

Fire risks associated with batteries

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Abstract

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This report summarizes possible fire risks related to batteries while not in use, i.e. in storage or in idle mode in equipment or in recycling collection facilities. The risks also include possible abuse situations in these circumstances such as water exposure or mechanical abuse. The risks are also discussed in relation to handling of batteries in collection for recycling, both of batteries themselves and when incorporated into electronic waste.

Key words: Batteries, Fire, Recycling, Risk

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Preface

This report has been sponsored by Stena Technoworld and Elkretsen in Sweden. Stena Technoworld is one of the largest recyclers of electronic waste in Sweden and Elkretsen is responsible for the battery collection in Sweden. This support is gratefully acknowledged. In addition, Stena Technoworld and Elkretsen have provided us with information concerning the recycling process as input to the work presented in this report.

Summary

This report summarizes possible fire risks related to batteries while not in use, i.e. in storage or in idle mode in equipment, or in recycling collection facilities. The risks also include possible abuse situations in these circumstances such as water exposure or mechanical abuse. The risks are also discussed in relation to handling of batteries in collection for recycling, both of batteries themselves and when incorporated into electronic waste.

The work has been conducted as a collaboration between the departments of Chemical and Materials Technology, Electrical Technology and Fire Technology at SP Technical Research Institute of Sweden (SP Sveriges Tekniska Forskningsinstitut). This collaboration draws on the specific expertise of each department to bring together a mix of information which we feel provides a better overall understanding of battery risks than is typically the case when considered from a more narrow perspective.

This report represents a summary of both data from the literature data, news reports of fire incidents, and a collation of textbook information concerning battery types and associated risks. The work is applied specifically to the recycling chain in Chapters 8 and 9 and some outlook to the future is given in Chapter 10.

The work is exploratory in nature (in particular concerning fire risks and reports concerning fire incidents) so the information contained is in some parts speculative and in many ways indicative of risks rather than aiming to provide an exhaustive picture.

1 Introduction

The use of batteries is expanding rapidly. Batteries are being included in many consumer appliances such as handheld tools, toys, kitchen appliances, computers, and even in clothes, at an ever growing rate. The risk of fire caused by batteries is also affected by advances in battery technology that allow an increased amount of energy to be stored in them. The presence, number, and location of batteries may not be obvious to the consumer due to clever designs that favour smaller, lighter weight, multifunctional products (and batteries) and this can lead to safety issues at the end of the product's life.

The increased use of batteries and the rapid exchange in society of consumer products containing integrated batteries means that a lot of batteries are present in facilities that process Waste Electrical and Electronic Equipment (WEEE). Special attention is given to the fire risks that batteries pose in these facilities. This includes fire risks in the entire recycling chain from collecting the waste, separating batteries from other material, storing and transporting the separated batteries, along with the fire risk associated with batteries that have not been separated but are processed together with other waste.

This report summarizes literature documentation of fire risks associated with batteries while not in use, with a particular focus on the recycling chain. In addition, a list is provided of some fire incidents caused by batteries or in which batteries played a significant role.

Chapter 2 describes the approach taken to collect and analyse the information contained in this report. Chapter 3 gives background information such as trends in battery use, including policies on battery recycling and recovery of materials, and battery and WEEE recycling in general. In Chapter 4 an overview is given of existing battery types, along with their chemistries and trends for the development of future batteries.

In Chapter 5 the risk of fire ignition associated with the various battery types and chemistries, as well as risks common to all batteries, are presented. Chapter 6 is a collation of experiences from real fire incidents associated with batteries, both nationally and internationally; this subject is generalized to fire spread in waste in Chapter 7.

Chapters 8 and 9 examine the recycling chain and apply the knowledge collected in previous chapters to the recycling chain. Lastly, in Chapter 10, future changes in the nature of batteries, recycling processes, and relevant fire safety precautions are explored.

2 Approach

The information contained in this report has been collated from internal reports, references, direct experience, and other communications within the Chemistry, Electrical, and Fire Technologies departments at SP Sveriges Tekniska Forskningsinstitut. A search of the general literature, conference proceedings, worldwide web, and governmental databases was conducted and additional information was also acquired from local recycling facility owners and operators. Once collected, the information was organized and used to create this report.

In general, there is very little detailed information available about the conditions that have led to fire caused by batteries in WEEE recycling facilities. The general literature, which leans more toward theoretical research, is not an ample source of information regarding this very applied topic. Therefore, most of the information presented in this report comes from sources other than the general literature and may or may not have undergone a rigorous review process.

The specific databases that were searched for information on battery fires in recycling facilities are: ScienceDirect, Scopus, and the US Department of Energy Information Bridge (which provides access to the Energy Citations Database, the Green Energy Knowledge Database, and the Office of Science and Technical Information).

3 Battery use and policy trends

It is predicted that the global market for consumer batteries will exceed \$55 billion by 2017 [1]. Europe is currently the leading consumer of batteries, however, the European market is expected to grow moderately in the next few years while China's demand for consumer batteries is expected to grow much more rapidly, making China the market leader by 2017. The growing popularity of mobile devices and consumer electronic products such as cell phones, laptops, and digital cameras has been the major driving force behind the increase in demand for consumer batteries.

Primary (non-rechargeable) battery consumption is higher than secondary (rechargeable) batteries, with primary alkaline batteries being the largest segment of the battery market. Among secondary batteries, lithium-ion (Li-ion) batteries have the best growth expectations while Nickel-Cadmium (NiCad) and Nickel Metal Hydride (NiMH) secondary battery use is declining [1].

From an industrial perspective, hybrid and electric transportation, such as trains, buses, cars, motorcycles, scooters, and bikes are expected to come into use or become more popular in the future and will promote the development of new smaller, lighter, more efficient, less environmentally problematic battery technology. Also, as more countries increase their reliance on renewable energy, batteries will have an important role as energy storage devices [2].

As the use of batteries has increased it has become apparent that proper battery disposal is important both from an environmental stewardship perspective and from the standpoint of recovery of valuable materials. These two factors work constructively to motivate the formation of recycling policies that work to protect the environment and help to diminish national dependencies on external resources [3, 4].

The WEEE Directive was created in 1996 and implemented in 2003 by the European Commission to promote strategies for the reuse and recovery of material or energy from electrical and electronic equipment waste [5]. The objective of this policy is to preserve, protect and improve the quality of the environment, protect human health and utilize natural resources prudently and rationally. The WEEE Directive has been very recently updated with improvements in regulations on the collection, re-use and recycling of used electronic devices, control of illegal exports of such waste from the EU, and incentives to enhance the performance of producers, distributors and consumers involved in the entire life cycle of electrical and electronic equipment.

In 2006, the European Battery Directive was established to require minimum battery collection and recycling regulations and to set up a consistent set of definitions and calculation methods used to comply with the regulations. The Directive has since been amended several times and transposed into national laws that are being implemented [6-8]. The Directive includes challenging goals in terms of battery collection rates and recycling efficiency; these goals are expected to become more stringent as materials become more valuable and pollution concerns deepen. The most recent development in the Directive is a 2012 proposal to limit the current exemption to 2016 for power tool batteries that contain cadmium [9].

In North America the Universal Waste Law was established in 1995 and governs proper handling of hazardous waste, including batteries [10]. The following year the Mercury-Containing and Rechargeable Battery Management Act was implemented in the US to phase out the use of mercury-containing batteries and encourage people to use rechargeable batteries [11]. Information about laws that have been implemented more

recently at the provincial, state and local levels regarding battery recycling in the US and Canada is available on the Call2Recycle¹ website. The overall trend in North America and Europe is to develop or strengthen legislation that encourages battery recycling, discourages accumulation of batteries in landfills, phases out batteries having the most environmentally toxic constituents, and shifts responsibility for collection, treatment, and salvaging of battery waste to manufacturers of consumer products and batteries.

¹ Call2Recycle is a North American grass-roots recycling program operated by a non-profit organization consisting of rechargeable battery and consumer electronics manufacturers. See their websites at Call2Recycle.org (USA) and Call2Recycle.ca (Canada).

4 Battery technology

Batteries are often divided into primary and secondary batteries. Primary batteries are those that are only used until they are empty and never recharged. These batteries represent the major battery type and have been used in consumer appliances for a long time in cameras, torch lights, radios etc. Secondary batteries are rechargeable. The use of rechargeable batteries has grown in consumer products during the last years in e.g. handheld tools and will most likely continue to grow [12].

Reserve batteries are a special type of primary battery. These batteries lack a component during storage and this component is added to the battery in order to activate it. These batteries do not age like normal batteries and hence they can be stored for very long times before they are used.

Several different types of primary and secondary batteries exist. The type of battery that is used for certain equipment or an specific application is determined by the requirements of the system in which it is used e.g. voltage, physical size and weight, capacity, load current, temperature requirements, shelf life, charging (if rechargeable), safety and reliability, cost, environmental conditions. [13].

A detailed description of different batteries can be found in several books, for instance Linden's Handbook of Batteries [14].

4.1 Primary batteries

Main components and cell reactions in different types of common commercial primary batteries are summarized in table 1. Lithium batteries can be of several different types and the most common are therefore summarized separately in table 2. A summary of more primary battery characteristics is available in the literature [15]. Often lithium batteries (that are normally primary) and lithium-ion batteries (that are normally secondary) are not considered to be of the same type since lithium-ion batteries do not contain metallic lithium. In addition to the main components, batteries also contain additional materials in the casing etc. The chemical composition is often different from manufacturer to manufacturer, and between batteries of different models, however typical compositions of some common primary batteries can be found in the document "Product information Primary and rechargeable batteries" from The European Portable Battery Association [16].

