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Incident Analysis and Identification of Key Risks During LIB's Battery Life: the Role of Accidents Databases in the Risk Prevention Actions

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The demands for Li-ion batteries (LIBs) have recently increased exponentially. They are used in a multitude of applications including electric vehicles (EVs), Energy Storage Systems (ESS) and consumer electronics. However, their chemical composition, high energy content and behaviour under abuse conditions pose a significant risk to safety, human health and the environment. This risk is particularly pronounced with the amount of active materials, especially the organic electrolyte and consequently, with the number of cells constituting the battery. To mitigate the risk, critical points throughout the entire life cycle of a lithium battery must be identified. For this purpose, the analysis of accidents occurring around the world acquires a fundamental importance. The evaluation of the main risks associated with the transport, use and storage of LIBs would allow the improvement of specific prevention measures to reduce the risk of fire and explosion during their use and their storage. Additionally, the improvement of safety procedures to manage accidents involving lithium ion batteries should be considered. Furthermore, it enables the updating of legal and technical standards and the development of more reliable storage systems. The aim of this study is to enhance current knowledge on the factors that may trigger fire involving LIBs through the analysis of accidents and recall databases analysis. An Italian database has been developed which includes data on accidents that occurred during the normal use of batteries, as well as those that occurred in storage facilities, during transport and in the disposal of batteries. One example of the reconstruction of data necessary to enhance a database is presented in this work.

1. Introduction

LIBs are currently the most prevalent type of battery on the market. They are particularly suitable for applications that require portable electronics, for battery electric vehicles and for aerospace applications. These batteries offer several advantages over other battery types, including faster charging times, longer battery life and a higher energy density (Tarascon and Armand, 2001).

However, in recent years, several accidents have been reported in which lithium-ion batteries have been identified as the source of fires and of the emission of hazardous substances. This is due to LIBs chemical composition and their high energy density which, in the case of misuse or failure, can result in the development of undesired chemical reactions, leading to the release of toxic and flammable substances (Wang et al., 2012). Manufacturing defects, environmental contamination, misuse and abuse (e.g. overcharging, overdischarging, exposure to excessively low or high temperatures, mechanical shock) can lead to failures that can develop into the "worst case" of thermal runaway, which can lead to explosion and/or fire. For used batteries, other potential sources of abuse include improper disassembly processes, accidental puncture, deterioration or damage due to improper discharge and even battery ageing. It is possible for these batteries to retain a residual charge which, if not handled properly, could result in overheating, fire or short circuit.

The rapid increase in use increases the likelihood of accidents. The risk is pervasive, and the extent of the damage increases in proportion to the increase in the use of batteries and/or with the size of the batteries used, which in turn correlates with the amount of material and energy involved. Any accident has the potential to cause damage to people, property, the environment, and the brand image. The study of past accidents, including an

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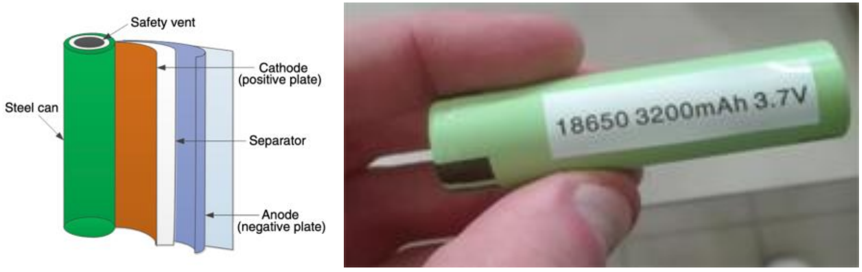
understanding of the root causes, is fundamental to the development of a risk analysis and the appropriate definition of risk management and prevention policies. In fact, the data obtained from accident investigation allows for the correct implementation of risk analysis activities, the development of appropriate operating instructions, the review of the system design and the provision of fundamental indications for legislative and standardisation activities.

In January 2020, the National Fire and Rescue Service (CNVVF-Corpo Nazionale Vigili del Fuoco), in collaboration with ENEA (Ente Nuove tecnologie, Energia e Ambiente), published the first Italian study on the safety of LIBs (Di Bari et al., 2020). The study focused on the assessment of the risks associated with the storage of lithium-based electrochemical energy storage systems and on the identification of specific prevention, protection, and management measures to reduce the risk of fire and explosion during their storage. As part of the activities, a preliminary study has beenpublished (Di Bari et al., 2020) on the safety issues related to lithium batteries throughout their life cycle. The study presents a non-exhaustive compilation of national and international accidents. These incidents have been catalogued in a database (ENEA-CNVFF DB). In addition, institutional sources and consumer product recall databases were examined, including EU-RAPEX (Rapid Exchange Information System for Dangerous Products), based on the Directive 2001/95/EC of the European Parliament and of the Council of 3 December 2001 on general product safety, and the US-CPSC (Consumer Products Safety Commission).