Table 1 Main components and cell reactions in primary batteries [14]

Battery type	Positive pol	Negative pol	Electrolyte	Cell reaction
Zinc carbon batteries ("brunstenbatterier")	Manganese dioxide (MnO ₂)/carbon (C)	Zinc (Zn)	Ammonium chloride (NH ₄ Cl) and/or zinc chloride (ZnCl ₂)/water	$\text{Zn} + 2\text{MnO}_2 + 2\text{NH}_4\text{Cl} \rightarrow 2\text{MnOOH} + \text{Zn}(\text{NH}_3)_2\text{Cl}_2 \text{ (light discharge)}$ $\text{Zn} + 2\text{MnO}_2 + \text{NH}_4\text{Cl} + \text{H}_2\text{O} \rightarrow 2\text{MnOOH} + \text{NH}_3 + \text{Zn}(\text{OH})\text{Cl} \text{ (heavy discharge)}$ $\text{Zn} + 6\text{MnOOH} \rightarrow 2\text{Mn}_3\text{O}_4 + \text{ZnO} + 3\text{H}_2\text{O} \text{ (prolonged discharge)}$ <p style="text-align: center;">or</p> $\text{Zn} + 2\text{MnO}_2 + 2\text{H}_2\text{O} + \text{ZnCl}_2 \rightarrow 2\text{MnOOH} + 2\text{Zn}(\text{OH})\text{Cl} \text{ (light or heavy discharge)}$ <p style="text-align: center;">or</p> $4\text{Zn} + 8\text{MnO}_2 + 9\text{H}_2\text{O} + \text{ZnCl}_2 \rightarrow 8\text{MnOOH} + \text{ZnCl}_2 \cdot 4\text{ZnO} \cdot 5\text{H}_2\text{O} \text{ (light or heavy discharge)}$ $\text{Zn} + 6\text{MnOOH} + 2\text{Zn}(\text{OH})\text{Cl} \rightarrow 2\text{Mn}_3\text{O}_4 + \text{ZnCl}_2 \cdot 2\text{ZnO} \cdot 4\text{H}_2\text{O} \text{ (prolonged discharge)}$
Alkaline batteries	Manganese dioxide (MnO ₂)	Zinc (Zn)	Potassium hydroxide (KOH)/water	$2\text{MnO}_2 + \text{Zn} + 2\text{H}_2\text{O} \rightarrow 2\text{MnOOH} + \text{Zn}(\text{OH})_2$ <p style="text-align: center;">or</p> $3\text{MnO}_2 + 2\text{Zn} \rightarrow \text{Mn}_3\text{O}_4 + 2\text{ZnO}$
Silver oxide zinc batteries	Silver oxide (Ag ₂ O or AgO)	Zinc (Zn)	Potassium hydroxide (KOH) or sodium hydroxide (NaOH)/water	$\text{Zn} + \text{Ag}_2\text{O} \rightarrow 2\text{Ag} + \text{ZnO}$ <p style="text-align: center;">or</p> $\text{Zn} + \text{AgO} \rightarrow \text{Ag} + \text{ZnO}$
Mercury batteries	Mercury oxide (HgO)	Zinc (Zn)	Potassium hydroxide (KOH) or sodium hydroxide (NaOH)/water	$\text{Zn} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$
Zinc air batteries	Oxygen or air (O ₂)	Zinc (powder) (Zn)	Potassium hydroxide (KOH)/water	$2\text{Zn} + \text{O}_2 + \rightarrow 2\text{ZnO}$
Lithium batteries ¹	Various, see table 2	Lithium (Li)	Various, see table 2	Various, see table 2

1) Often lithium batteries and lithium-ion batteries are not considered to be the same type of battery.

Table 2 Main components and cell reactions in lithium batteries [14] (primary batteries) ¹

Battery type	Positive pol	Negative pol	Electrolyte ²	Cell reaction
Lithium manganese dioxide batteries	Manganese dioxide (MnO ₂)	Lithium (Li)	Lithium salt (e.g. lithium perchlorate (LiClO ₄)) in organic solvent (e.g. propylene carbonate and 1,2-dimethoxyethane)	$x\text{Li} + \text{Mn(IV)O}_2 \rightarrow \text{Li}_x\text{Mn(III)O}_2$
Lithium carbon monofluoride batteries	Polycarbon monofluoride (CF _x)	Lithium (Li)	Lithium salt (e.g. lithium tetrafluoroborate (LiBF ₄)) in organic solvent	$x\text{Li} + \text{CF}_x \rightarrow x\text{LiF} + x\text{C}$
Lithium iron disulfide batteries	Iron disulphide (FeS ₂)/carbon (C)	Lithium (Li)	Lithium salt (lithium iodide (LiI)) in organic solvent (e.g. mixture of 1,3-dioxolane and 1,2-dimethoxyethane)	$4\text{Li} + \text{FeS}_2 \rightarrow \text{Fe} + 2\text{Li}_2\text{S}$
Lithium thionyl chloride batteries	Carbon (C)/thionyl chloride ³ (SOCl ₂)	Lithium (Li)	Lithium tetrachloroaluminate (LiAlCl ₄) in thionyl chloride ³ (SOCl ₂)	$4\text{Li} + 2\text{SOCl}_2 \rightarrow 4\text{LiCl} + \text{S} + \text{SO}_2$
Lithium sulphur dioxide batteries	Carbon (C)	Lithium (Li)	Sulphur dioxide (SO ₂) in solution of lithium bromide (LiBr) in acetonitrile	$2\text{Li} + 2\text{SO}_2 \rightarrow \text{Li}_2\text{S}_2\text{O}_4$
Lithium copper oxide batteries ⁴	Copper oxide (CuO)	Lithium (Li)	Lithium perchlorate (LiClO ₄) in organic solvent	$2\text{Li} + \text{CuO} \rightarrow \text{Li}_2\text{O} + \text{Cu}$

- 1) Approximately 10 additional types of lithium batteries exist, however they are considered to be rare and are therefore not included here.
- 2) Many of the organic solvents are flammable.
- 3) Thionyl chloride (SOCl₂) reacts with many compounds, for instance water, and will then produce hydrogen chloride (HCl) and sulphur dioxide (SO₂) (that are not flammable) according to: $\text{SOCl}_2 + \text{H}_2\text{O} \rightarrow 2\text{HCl} + \text{SO}_2$
- 4) No longer commercially available [14].

4.2 Secondary batteries

Common commercial secondary batteries are summarized in table 3 where main components and cell reactions are given. A summary of more secondary battery characteristics is available in the literature [17]. Since hydrogen evolution can be a major fire risk, and since many secondary batteries can produce hydrogen gas, the possibility for hydrogen gas production for the different batteries is also noted in table 3. In addition to the main components, batteries also contain additional materials in the casing etc. The chemical composition is often different from manufacturer to manufacturer, and between batteries of different models, however typical compositions of some common secondary batteries can be found in the document "Product information Primary and rechargeable batteries" from The European Portable Battery Association [16].

Table 3 Main components and redox reactions in secondary batteries (rechargeable batteries) [14]

Battery type	Positive pol	Negative pol	Electrolyte	Cell reaction (discharge →, charge ←)	Possible hydrogen evolution
Lead-acid batteries ¹	Lead dioxide (PbO ₂)	Lead (Pb) ²	Sulphuric acid (H ₂ SO ₄) ³ /water	$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$	Yes
Nickel cadmium batteries ⁴	Nickel oxide hydroxide (NiOOH)	Cadmium (Cd)	Potassium hydroxide (KOH)/water	$Cd + 2NiOOH + 2H_2O = Cd(OH)_2 + 2Ni(OH)_2$ or $Cd + 2NiOOH \cdot xKOH \cdot (H_2O) = Cd(OH)_2 + 2Ni(OH)_2 + 2xKOH$	Yes
Nickel metal hydride batteries (NiMH)	Nickel oxide hydroxide (NiOOH)	Different alloys ⁵	Potassium hydroxide (KOH)/water	$MH + NiOOH = M + Ni(OH)_2$ M is an alloy ⁵	Yes
Lithium-ion batteries ^{6,7}	Different metal oxides or phosphate ⁸ (e.g. lithium cobalt oxide (LiCoO ₂), lithium iron phosphate (LiFePO ₄) or lithium manganese oxide (LiMn ₂ O ₄))	Often carbon (graphite) ⁹	Lithium salt (e.g. lithium hexafluorophosphate (LiPF ₆)) in mixtures of organic solvents ¹⁰	$x/yLi_yC + Li_{1-x}MO_2 = LiMO_2 + x/yC$	See footnote ¹¹
Lithium (ion) polymer batteries	Different metal oxides ⁸ (e.g. lithium cobalt oxide (LiCoO ₂) or lithium manganese oxide (LiMn ₂ O ₄))	Often carbon (graphite) ⁹	Lithium salt (e.g. lithium hexafluorophosphate (LiPF ₆)) in polymer	$x/yLi_yC + Li_{1-x}MO_2 = LiMO_2 + x/yC$	See footnote ¹¹
Nickel iron batteries or iron electrode batteries	Nickel oxide hydroxide (NiOOH) ¹²	Iron (Fe)	Potassium hydroxide (KOH) together with lithium hydroxide (LiOH)/water	$3Fe + 8NiOOH + 4H_2O = 8Ni(OH)_2 + Fe_3O_4$ ¹²	Yes
Nickel zinc batteries	Nickel oxide hydroxide (NiOOH)	Zinc (Zn)	Potassium hydroxide (KOH)/water	$Zn + 2NiOOH + 2H_2O = Zn(OH)_2 + 2Ni(OH)_2$ or $Zn + 2NiOOH + 2OH^- = ZnO_2^{2-} + 2Ni(OH)_2$ or $Zn + 2NiOOH + H_2O = ZnO + 2Ni(OH)_2$	Yes

- 1) Lead-acid batteries are often divided into open lead-acid batteries or valve regulated lead-acid (VRLA) batteries. In lead-acid batteries, hydrogen gas ($H_2(g)$) and oxygen gas ($O_2(g)$) can be produced through electrolysis of water. In open batteries $H_2(g)$ and $O_2(g)$ can be lost and therefore these batteries must be refilled with water. In VRLA batteries, gases are recombined to reform water (H_2O). VRLA batteries can be divided into gel batteries or absorptive glass mat (AGM) batteries dependent on how the electrolyte is immobilized.
- 2) Often low concentrations of calcium (Ca) (most common), antimony (Sb), tin (Sn) or selenium (Se) can be present.
- 3) Concentration of sulphuric acid varies during the charging/discharging cycle.
- 4) Several variants of nickel-cadmium battery exist including sealed and vented batteries.
- 5) Consists of mixtures written as AB_5 , A_2B_7 , or AB_2 . AB_5 consists of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), nickel (Ni), cobalt (Co), manganese (Mn), and aluminum (Al). A_2B_7 consists of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), magnesium (Mg), nickel (Ni), cobalt (Co), manganese (Mn), aluminum (Al), and zirconium (Zr), or consists of neodymium (Nd), magnesium (Mg), nickel (Ni), cobalt (Co), aluminum (Al), and zirconium (Zr). AB_2 consists of vanadium (V), titanium (Ti), zirconium (Zr), nickel (Ni), chromium (Cr), cobalt (Co), and manganese (Mn), or consists of vanadium (V), titanium (Ti), zirconium (Zr), nickel (Ni), chromium (Cr), manganese (Mn), and tin (Sn), or consists of vanadium (V), titanium (Ti), zirconium (Zr), nickel (Ni), chromium (Cr), cobalt (Co), manganese (Mn), aluminium (Al), and tin (Sn).
- 6) Lithium-ion batteries and lithium batteries are often not considered to be the same type of battery.
- 7) Lithium-ion batteries have several different safety mechanisms built into the batteries.
- 8) Several different metal oxides exist.
- 9) Other materials are also used.
- 10) Different electrolytes in different mixtures of organic solvents exist. Common organic solvents are e.g. ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), and dimethyl ether (DME). Many of the organic solvents are flammable.
- 11) These batteries do not contain an aqueous electrolyte, however hydrogen gas ($H_2(g)$) can still be released when lithium-ion batteries vent after abuse.
- 12) Other materials exist, for instance silver oxide could be substituted for nickel oxide hydroxide, however nickel oxide hydroxide is the most common material.

4.3 Reserve batteries

Water-activated reserve batteries are the most common type. The battery is activated by addition of water or an aqueous electrolyte to the battery. This is performed by immersion of the battery in the aqueous liquid, or by forcing a flow of the aqueous liquid or pouring the aqueous liquid into the battery. Water-activated reserve batteries are summarized in table 4 where main components and cell reactions are given. Water-activated batteries are presently manufactured for specific applications such as aviation and marine life jacket lights, lifeboat emergency equipment, sonobuoys, radio and light beacons, underwater ordnance and radiosonde units [18]. More water-activated reserve battery characteristics and description of other types of reserve batteries are available in the literature [19, 20].

Table 4 Main components and cell reactions in water-activated reserve batteries

Battery type	Positive pol	Negative pol	Cell reaction ¹
Magnesium-silver chloride batteries	Silver chloride (AgCl)	Magnesium (Mg)	$Mg + 2AgCl \rightarrow MgCl_2 + 2Ag$
Magnesium-cuprous chloride batteries	Cuprous chloride (CuCl)	Magnesium (Mg)	$Mg + 2CuCl \rightarrow MgCl_2 + 2Cu$
Magnesium-lead chloride batteries	Lead chloride (PbCl ₂)	Magnesium (Mg)	$Mg + PbCl_2 \rightarrow MgCl_2 + Pb$
Magnesium-cuprous iodide-sulphur batteries	Cuprous iodide (Cu ₂ I ₂)	Magnesium (Mg)	$Mg + Cu_2I_2 \rightarrow MgI_2 + 2Cu$
Magnesium-cuprous thiocyanate-sulphur batteries	Cuprous thiocyanate (CuSCN)	Magnesium (Mg)	$Mg + 2CuSCN \rightarrow Mg(SCN)_2 + 2Cu$
Magnesium-manganese dioxide	Manganese dioxide (MnO ₂)	Magnesium (Mg)	$Mg + 2MnO_2 + H_2O \rightarrow Mn_2O_3 + Mg(OH)_2$

1) In addition, the following reaction takes place $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$

4.4 Other less common batteries

Several other batteries not included in tables 1 to 4 exist and these can be used in special applications (such as at extreme temperatures, in unusual equipment, or when extra high demands exist concerning, for instance, reliability or storage times). Examples of such batteries include: mercury-cadmium batteries (primary), magnesium-manganese dioxide batteries (primary), nickel-hydrogen batteries (secondary), rechargeable silver oxide batteries (secondary), zinc-alkaline-manganese dioxide batteries (secondary), rechargeable lithium metal batteries (secondary), zinc-silver oxide reserve batteries, ambient-temperature lithium anode reserve batteries, spin-dependent reserve batteries, and thermal batteries (reserve batteries) [14]. These batteries are considered to be rare and are not discussed further but are described in the literature [14].

4.5 Future batteries

A lot of research and development is performed on batteries by universities, research institutes and battery manufactures. It is expected that battery technology will continue to develop rapidly. However, for many batteries that are under development several problems exist. Hence, it is difficult to predict the future and whether new types of

batteries will be commercialized and reach the market. Despite this, a few predictions of the future will be given here.

Lithium based battery technology is evolving extremely rapidly and it is expected that these batteries will be improved and further developed with respect to power, lifetime, reliability, and safety in the future [2]. Much effort is directed to finding new electrode materials and electrolytes. An example of a future lithium based battery with high expectations is the lithium-air battery [2, 21, 22].

Lithium based batteries are today widely used in the consumer electronic market and it is not likely that they will be replaced by other battery types in the near future [2]. In the electric automotive transportation market it is also expected that lithium based batteries will dominate [2].

Micro fuel cells [11, 23, 24] are sometimes mentioned as a future alternative to traditional batteries, however it is believed that it will take several years before they are ready to be introduced widely as a primary power source for e.g. computers and mobile phones [11, 23].

4.6 Storage, transport and handling procedures for batteries

Safe storage and handling of batteries is the subject of international, national, and regional regulations, policy statements, and guidelines, as well as recommendations from the manufacturers of the batteries. Most of these documents deal with issues of labelling, protection against short circuits, containment of leakage from the batteries, and safety training of responsible personnel. Special attention is given to lithium-containing batteries in all of the safety requirements/ guidelines as they are considered to represent a potentially greater risk than other battery types.

Shipping companies, universities, governmental organizations, battery manufacturers and associations, and other large end users of batteries also provide handling, storage, packaging, transport, and disposal guidance for their customers and staff [25-31]. Material Safety Data Sheets (MSDS) are required to be provided by battery manufacturers, and are usually available online, which clearly state the hazards associated with the product.

4.6.1 Storage

As battery recycling becomes more prevalent in society, collection points are being established in stores and other public places to make it easy for people to properly dispose of their used batteries. Canada and the United Kingdom are leaders among nations in developing functional systems by which to collect, transport, and recycle used consumer batteries [32].

The US Army guidelines [33] on battery storage are representative of precautions used for bulk storage of batteries and include the following useful guidance:

1. Store new batteries in original packaging. This helps to identify damage such as swelling or leakage of batteries. Swelling of the bag indicates a battery that has vented.
2. Do not mix new and used batteries since it is difficult to distinguish between them.
3. Do not accumulate used batteries, dispose of them on a regular basis.

4. Segregate storage from other hazardous materials and other battery chemistries. It is critical that lead acid batteries be kept away from nickel cadmium or nickel metal hydride batteries.
5. Protect from crushing, punctures, and shorting.
6. Keep in a cool, dry, well-ventilated area, below 54°C (130° F).
7. Thermal runaway of nickel cadmium batteries may occur if temperatures exceed 54°C (130° F).
8. Coordinate battery storage locations with your local fire department/safety office and have periodic inspections conducted by fire department/safety office.
9. Protect bulk storage of batteries with sprinklers.
10. No smoking or eating.
11. Ensure that fire extinguishers are available. Use a type "AB" (H₂O) extinguisher to fight fires involving small quantities of batteries. A type "D" extinguisher would be used to fight a lithium fire by professional fire fighters.

4.6.2 Transport

On an international level, there are many United Nations (UN) regulations that apply to the classification of dangerous goods and hazardous materials, which has an important impact on the transport of batteries, among these are UN2794, UN2795, UN2796, UN2797, UN2800, UN3028, UN3090, UN3091, UN3292, UN3480, and UN3481, all dealing with classification and safe packaging of batteries for transport, including protection from short circuits and leakage [34, 35]. The UN requirements for lithium batteries include altitude, thermal, vibration, shock, external short circuit, impact, overcharge, and forced discharge tests that ensure the batteries are safe for transport.

The International Civil Aviation Organization (ICAO) publishes broad principles governing the international transport of dangerous goods (including batteries) by air [36]. They also publish technical instructions based on these principles which have become incorporated into national legislation for many countries. The technical instructions are intended for use by all parties involved in the transport chain, e.g., shippers, operators, government authorities, etc.

When batteries are imported/exported to the European Community for treatment and recycling the transport must comply with the requirements, or with equivalent conditions, of the Batteries Directive (2006/EC) [37] and evidence must be provided that:

- The applied technology is the best available, or equivalent.
- The existing approved guidelines are fulfilled.
- There is no danger to human health or the environment.
- Minimum treatment requirements are met.
- Minimum recycling efficiencies are fulfilled.
- Health and safety and waste management conditions for recycling, treatment, transport, and storage are fulfilled.

In Canada, the Transportation of Dangerous Goods (TDG) Act and Regulations [38, 39] promotes public safety when dangerous goods are transported by rail, road, sea, or air. With regard to batteries, the TDG requires that proper documentation accompany the shipment, the packages and vehicles are properly marked, the responsible person is adequately trained, and the packaging is spill-proof.

In the US, the National Transportation Safety Board (NTSB) is responsible for the safety of transported goods. The US regulations are codified in the Hazardous Materials Regulations (HMR) 49 CFR Parts 100 – 185 which generally follow the ICAO requirements mentioned above. This legislation includes provisions for packaging, hazard

communication, and handling batteries and battery-powered devices. The Call2Recycle program mentioned in Section 3 operates in both Canada and the US and provides many guidelines on the safe transport of consumer batteries from collection points to recycling facilities.