2. Lithium-ion batteries and their safety

LIBs are composed of cells that can be cylindrical, prismatic or pouch: all these cell have a layered structure and variable chemical composition. A visual representation of a cylindrical cell is presented in Figure 1 (Wang et al., 2019).



a) b)

Figure 1: a) a schematic view of a cylindrical cell 18650 and b) a picture of it.

A non-exhaustive list of the components and materials of the commercial LiB is given in Table 1. LiBs are usually categorised on the basis of the composition of the cathode, and each specific combination of active materials is associated with different electrical and safety properties.

Table 1: main components and materials of Lithium-ion cells:

Anode	Carbon/graphite or Li_2TiO_3 (LTO) deposited on a copper current collector
Cathode	Lithiated mixed metal oxide deposited on an aluminum current collector: LCO (Li Cobalt Oxide) 3.7V; LMO (Li Manganese Oxide) 3.9V; NCM (Li Nickel Cobalt Manganese Oxide) 3.6V; NCA (Li Nickel Cobalt Aluminum Oxide) 3.6V; LFP (Li Iron Phosphate) 3.2V
Separator	A polymer placed between the anode and cathode that allows the conduction of lithium ions.
Electrolyte	Lithium salt, usually $LIPF_6$ dissolved in an organic solvent or a mixture of organic solvents.
Additives	Flame retardants, binders, corrosion inhibitors, lithium deposition inhibitors, etc.
Safety Devices	SEI (solid-electrolyte interphase): a protection layer which covers the anode. It is formed during the first charge, carried out by the manufacturer; PTC (Positive Temperature Coefficient expansion device); Venting device; CID (Current Interruption Devices); separator with shut-down effect

Deviations from the values that define the operating window(Fig.2a) in terms of maximum and minimum voltage (V_{max}, V_{min}) and maximum and minimum temperature (T_{max}, T_{min}) can be attributed to a number of factors, including production/design defects; misuse (use in conditions other than those specified by the manufacturer);

abuse (electrical, thermal or mechanical); internal short circuit caused by prolonged misuse phenomena leading to the formation of metallic lithium deposits on the anode (i.e., over-charging; charging below T_{min}), ageing as shown in Figure 2b (Garche & Brandt, 2019).Most of these deviations (including excessive charge or discharge rate) cause an increase in internal temperature, leading to permanent deformation (swelling) and/or venting, or catastrophic cell failure (physical explosion or chemical explosion for runaway reactions).

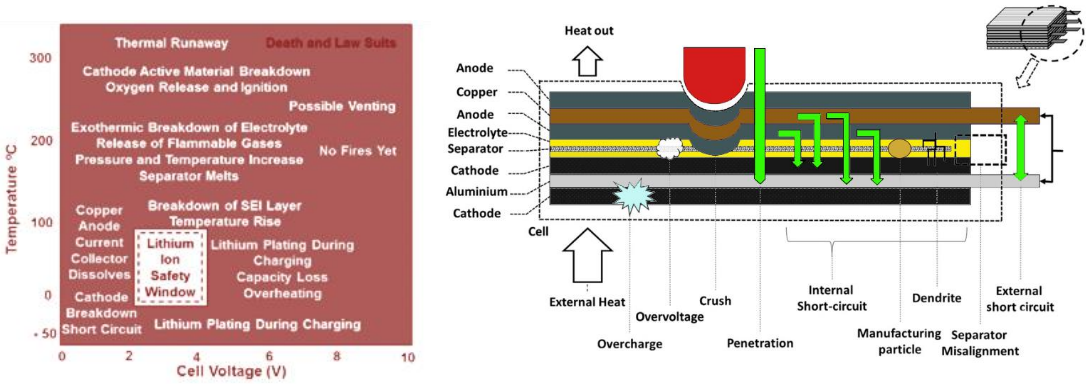


Figure 2: a) Li-ion cell operating window (Di Bari et al.,2020) b) Example of abuses (Garche et al., 2019).

In addition, emissions include toxic, harmful and flammable substances such as H_2, HF, phosphorus and chlorine, as well as oxygenated compounds and carbonyl complexes of heavy metals and respirable particles (Ubaldi et al., 2023a, 2023b; Willstrand et al., 2020).