4.6.3 Recycling

Article 15 of the Batteries Directive (2006/66/EC) [37] concerns the safe storage of batteries before/during the recycling process, among other battery recycling topics. This document requires all fluids and acids to be removed from batteries to be treated prior to storage. The treatment/storage sites must also have impermeable surfaces, suitable weatherproof covering or clearly labelled, leak-proof containers. Notably, Article 15 does not mention external short circuit protection.

5 Fire risks

Several fire risks associated with batteries have been identified including:

- 1) Hydrogen gas production from batteries
- 2) Flammable compounds in lithium and lithium-ion batteries
- 3) Thermal runaway
- 4) Electrical fire risks
- 5) Reaction of metallic lithium
- 6) Reaction of sulphuric acid
- 7) Fire risks due to contact with water
- 8) Extreme temperatures
- 9) Accidental activation of reserve batteries

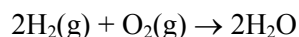
These risks are described and discussed below.

5.1 Hydrogen gas production from batteries

Many different types of batteries can produce hydrogen gas ($\text{H}_2(\text{g})$), which is highly flammable.

5.1.1 Properties of hydrogen gas

Hydrogen gas ($\text{H}_2(\text{g})$) easily ignites in oxygen gas ($\text{O}_2(\text{g})$) or air and produces water (H_2O) according to:

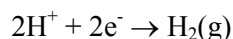


Oxygen gas (O_2) can be produced electrochemically but is of course also present in the ambient air.

Hydrogen gas is the lightest of all gases and is therefore quickly dispersed which also means that it is diluted quickly. Hydrogen gas is free from odour and colour [40]. Hydrogen gas ignites relatively easy and is flammable over a relatively large concentration range, i.e. 4 - 75 vol-% in air (4.5 - 94 vol-% in oxygen gas) and prone to detonation in the concentration range 18 - 59 vol-% in air (15 - 90 vol-% in oxygen gas) [40]. The flame is almost invisible [40]. Clearly, hydrogen gas and hydrogen gas flames are not easily detected and represent a significant risk.

5.1.2 Production of hydrogen gas by batteries

Evolution of hydrogen gas ($\text{H}_2(\text{g})$) takes place when hydrogen in the +1 oxidation state is reduced to elementary hydrogen with the oxidation state 0 according to:



This can take place in different ways from different types of batteries if the batteries are abused, used incorrectly or if some compounds in the batteries come into contact with certain other compounds or materials. Many batteries produce hydrogen gas as a by-product but the amount of gas is typically negligible under normal operation. For batteries, five different possible modes of hydrogen gas production have been identified:

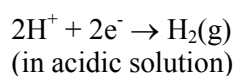
- 1) Production through reduction of hydrogen ions or water at one of the electrodes in a battery

- 2) Production through reaction between sulphuric acid and metals
- 3) Production when metallic lithium comes in contact with water
- 4) Production when hydroxide solutions come in contact with some metals
- 5) Production in lithium-ion batteries

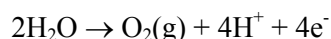
These different modes of hydrogen gas production are discussed below.

5.1.2.1 Hydrogen gas production through reduction of hydrogen ions or water at one of the electrodes in a battery

Evolution of hydrogen gas can take place through reduction of hydrogen ions (H^+) when sulphuric acid is used as an electrolyte or water (H_2O) at one of the electrodes in a battery:



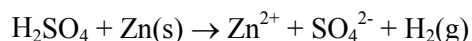
Water (H_2O) can simultaneously be oxidized at the other electrode and form oxygen gas ($O_2(g)$):



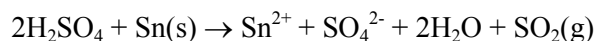
Production of large amounts of hydrogen and oxygen gas can occur during charging of secondary batteries that contain aqueous electrolytes. Some secondary batteries with aqueous electrolytes (e.g. many lead-acid, nickel metal hydride, and nickel cadmium batteries) have systems where oxygen gas can be reduced back to water and at the same time prevent formation of hydrogen gas during charging. However, excessive over-charging, a deficiency in the battery, or the absence of a system allowing recombination of the gases back to water, can result in formation of hydrogen and oxygen gases that are released from the battery during charging. Even during normal operation of VRLA (valve regulated lead-acid) batteries, small amounts of hydrogen gas are released from the batteries [41].

5.1.2.2 Hydrogen gas production through reaction between sulphuric acid and metals

Hydrogen gas ($H_2(g)$) can also be produced through reaction between sulphuric acid (H_2SO_4) and many metals such as zinc (Zn) or iron (Fe). Using zinc (Zn) as an example the reaction can be written as:



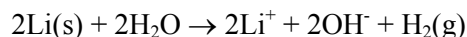
Concentrated and hot sulphuric acid (H_2SO_4) can also produce sulphur dioxide (SO_2) in contact with a few metals. Using tin (Sn) as an example this reaction can be written as:



Hydrogen gas evolution (and evolution of sulphur dioxide (SO₂(g))) could take place if batteries containing sulphuric acid (H₂SO₄) begin to leak acid that will come into contact with some other metals.

5.1.2.3 Hydrogen gas production when metallic lithium comes in contact with water

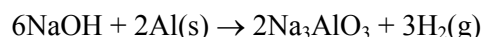
Evolution of hydrogen will also occur if metallic lithium (Li) comes into contact with water (H₂O) according to:



Hydrogen gas can then easily ignite. Metal will normally not burn spontaneously with water (unless the metal is finely divided) [42]. However, lithium metal can ignite if heated [42].

5.1.2.4 Hydrogen gas production when hydroxide solutions come in contact with some metals

Hydrogen gas production will also occur if strongly basic solutions like hydroxide solutions, e.g. solutions of sodium hydroxide (NaOH) or potassium hydroxide (KOH), come into contact with some metals such as aluminium (Al). This can be described, using sodium hydroxide as an example, as:



Potassium hydroxide solutions are used as electrolytes in several types of batteries and leakage of such electrolyte could possibly result in the production of hydrogen gas if the electrolyte comes into contact with aluminium (Al).

In batteries containing zinc (Zn) as electrode material and an alkaline electrolyte (e.g. alkaline batteries and silver oxide zinc batteries), zinc will slowly oxidize and produce hydrogen gas in the battery [14] but the amount of gas is typically negligible under normal operation. However, if the battery is located in a sealed container (such as water proof compartments) without venting possibilities, hydrogen gas levels can be so high that the gas can be ignited [43].

5.1.2.5 Production in lithium-ion batteries

When lithium-ion batteries vent after abuse, hydrogen gas together with other gases are released [44, 45], as described in more detail in section 5.2 “Flammable compounds in lithium and lithium-ion batteries”. It is likely that hydrogen gas is formed in the decomposition reactions of the electrolyte (that consists of a lithium salt in a mixture of organic solvents).

5.1.3 Estimation of the amount of hydrogen gas that can be produced from a battery

The amount of hydrogen gas that can be produced from a battery under different circumstances can be estimated using the ideal gas law in combination with some other physical laws such as Faradays’ law of electrolysis and the relationship between electric current, charge and time.

5.1.3.1 Estimation of the amount of hydrogen gas that can be produced from sulphuric acid and water

The volume of hydrogen gas ($H_2(g)$) (V_{H_2}) that can be produced from a certain amount of sulphuric acid (H_2SO_4) or water (H_2O) can be estimated from (the ideal gas law):

$$H_2SO_4: \quad V_{H_2} = \frac{R \times T \times m_{H_2SO_4}}{P \times M_{H_2SO_4}}$$

$$H_2O: \quad V_{H_2} = \frac{R \times T \times m_{H_2O}}{P \times M_{H_2O}}$$

where R is the universal gas constant (8.3143 J/(mol K), T is the absolute temperature, P is the gas pressure, $m_{H_2SO_4}$ and m_{H_2O} are the mass of H_2SO_4 and H_2O respectively, and $M_{H_2SO_4}$ and M_{H_2O} are the molar mass for H_2SO_4 and H_2O , respectively. Table 5 shows the amount of (concentrated) sulphuric acid (H_2SO_4) or water (H_2O) that is needed in order to produce 1 dm³, 10 dm³, 100 dm³, 1 m³ and 10 m³ of 4 % hydrogen gas ($H_2(g)$) at normal air pressure and at room temperature (20 °C).

Table 5 Mass of (concentrated) sulphuric acid (H_2SO_4) or water (H_2O) that is needed in order to produce a certain volume of 4 % hydrogen gas ($H_2(g)$) at normal air pressure and at room temperature (20 °C).

Produced volume of 4 % $H_2(g)$	Mass of (concentrated) H_2SO_4	Mass of H_2O
1 dm ³	0.16 g	0.030 g
10 dm ³	1.6 g	0.30 g
100 dm ³	16 g	3.0 g
1 m ³	0.16 kg	30 g
10 m ³	1.6 kg	0.30 kg

The chemical composition of different batteries will of course vary between different manufacturers and between different types of batteries but typical content of water in common batteries is listed in Table 6 based on the information in the document "Product information Primary and rechargeable batteries" from The European Portable Battery Association [16]. Lead-acid batteries contain 17 % Sulphuric acid according to the same document but it is not clear whether this refers to concentrated sulphuric acid or a water acid solution.

Lead acid battery's electrolyte typically consists of 37 weight-% sulphuric acid when fully charged [46].)

Table 6 Water content in some batteries.

Battery type	Water content weight%
Zinc carbon batteries ("brunstensbatterier")	6 %
Silver oxide batteries	2 %
Zinc air batteries	10 %
Nickel metal hydride batteries	8 %

5.1.3.2 Estimation of the amount of hydrogen gas that can be produced from electric charge

The volume of hydrogen gas ($\text{H}_2(\text{g})$) (V_{H_2}) that can be produced from electric charge (Q) when water (in excess) is electrolyzed can be estimated (by combining the ideal gas law and Faradays' law of electrolysis) from:

$$V_{\text{H}_2} = \frac{Q \times R \times T}{P \times 2 \times F}$$

where F is the Faraday constant (96485 As/mol). Table 7 shows the volume of pure hydrogen gas ($\text{H}_2(\text{g})$) and volume of 4 % hydrogen gas ($\text{H}_2(\text{g})$) that can be produced when water (in excess) is electrolyzed using different amounts of charge at normal air pressure and at room temperature (20 °C).

Table 7 Volume of pure hydrogen gas ($\text{H}_2(\text{g})$) and 4 % hydrogen gas ($\text{H}_2(\text{g})$) that can be produced from different amount of charge at normal air pressure and at room temperature (20 °C).

Charge	Volume $\text{H}_2(\text{g})$	Volume 4 % $\text{H}_2(\text{g})$
100 mAh	0.045 dm ³	1.1 dm ³
1 Ah	0.45 dm ³	11 dm ³
10 Ah	4.5 dm ³	0.11 m ³
100 Ah	45 dm ³	1.1 m ³
1000 Ah	0.45 m ³	11 m ³

In the literature, the maximum rate of hydrogen formation per ampere-hour is stated to be 0.42 dm³ at standard temperature and pressure [46]. Many smaller batteries (e.g. batteries in cellular phones and cameras, or rechargeable batteries of size AAA) have a charge (capacity) of approx. 600 - 2000 mAh. Hence, one such battery could produce approx. 0.3 – 1 dm³ pure hydrogen gas ($\text{H}_2(\text{g})$) or approx. 6 – 20 dm³ 4 % hydrogen gas ($\text{H}_2(\text{g})$) by decomposition of water.

5.1.3.3 Estimation of the amount of hydrogen gas per time that can be produced from electric current

The volume of hydrogen gas ($\text{H}_2(\text{g})$) per time ($\frac{V_{\text{H}_2}}{t}$) that can be produced from (constant) electric current (i) when water (in excess) is electrolyzed can be estimated by combining the ideal gas law, Faradays' law of electrolysis, and the relationship between current, charge and time, i.e.:

$$\frac{V_{\text{H}_2}}{t} = \frac{i \times R \times T}{P \times 2 \times F}$$

Table 8 shows the volume of pure hydrogen gas ($\text{H}_2(\text{g})$) per time that can be produced when water (in excess) is electrolyzed using different currents at normal air pressure and at room temperature (20 °C).

Table 8 Volume of pure hydrogen gas (H₂(g)) per time that can be produced from different currents at normal air pressure and at room temperature (20 °C).

Current	Volume H ₂ (g) per time
1 mA	1.2×10^{-4} ml/s
10 mA	1.2×10^{-3} ml/s
100 mA	1.2×10^{-2} ml/s
1 A	1.2×10^{-1} ml/s
10 A	1.2 ml/s

5.2 Flammable compounds in lithium and lithium-ion batteries

Lithium and lithium-ion batteries contain organic solvents that are flammable [44, 47]. Lithium-ion batteries can contain for instance propylene carbonate (PC) (flash point 135 °C), ethylene carbonate (EC) (flash point 145 °C), di-methyl carbonate (DMC) (flash point 18 °C), di-ethyl carbonate (DEC) (flash point 25 °C), and ethyl methyl carbonate (EMC) (flash point 25 °C) [44]. According to the document "Product information Primary and rechargeable batteries" from The European Portable Battery Association [16], lithium-ion batteries typically contain 1-10 % of organic solvents. Lithium batteries can contain organic solvents such as acetonitrile (flash point 5 °C), 1,2-dimethoxyethane (DME) (flash point 1 °C), and 1,3-dioxolane (1,3-D) (flash point 2 °C) [47].

It has been shown that punctured lithium-ion batteries release the electrolyte solvent together with several other gases such as hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂) and methane (CH₄) [44]. It has also been shown that gases released when a lithium-ion battery vents during heating include hydrogen (H₂), carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), ethene (C₂H₄), and ethane (C₂H₆) [44, 45].

5.3 Thermal Runaway

The temperature can, in some batteries, increase in an uncontrolled way called "thermal runaway" and can result in an explosion or a fire in the battery. Furthermore, thermal runaway can propagate to adjacent cells.

5.3.1 Thermal runaway in lithium-ion batteries and lithium batteries

There are many reports about lithium-ion batteries that have started to burn or exploded even if they have not been abused or used incorrectly. This is due to thermal runaway where the temperature increases rapidly as a result of exothermic reactions in the batteries. This has been summarized in several reports [44, 48-51] and a detailed description of the processes is complex. Temperatures when exothermic reactions can start and result in thermal runaway are cited as: 150-170 °C [50], 90 °C [48], approx. 150 °C (cobalt cathode) or 250 °C (manganese cathode) [52], 130-150 °C [49], 70-90 °C [44], 130-150 °C [51]. Such temperatures can be reached as a result of e.g. overcharging, physical abuse, thermal abuse, short circuit, and internal cell faults [44, 48-50]. When lithium-ion batteries are packed together, thermal runaway in one battery cell can induce

thermal runaway in a neighbouring cell due to heat transfer [44]. Hence, thermal runaway can propagate through a battery pack. Propagation of thermal runaway in a lithium-ion battery pack can also result in re-ignition of an extinguished fire [44]. Thermal runaway can also be delayed for long times after physical abuse and cause a fire at a later stage [44].

According to a Swedish report [50], many accidents with lithium-ion batteries in computers have in common that the computers have been placed so that ventilation has been restricted, and/or have taken place during charging of the batteries. It has also been observed that most thermal runaway reactions occur during or shortly after cell charging, i.e. when the battery is fully charged [44]. It has also been found that thermal runaway is dependent on the state of charge (i.e. thermal runaway starts at lower temperatures when the battery is fully charged) [44].

Thermal runaway has also been found to be a result of the presence of microscopic metallic particles in the batteries that can result in short circuit in the batteries [52, 53]. Manufacturers of such batteries have been forced to recall large quantities of lithium-ion batteries or computers containing lithium-ion batteries. Such batteries can of course still be present in old electronic equipment.

In order to avoid thermal runaway, lithium-ion batteries might have several different safety devices such as charge interrupt devices and positive temperature coefficient switches [44, 49, 51].

Thermal runaway can also occur in lithium batteries and it has been reported to occur at temperatures of approx. 150 °C [48].

5.3.2 Thermal runaway in non-lithium containing batteries

Thermal runaway can also occur in lead-acid batteries, nickel cadmium batteries, nickel metal hydride batteries, and nickel iron batteries mainly during charging [14].

5.4 Electrical fire risks

5.4.1 A battery's capability to store energy

Modern batteries have the ability to store a lot more energy than in previous times and therefore will also be a greater hazard if they are handled during abnormal conditions. Hence batteries will be a hazard if they are not carefully designed or if they are abused.

To illustrate this point, let us make a comparison between a “Sony Stamina Plus” alkaline battery and a “Boston Power Swing” lithium-ion battery, as shown in Figure 1. The size of these batteries is almost the same. The difference between these cells is that the cell voltage of the alkaline battery is 1,5 V and is 3,7 V in the lithium-ion battery. The capacity in the alkaline battery is 2,5 Amp hours (Ah) and 4,4 Ah in the lithium-ion battery. The fully charged alkaline battery contains 13500 Joules of energy and the fully charged lithium-ion battery contains 58608 Joules, i.e. the ability to store energy is approximately four times higher in the lithium-ion battery than in the alkaline battery.



Figure 1 “Sony Stamina Plus” alkaline battery on left and “Boston Power Swing” lithium ion battery on the right.

In the automotive field of battery application, it is critically important to have batteries which are able to store a high amount of energy and in this area the lithium-ion batteries have been developed to be as effective as possible, e.g. today there are several “pouch cell” batteries intended to be used in automotive applications. Two examples of pouch cells are shown in Figure 2.



Figure 2 Two examples of lithium-ion pouch cells.

This type of battery cell has a typical capacity of between 20-40 Ah. A 40 Ah 3,6 V pouch cell contains 518400 Joules of energy. This is about 38 times more energy than in the alkaline battery used in the previous comparison.

Battery operated hand tools have also gone through an impressive development phase regarding the ability to store more energy. A battery pack for an ordinary battery operated screwdriver can have a voltage of 18 V and a capacity of 3 Ah. In this case the fully charged battery contains 194400 Joules of energy.

This increase of energy storage will obviously create a higher hazard if the batteries are handled in an unintended way and if the batteries are not equipped with safety protection systems.

5.4.2 Safety protection systems in batteries

There are many different types of safety protection systems for batteries that may or may not be built into the batteries themselves, their chargers, and/or control techniques such as Battery Management Systems (BMS). The risk of fire depends heavily on the type and effectiveness of the protection system used, for example, in short circuit testing of 9 volt

alkaline batteries the results depend on the brand and model of battery but the batteries may look outwardly identical.

To prevent overcharge, reversed polarity or short circuit there are some protective devices used. Those devices are either placed within the battery or outside the battery. Many of the control devices are placed outside the battery since both the current and the voltage can be sensed in the battery charger.

According to Linden's Handbook of Batteries [14], in some batteries thermal devices are used to cut off or reduce the current:

- Thermostat (Temperature Cut off TCO). This device operates at a fixed temperature and is used to cut off the charge (or discharge) when a pre-established internal battery temperature is reached. TCOs are usually resettable. They are connected in series within the cell stack.
- Thermal fuse. This device is wired in series with the cell stack and will open the circuit when a predetermined temperature is reached. Thermal fuses are included as a protection against thermal runaway and are normally set to open at approximately 30-500°C above the maximum battery operating temperature.
- Positive Temperature Coefficient (PTC) device. This is a resettable device, connected in series with the cells, whose resistance increases rapidly when a pre-established temperature is reached, thereby reducing the current in the battery to a low and acceptable current level.
- Circuit Interrupt Device (CID). Some cells also incorporate a CID which interrupts the current if the internal gas pressure in the cell exceeds specified limits.

Also, some batteries are provided with safety vents. If a cell overheats, the safety vents will open if there is a chemical reaction that will build up pressure inside the battery.

5.4.3 Short circuit

A short circuit may arise if a low resistance connection between the positive and negative electrodes occurs. According to Ohms law $I=V/R$ (I : Current [A], where V = Voltage [V] and R = Resistance [Ω]), the current will increase proportionally with the decrease of the resistance.