3. ENEA-CNVVF Database

The ENEA-CNVVF DB (Di Bari et al., 2020) contains 102 accidents that occurred in different countries around the world and involved different products as follows: A total of 11 e-bikes, 9 consumer electronics, 2 ESSs, 60 electric vehicles, and 16 accidents involving WEEE (Waste of Electric and Electronic Equipment) or battery waste. The data is divided into 5 different categories: 1) the date and location of the accident; 2) the type of batteries, accumulators and equipment involved; 3) a description of the accident; 4) the damage caused ; 5) the sources of the accident information. A case study is presented in the following section. The implementation of this database will be based on the daily input accident information with the addition of a new format.
Other important databases are currently available such as the FAA DB, Verisk, the EPRI BESS Failure Event Database, the BARPI but they are not specific to accidents involving batteries or are only related to specific battery application.

4. Case Study

Examining the ENEA-CNVVF DB, a cluster of 5 accidents was selected. They occurred in a lithium-ion battery recycling plant located in Darlaston, West Midlands England, and are now described. These incidents have occurred over the years and they are an example of the successful implementation of fire prevention and mitigation procedures and strategies.

4.1 The Company and the industrial site

The company has a global reach and a leading position in the production of lead, lead alloys and the recycling of lead batteries. The company began collecting of lithium and other non-Pb batteries in 2005. The company collects waste and end-of-life batteries from across the country. These, batteries are returned to the Company's site where they are manually sorted by chemistry and stored in preparation for export or shipment for recycling. The main off-site storage area is used to store spent batteries. The storage buildings within the yard area are used to store lithium batteries. The site layout is shown In Figure 3.

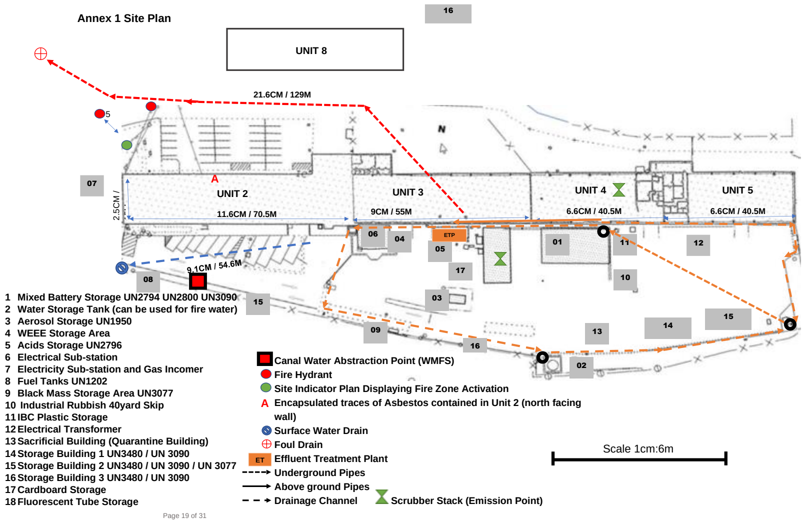


Figure 3: site plan

The different units of the site facility are described below:

- Unit 2 is used to manually sort mixed household batteries of the following chemistries: alkaline, nickel-cadmium, nickel-metal hydride, lithium-ion, and lithium-metal. At the end of each shift, the lithium is extracted from the units and transferred to off-site storage facilities.
- The lithium shredder, with a capacity of 6 tons per hour, is located in Unit 3. Within the Unit is a crashing plant on a water circuit with a nitrogen generator. The plant includes a primary shredder, secondary shredder, density and magnetic separation system, and drying augers.
- Unit 4 contains a small-scale lithium shredder with a daily capacity of 2 tons per hour and a sorted material storage area. The lithium-ion cells collected from the EVs are shredded by the lithium shredder, which also produces black matter and ferrous and non-ferrous fractions. The equipment operates in a CO_2-filled environment to prevent fires. Eight storage bays with metal stillages are used to sort the unit's alkaline storage space.
- Unit 5 is where the EV's LIB battery pack is tested and disassembled. The unit consists of an office area, a technical room where test equipment is stored in an internal aerosol fire suppression system, and an internal segregated warehouse. It is company policy that no materials are stored within the main unit outside of working hours. The internal storage area is equipped with two sets of shelving to store safe and low-voltage lithium-ion vehicle modules that have tested, de-energised and deemed safe for reintroduction to the market.

Each unit has a minimum of two 6 kg powder extinguishers at each entrance door. A minimum of two 6-liter Lith-Ex fire extinguishers are required for each workstation in Unit 5 and Unit 4.

The on-site wastewater treatment plant, located on a concrete pad outside Unit 3, is responsible for treating all surface water from the outside yard and units. The effluent is then discharged into the two foul sewers.