A short circuit in a battery will cause a high current flow and the battery will be discharged very quickly. This rapid discharge will heat up the battery due to the high current flow. The current flow in a short circuit depends on the internal resistance in the battery while the external resistance in the material is causing the short circuit.

If we assume that a battery is perfect, with no internal resistance (0Ω) then, according to Ohms law, this battery would be able to supply an infinite amount of current. In the real world there are no perfect batteries and they will always have some internal resistance reducing the ability to supply current. The internal resistance will be different depending on the cell chemistry and the battery's ability to supply high current is also dependant on the kind of protection systems that are built in into the battery.

5.4.3.1 External Short circuit

An external short circuit will occur if a low resistance path between the two poles of the battery is present. This can happen during disassembling an electronic device where a

battery is incorporated into the product. If a metallic tool, for example a screw driver, is causing a short circuit between the two poles of the battery, a very high current will flow through the screwdriver from the positive pole to the negative pole of the battery.

It is obvious that the risk for external short circuit in a battery is much higher at a recovery plant where a lot of used batteries are stored together than the risks associated with normal use. The probability of an external short circuit is also increased as the batteries might be placed in metallic bins and containers and the poles of the batteries are not provided with insulating tapes or other protective measures.

Figure 3 shows the current during the initial second in a short circuit test of a lithium-ion battery cell. As seen, the current is on the order of 3000 A. During this short circuit the temperature in the battery cell will increase and the internal heating could cause the cell to exceed thermal stability limits [44].

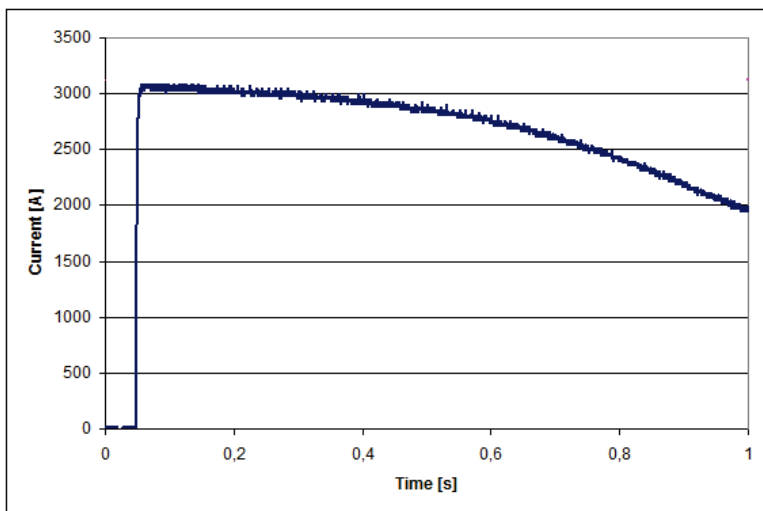


Figure 3 First second of a short circuit test of a lithium-ion battery cell.

This short circuit test could simulate a real scenario when a battery is thrown into a metallic container and a short circuit occurs between the poles through the metal in the container. It could also simulate a short circuit between the poles through the metal in another battery's casing.

The consequence from the short circuit is shown in Figure 4. The short circuit test was performed on a lithium-ion pouch cell. The normal thickness of the cell is approximately 8 mm. During the test the cell started to build up gas inside the pouch and after a few minutes the cell ruptured and vented.



Figure 4 Ruptured lithium-ion pouch cell.

We can only speculate about the potential consequences of such an incident in real life, although we can note that in this case high temperatures can cause a fire in other materials in close vicinity to the battery. Another possible scenario is that the cell itself will start a fire. The third possible scenario is that the exposed lithium in the cell will react to water and cause a fire.

It is widely known that a short circuit in a 12 V lead acid car battery will create a very high current and cause a risk that an electric arc will occur. Tests at SP show that lead acid batteries can supply current exceeding 1000 A during a short circuit.

A discussion of lead acid battery hazards is found in Taylor [54], an excerpt follows:

“If a shorted battery cell does not clear the external short, the electrical connection between the battery terminals allows for a very rapid chemical reaction as the sulfuric acid converts the lead and lead dioxide to lead sulfate. Now the electrical energy is not dissipated externally, but internally in the form of heat. The resulting temperature rise inside the battery cell literally destroys the cell and actually may vaporize the battery materials including the electrolyte and lead.”

Friedrich and Ramirez [55] gives the example of a Duracell 9 Volt Alkaline battery type PP3 that was short circuited with a wire which resulted in a current of 4.2 amps measured through the wire. In this case this was enough current to make the wire glow. They also report on some incidents with batteries that had been exposed to short circuit tests. One battery had been exposed to a short circuit test one and a half weeks previously and had since been lying on a desk for a week when one of the cells explosively ruptured without any electrical, mechanical or any other form of contact.

5.4.3.2 Internal Short circuit

Charging of lithium-ion batteries can result in formation of metallic lithium dendrites that can cause internal short-circuit of the batteries [44]. It has also been reported that the presence of microscopic metallic particles in lithium-ion batteries has resulted in short circuit and thermal runaway of the batteries [52, 53].

An internal short circuit can also appear if the battery is exposed to physical abuse caused, for example, by wheel-loaders and industrial trucks. If a battery is exposed to mechanical crush or other damage it is very likely that an internal and/or external short circuit will occur and safety protection systems associated with the battery may become disabled.

5.4.4 Over discharge

Lithium-ion batteries have a specific working range regarding the voltage. A discharge deeper than the specified cut of voltage will cause damage to electrodes and current collectors. If a lithium-ion battery is discharged below its stated cut off voltage, thermal runaway may occur when the battery cell is recharged.

Another scenario that could possibly occur in the recycle process is forcing a battery into reversed polarity. This could happen if a battery is thrown into a waste bin or a container without insulating tape or other protective measures on the poles. The poles of one battery could then come into contact with the poles of another battery. In this case the battery with the highest state of charge (SOC) will start to recharge the battery with lower SOC. This scenario could result in reversed polarity and thermal runaway. Depending on the

built-in protection systems in the battery and the ability to create thermal runaway this scenario could be possible in nickel cadmium batteries, nickel metal hydride batteries, and nickel iron batteries.

5.5 Reaction of metallic lithium

As described in section 5.1 lithium metal will react with water and form hydrogen gas. Lithium metal can also ignite if heated [42, 56].

5.6 Reaction of sulphuric acid

If sulphuric acid (H_2SO_4) leaks from a battery it can react with many metals and produce hydrogen gas ($H_2(g)$) (and also sulphur dioxide (SO_2) in some cases). Hydrogen gas in contact with oxygen gas ($O_2(g)$) or air can then ignite as described above.

Concentrated sulphuric acid (H_2SO_4) will also react vigorously with many organic compounds. Concentrated sulphuric acid will also generate a lot of heat when mixed with some materials such as water or organic materials that will result in a temperature increase.

5.7 Fire risks due to contact with water

A possible scenario in the recycling chain is that batteries are stored outdoors in containers or barrels without lids or with leaking lids. A possible consequence is that the batteries will be stored in barrels or containers along with water.

The conductivity of ordinary tap water it is not very high. This means that tap water does not have the ability to lead high currents if you immerse a battery into the water. Sea water has a much higher conductivity and thus higher ability to lead the current if a battery is immersed in it.

SP has conducted some experiments to evaluate the current flow in different types of water, i.e. deionized water, tap water and sea water (36g NaCl/kg H_2O). The goal was to determine what will happen if a battery with the terminal voltage 12 V is immersed and the gap between the two poles is 10 centimetres. The resistance between the two poles will depend on the conductivity of the different types of water. Table 9 shows the results of these tests.

Table 9 Immersion of 12 V batteries in different types of water.

Type of water	Voltage [V]	Resistance [Ω]	Current [A]
Deionized water	12	$5,9 \times 10^4$	$2,0 \times 10^{-4}$
Tap water	12	$4,0 \times 10^3$	$3,0 \times 10^{-3}$
Sea water (36g NaCl/kg H_2O)	12	12	1,0

The results from these tests show that the current is not very high even if the battery is immersed in sea water and it is quite unlikely that a battery would rupture or cause a fire because of a short circuit in water.

A more probable risk with batteries in contact with water would be that the batteries are physically/mechanically damaged in some way and a chemical reaction occurs between the substances inside the battery and the water. Other failure modes include the increased spread of liquids from leaking batteries with the water which then would increase corrosion on other batteries and thus increase the leakages further.

Another possible risk with batteries stored in containers filled with water is the production of hydrogen gas during electrolysis of water (see section 5.1.2.1). If a battery is immersed in water it will start to create hydrogen at the negative pole and oxygen will appear at the positive pole. Assuming tap water is similar to rain, there will be a current of about 3mA when a 12 V battery is placed in rain water. According to section 5.1 this would result in 3.6×10^{-4} ml/s of hydrogen, i.e. slightly more than 1 ml hydrogen per hour, i.e. a very low hydrogen production. If there are air pockets inside the container there is a possible risk for build-up of hydrogen and an explosion if a spark occurs inside the container.

The risks associated exposure to mist, fog, ice and frost are similar. Even if the water contains a lot of salt, we will not have such high current that it will damage the battery. The literature contains no information on safety issues concerning ice and the potential for short circuits. Instead, the major risk is that batteries with aqueous electrolytes will freeze and thus perhaps start leaking.

5.8 Exposure to Extreme temperatures

As discussed above, lithium-ion and lithium batteries can undergo thermal runaway at relatively high temperatures. The onset temperature varies in the literature (from 70 to 250 °C), and is also different from battery type to battery type. At low temperatures, batteries containing aqueous electrolytes can possibly freeze and this can in rare cases result in cell rupture due to expansion of the electrolyte. If the temperature then rises above the freezing point, electrolyte will leak from the battery and this can result in a short-circuit of other batteries, and possibly also formation of hydrogen gas as described above. It is not clear if this is a significant problem.

The freezing temperature of batteries is dependent on the battery type and electrolyte. In lead-acid batteries, the sulphuric acid content in the electrolyte will vary during charging and discharging, and the electrolyte will contain much more sulphuric acid when charged than when discharged. As a result, the freezing point of the electrolyte will be much lower for a charged lead-acid battery than for a discharged battery (where the electrolyte will have a freezing temperature close to pure water (0 °C)). It is therefore difficult to give a general freezing temperature of electrolytes, but aqueous electrolytes typically have freezing temperatures below the freezing temperature of pure water (0 °C). In a literature source, the recommended storage temperature for most batteries in general is 15 °C with extreme allowable temperature of -40 °C to 50 °C [57]. However, temperatures as low as -40 °C will likely result in freezing of many aqueous electrolytes.

5.9 Accidental activation of reserve batteries

If reserve batteries are activated unintentionally, for instance by water-activated reserve batteries coming in contact with water, a fully charged battery is suddenly obtained unwittingly. Improper handling of such a battery would pose a fire risk in the same way that improper handling of any charged battery would.

6 Fires in recycling facilities and recycling chain

Over the years many fires have occurred and some of them reach the news. The listings here are not complete but only contain the information gained from searching on the web and literature databases and information from STENA and Elkretsen. The conclusions cited are the conclusion made in the articles, the citation here does not mean that the authors of this report agree with the conclusion.

It should be noted that there are many reports of fires in laptops [50] and mobile phones. However, fires that have occurred while charging are not relevant for this study and have not been included below.

6.1 Fires in Sweden

The Swedish rescue service journal Sirenen [58] reported three incidents in issue nr 7 in 2003:

- An explosion occurred in a paper collection bin. It turned out that the bin was equipped with a sensor to recognize when the bin was full. Water had entered the sensor's two lithium batteries through a safety opening. The battery exploded during extinguishing of a fire in the container and exited as a projectile through an opening of the container. It was concluded that extinguishing water had entered the safety hole, reacted with the lithium and caused the violent reaction.
- An employee at an office noticed smoke coming out of the paper shredder. When the fire was extinguished small pieces of a 9 volt ("smoke alarm") battery was found in the shredder, it had probably been placed there by mistake.
- A man had changed batteries in the TV remote control. The batteries were of button type. The batteries were placed in a box in a cupboard together with other batteries. Later a bang was heard and a fire started. The fire was extinguished quickly. It is possible that the button battery short circuited a 9 V battery and thus heat was created.

Several other reports are available in Sirenen over the years;

- The fire alarm and sprinkler was activated in a rather new office building in 2007 [59]. When the fire brigade arrived at the site the fire had been extinguished by the sprinkler system. The fire had started in a plastic basket used for storing used batteries.
- Five different remote control fires are reported, three in 2001, one in 2002 and one in 2007 [60]
- A cell phone laying in a bed started to burn. According to the user the phone was turned off and not being charged [61].

In the middle of March in 2010 a fire started in a bin with primary lithium batteries. The date of the batteries had expired and were thus removed from their packages and put into a bin unused and thus probably fully charged. A popping sound was heard from the bin after a while and the bin was warm. The bin was thus moved out to cool down but was placed next to a wall. The bin ignited and damaged the nearby wall. The personnel noticed the fire and tried to extinguish it without success. The barrel was moved out to the yard, the rescue service was called and extinguished the fire.

6.2 Fires internationally

It is difficult to obtain detailed or reliable data concerning fires internationally. The work presented in this section of the report has been based on direct contacts with some sources in the US and through internet searches. Fires that make it to the news (internet) are generally large fires but it can be difficult to determine the cause of these fires due to the nature of information available. A selection of battery related fires is discussed below, the selection being based both on information availability and significance of the fire.

6.2.1 Fires in battery recycling facilities

Fire incidents in battery recycling facilities in the US, Canada, and UK have been reported over the past 15 – 20 years. It can be difficult to determine the cause of these fires, even if facility staff is present when the fire starts; in most cases the cause of the fire is inferred from whatever information is available after the fire has been extinguished. The major reported fires in battery recycling facilities are listed in Table 7 together with relevant information regarding their cause if it exists.

Table 10 Fires in recycling facilities

Year	Location	Battery Type	Cause
1995	Trail, Canada [62]	Mixed	
2000	Trail, Canada [62]	Mixed	
2000	Trail, Canada [62]	Mixed	
2000	Trail, Canada [62]	Mixed	
2002	Clarence, NY [63]	Lithium	Storage in 55 gal drums, moisture?
2007	Thorold, Canada [64]	Lithium	Storage in containers, moisture?
2008	Trail, Canada [62]	Mixed	
2009	Trail, Canada [62]	Lithium	Storage in earth mounds.
2011	Basingstoke, UK [65]		
2011	Cartersville, GA [66]		Batteries in containers shipped to facility.

The cause of the first five fires at the Trail, Canada battery recycling facility was not reported in newspaper accounts that are currently available.

6.2.2 Other fires caused by batteries

There is a significant amount of anecdotal information on the internet concerning battery fires in consumer appliances (computers, telephones, hair dryers, power tools etc.) but these occur during charging or use and have not been included here.

Little information is available concerning fires initiated in batteries in other situations. One exception is the work that has been done concerning battery fires during air transportation. The FAA has collated a significant number of incidents, not only in the US, which have occurred during air transport or in conjunction with air transport (e.g. loading and unloading, storage while waiting for transportation) [67]. In a report from the FAA published in 2012 a total of 132 incidents are reported, some of which are significant. The proportion of these incidents which occurred on cargo planes or passenger planes is shown in Figure 5a. The relative proportion of different battery types involved in the incidents is shown in Figure 5b.

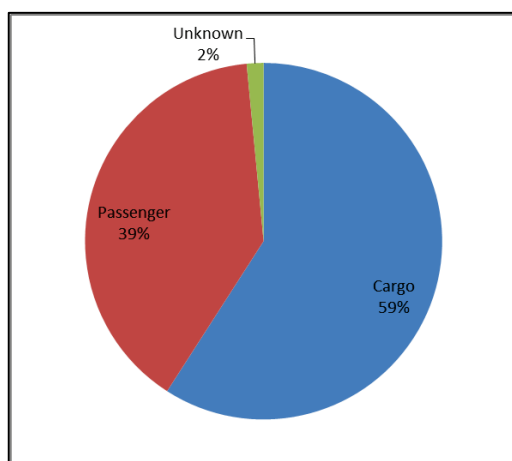


Figure 5a Proportion of incidents on cargo or passenger planes

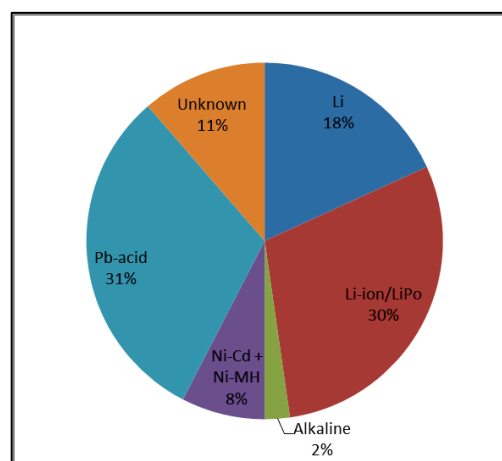


Figure 5b Types of batteries involved in the incidents

As can be seen from Figure 5b the majority of incidents occurred on cargo vessels. Further, the major category involved in the incidents was rechargeable batteries (lead acid batteries were involved in 30% of all incidents, and Lithium-ion/Lithium polymer in 30% or all incidents). Lithium batteries (primary and secondary) were involved in almost 50% of all incidents.

Approximately 50% (68 cases) of the incidents were minor, involving only the release of smoke. In approximately 25% (31 cases) of the incidents some scorching or melting was also seen while in the remainder of cases (33 cases) flames were seen. In the final category there are specific examples where extinguishing was attempted but unsuccessful and a large fire was the result. Table 10 contains a selection of major incidents. In most cases the fire is caused by a short circuit of the battery terminals, often due to poor packaging. In some cases a fire is caused by damage being inflicted to the package containing the battery either by impact (e.g. 28th April 1999 when a pallet containing 60 000 batteries was dropped during unloading) or other harm (e.g. 11th December 2007 when a customs official damaged a battery pack with a knife during a routine inspection).

Table 11 Summary of some major aviation incidents

Date/source	Type of Battery	Aircraft	Incident summary
7 Sept/2008 UK CAA report	Pb-acid	Passenger	Battery-powered wheelchair burst into flame as it was being unloaded, cause unknown
14 Feb/2008 US TSA report	Unknown	Passenger	Fire in overhead bin caused by flashlight battery
27 Dec/2007 UPS incident report	alkaline	Cargo	Package spontaneously combusted on the conveyor belt at a UPS package sort facility, cause unknown
11 Dec/2007 UPS incident report	Li-ion/LiPo	Cargo	Customs inspection of package with a knife accidentally cut the battery which then caught fire.
5 Jun/2007 DOT report #2007070001	Li-ion/LiPo	Passenger	Laptop computer burst into flames. Fire was suppressed with hand held extinguisher but difficult to extinguish
22 Mar/2007 FAA report	Unknown	Cargo	Battery pack caught fire at FedEx facility due to manufacturing error
1 Mar/2007 Australian CASA report	Li-ion/LiPo	Passenger	US mail package from EBay containing batteries was transported on a passenger flight. Caught fire at the Sydney mail gateway.

17 Jul/2006 FedEx report	Li-ion/LiPo	Cargo	Package caught fire during customs clearance
15 Jul/2006	Pb-acid	Cargo	Package caught fire during unloading, terminals unprotected
2 Jun/2006 China CAA report	Li-ion/LiPo	Passenger	Fire in the cargo hold of a passenger plane. Extinguishers released. Cause found to be a package containing LiPo batteries. Possible short circuit with cargo ceiling where burn marks were seen.
15 May/2006	Li-ion/LiPo	Passenger	Fire in extra battery for computer
4 Oct/2005 UK CAA report	Unknown	Passenger	Fire in domestic flight after package caught fire due to activation of power drill
14 Sept/2005 FAA report	Pb-acid	Cargo	Package dropped during loading causing fire
14 Sept/2004 FAA report	Pb-acid	Cargo	One battery caught fire when terminals came into contact with metal tape due to poor packaging
4 Sept/2004 FAA report	Li	Passenger	Flashlight battery fire due to faulty installation
21 Jul/2000	Li	Passenger	Small battery powered toys involved in fire in a bag where a bottle of cologne had broken causing short circuit
24 Aug/1999 Taiwan aviation report #ASC-AAR-00-11-001	Pb-acid	Passenger	Fire due motorcycle battery, passenger had both battery and petrol in hand luggage.
4 Jun/1999 FAA messages	Li	Cargo	Fire during offloading due to short circuit in batteries packaged with a steel rod
28 Apr/1999	Li	Passenger	120 000 Li batteries were transported on 2 pallets. One pallet dropped during unloading leading to a fire.