The main yard area comprises three main lithium batteries storage buildings. Storage buildings 1 and 2 are used to store material awaiting processing and processed stock. All batteries stored in these buildings have undergone the necessary safety checks. The sacrificial building in the yard is used to store all incoming lithium batteries to ensure stability and complete safety checks (ECOBAT solution, 2023).

4.2 Five accidents at battery recycling plant

In March 2008, around 80 firefighters from various locations were called out to tackle a major fire that reached 100 feet in height (Express and Star, 2008). Up to 15 tons of lithium batteries and cylinders were destroyed as part of the warehouse collapsed. There were two other significant fires at the plant in 2014 (Express and star journal,2014). The first occurred in January, when up to 50 firefighters were called to extinguish a fire that broke out in the outdoor yard in the early hours of the morning. The fire was believed to have originated from the storage of leftover batteries in the yard, resulting in the combustion of a significant number of batteries. Twenty days later, in February, 50 firefighters were again called out to extinguish a fire that had broken out, resulting in the evacuation of 40 employees. This time the fire involved lithium batteries in a warehouse. The large fire quicky gained momentum, but the firefighters were able to extinguish it with the help of 10 fire engines supplied with pumped water from the nearby canal (Figure 4).

Figure 4: Firefighter pumping water from the canal

The fourth fire occurred on 23 May, 2017 (Cole 2017), at approximately 1:45 pm when a large fire broke out in the plant that housed four tons of batteries. Several discarded lithium batteries which had been packaged for later shipment, caught fire unexpectedly. The intense heat generated by the fire also ignited other batteries awaiting recycling. A fire and subsequent explosion resulted in multiple injuries to a 26-year-old man. The man suffered burns, bruises and lacerations to his hands. The fire was completely extinguished by the fire brigade the following morning.

The most recent incident occurred on 18 July 2022 at 2:00 pm (Parkes T.,2022). Crews arrived at the plant as temperatures began to rise. The incident involved a significant number of pallets of end-of-life lithium-ion and lithium-metal batteries. Due to the elevated ambient temperature, which reached a maximum of 36°C, a critical battery temperature was reached which posed significant fire risk. Local staff acted quickly to identify the threat, allowing the fire brigade to intervene before the situation escalated. To mitigate the fire risk, the firefighters used a strategy involving the use of water from a nearby canal, in conjunction with the site staff and Hazmat team. As a result of this intervention, the temperature was reduced to a non-hazardous level, preventing the situation from developing into a more catastrophic scenario.

4.3 Fire Detection Plan

Following incidents between 2008 and 2017, the Company implemented a fire detection plan, which was due for review and update in May 2023. The on-site fire detection systems are installed and maintained by third-party contractors who are appropriately accredited. The detection systems installed on-site include: optical smoke detectors, heat detectors, infrared smoke beams, continuous thermal imaging monitoring in all sorting/dismantling stations and flame detectors in all storage areas. The recently implemented fire prevention plan was crucial in preventing the 2022 quasi-accident from worsening, allowing personnel to respond quickly and effectively, thereby limiting the extent of the damage.

5. Conclusions

The case study analysis demonstrates the critical importance of investigating the factors that cause a Li-ion battery fire to start and spread in order to develop and implement strategies to mitigate the risk of fire and explosion damage. In fact, the experience gained from analysing the numerous incidents that occurred in the Li-ion battery recycling plant enabled the implementation of a strategic plan to prevent the fire from developing. This included the adoption of appropriate detection systems and the implementation of rapid and effective intervention procedures. Indeed, the accident that occurred in 2022 serves as a proof of the effectiveness of the measures implemented. It is therefore of paramount importance to study accidents that have occurred worldwide, although it must be emphasised that obtaining comprehensive accident data is a challenge, particularly in order to determine the underlying causes and the dynamics of accidents. It is also very important to expand data collection in countries such as China and Korea, where battery use and production is most concentrated.

To gather accurate accident data, it is essential to have comprehensive information on the plant site where cells, batteries, and portable devices are produced. For example, it is crucial to involve manufacturers of electric vehicles in the data collection process, as they are in a unique position to provide insight into the entire production chain, including vehicle transport, as well as data on accidents occurring during the various modes of transport and their intermediate storage.

The analysis of the incidents showed the importance of effective preventive measures, the importance of early detection of malfunctions, the prompt intervention of trained personnel with the appropriate skills to deal with lithium-ion battery emergencies, and the identification and maintenance of safe distances appropriate for this type of material. To achieve this objective, the Italian database developed by ENEA and CNVVF, will be soon updated by the authors. The ultimate goal of the project is to develop both regulatory and preventive measures, risk reduction and emergency management measures, which can only be achieved through the systematic analysis of incidents that have occurred.

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