7 Fire spread in waste

Fires in waste or other large piled storage are in many cases difficult to extinguish and produce a significant amount of toxic fumes. Extinguishment can take several weeks. In some cases the pile must be dug out in order to extinguish it.

In Sweden one fire occurred at the STENA recycling facility in Malmö in 2009, the fire started in a mattress but spread to the electronic waste, the fire started at 8.45 and was extinguished at 18.15, 50 persons participated in the extinguishing.

In Japan a fire started in a landfill in February 2004 that burnt for 13 months [68]. Japan uses landfills extensively as they would like to minimise dioxin emissions due to incineration.

Self heating is one major cause of fire in piled storage. The root cause is that some kind of heat is evolved in the pile from the beginning, this can be friction heat that comes with the material put into the pile or some biological, drying or chemical process that produces the heat. Depending on the size of the pile this heat is accumulated and other processes can start that produce even more heat until finally the pile ignites through auto-ignition. Data on self-heating and ignition of EE waste piles is scarce. Focus of this area has usually been on food or other biological goods that are stored or transported in bulk such as wood pellets for heating or the storage of harvested hay. With the increasing demand of storage for recycling there is a fear that these types of fires will increase. Clearly there is a data gap here when it comes to different types of waste [69]. Several studies have been conducted on pelleted Refuse Derived Fuel (RFD) mainly in Japan as there have been some severe fires including one fire that resulted in two explosions, the final one killed two fire fighters and the roof of the storage was detached [70].

Several studies are also available on different types of bio waste such as wood pellets. Biological material have special self-heating problems as humidity absorption, bacteria and fermentation processes produce heat which can cause temperatures up to 75°C if the heat is not transported away and then chemical oxidation processes start. Shimizu et al. [68] reports on self-heating start temperatures for RFD and car shredder dust (SD). The results reported are, however, difficult to transpose into useful data for a recycling plant and storage of recycling material. In addition EE recycling material is of a different constitution consisting mainly of plastic.

Electronic waste consists often of different kinds of plastics that can be ignited readily and fire spreads easily in this material. Large scale tests results are not available but Lönnermark and Blomqvist [71] conducted four tests on electronic waste stored in the typical collection cages used. In these test a propane burner was used as an ignition source for 2 minutes. The maximum heat release rate (about 1.7 MW) of the material was reached after 4-5 minutes. The ignition source in these cases was large as the purpose was to measure emissions and not to study ignition performance.

The requirements on ignition performance on IT-equipment and TV sets is low in Europe, with only a HB requirement on the casing [72]. This means that the outer material on much of the electronic waste is easy to ignite and one can expect a rapid fire growth should a fire start.

8 Recycling chain

Recycling processes differ between countries. A short description of the process in Sweden is given here as an example. Both the collection of batteries and the electronic waste collection are described as batteries are available in both.

8.1 Battery collection

In Sweden battery collection boxes are placed together with other waste collection bins nearby shopping areas etc. in order to make it easy for people to recycle. In some cities “battery-pipes” are also available inside shopping-malls, see Figure 6. There are also places where collection is organized by the building owner for apartment buildings. The small boxes/bins are placed in the open or in specially built sheds and are made of metal or plastic, while the battery pipes are indoors and made of plastic. How often these boxes or pipes are emptied varies considerably depending on the number of people who use them and the organization around it. In some instances they are emptied when full or otherwise they could be emptied when other recycling bins are emptied.

There are also larger boxes available at recycling stations in Sweden (there is usually one or two such stations in a city). Such a box is shown in Figure 7. These boxes are then transported to two places in Sweden there the batteries are sorted into seven fractions which are then transported to recycling facilities.



Figure 6 Battery collection pipe to be placed in shopping mall



Figure 7 Larger battery collection box.

Even if it is easy to hand in the batteries most people probably store their old batteries at home for a while and the same is also true for most offices. This means that the batteries can in many cases have started to leak acid etc. during “home storage” or even while in the equipment.

8.2 Electronic waste

Electronic waste (TVs, toys, CD-players, tools, etc.) should be handed in at larger recycling collection sites. They are typically put in steel cages (about 1-2 m³) or other containers. There is usually no staff controlling what is handed in, the consumers put the equipment in the collection boxes themselves.

The electronic waste is then transported by truck to a number of sorting facilities called pre-treatment facilities. At the pre-treatment facility the truck tips the cage and the material falls into a hopper as seen in Figure 8. After the hopper material is transported to a sorting belt where operators manually filter out material that should be removed like cables, circuit boards, batteries etc., see Figure 9. The operators smash the equipment with a hammer in many cases in order to be able to remove the items that should be sorted out. The batteries that are removed are placed in containers. On some sites batteries are sorted by type in this step (lead alone, Ni alone, etc.). On other sites all the batteries are put in the same vessel to be sorted later in the day (or next few days). The sorting here depends on the labelling of the battery, there can of course be instances when it is difficult to read the labelling and thus a limited mixing of batteries is possible in the bins. Some sites do not sort the batteries at all.



Figure 8 Handling the cages with EE



Figure 9 Sorting Electronic waste

The amount of material and equipment that passes the operators every day is massive and ever changing due to the rapid development in electronic equipment. Even if the operators are extremely efficient it is not possible to reliably sort out every battery manually.

The batteries that have not been sorted out follow the electronic waste to the shredder and defragmentation (defrag) facilities. At these facilities the material can be left in the open for up to two weeks as different types of waste are processed on different days or it can arrive in a container and be emptied into the process immediately, see Figure 10 to 12. In the defrag all material is ground into small pieces and then transported around in centrifuges and other sorting facilities in order to sort out material that is worth recycling, see Figure 13. In the end there is also manual sorting. The actual grinding process is constantly sprayed with water to cool the material and system and to minimize airborne dust.



Figure 10 Material arriving to the site to be grinded and sorted



Figure 11 Shuffling around the material



Figure 12 Material to be placed on belt to go to the grinding process



Figure 13 The large grinding mill

9 Application to the recycling chain

The recycling chain is almost the ultimate form of misuse/abuse of batteries. The batteries are stored mixed together under different temperatures and humidity, with no insulation protection on the poles. The batteries can in many cases be old and may already have started to leak acid or other liquids. They can also be exposed to liquids coming from other equipment like oil etc. On top of this they risk being grinded to small fragments if not sorted out beforehand. Given this it could be surprising that the number of fires is so limited. One mitigating factor is probably that the fire risks are larger when the batteries are fully charged, which is probably the reason why the number is relatively low.

9.1 Hydrogen gas emission

Chapter 5.1 gives examples of the potential for different batteries to produce enough hydrogen to create a flammable mixture. One rather common storage place for used batteries is barrels. A barrel is typically 200 litres in volume. Given the numbers in chapter 5.1 we can see that only a rather low amount of sulphuric acid or battery charge is needed, i.e. the energy in one fully charged AAA battery is sufficient to produce 20 litres of flammable hydrogen/air mixture. The time needed to produce the hydrogen based on electrolysis is, however, significant and thus the fire risk is not very large. The risk of hydrogen production is probably higher due to leaking batteries.

Hydrogen has a very large flammability range (4-75%) and any hydrogen release can potentially be ignited. Hydrogen is very easy to ignite, a small spark is sufficient which could be caused by e.g. some movement of the batteries. Similarly a small heating of the mixture could also cause a fire. In addition, hydrogen has a negative Joule Thompson coefficient that means that it heats itself up on release instead of, as most other gases, cooling down. The processes that produce the hydrogen can in some cases also produce heat.

Hydrogen disperses rapidly and a major factor in preventing hydrogen build-up is sufficient ventilation.

9.2 Weather exposure

In the WEEE recycling chain the batteries risk being exposed to all kinds of weather, including temperatures below zero, direct sunlight, rain, hail or snow.

Direct sunlight can raise the temperature of a surface to 70°C which is reported as a possible thermal runaway temperature for some batteries. This temperature is also above the 54°C referred to maximum storage temperature and potential thermal runaway temperature for Ni-Cd batteries according to the US army. In addition many of the batteries contain flammable electrolyte with a flashpoint below 70°C as discussed in Section 5.2. This gives a fire risk in particular in conjunction with moving of the material, which can create sparks.

Temperatures below 0°C mainly result in a potential for aqueous electrolytes freezing, resulting in a rupture of the cell, which then results in leakage of electrolyte and possible corrosion of other cells. Leaking electrolyte poses a fire risk, again in particular together with mechanical sparks which could be caused by shuffling of the material.

Rain, snow and hail all help possible leaking electrolyte and other liquids to spread in the waste pile and thus potentially increase the number of different liquids that are mixed and also possible further leakage of liquids due to corrosion.

9.3 Mechanical abuse

In the recycling chain many batteries are handled in an unintended way and therefore the probability to short circuit the batteries is high. This includes both external and internal short circuit. Both types of short circuit pose a large fire risk if they occur on fully charged batteries. On the other hand, most of the batteries are already used/discharged and therefore the energy in most of the batteries is low and the probability that a battery should cause a fire is reduced.

The steps taken to remove the batteries from the recycling chain can also result in mechanical damage so that electrolyte is released from the battery. This also poses a fire risk as many electrolytes are flammable.

The trucks and tractors used to shuffle the material at the sites produce both sparks and friction heat when used in the material. The ignition potential from sparks from different materials varies; examples of different sparks and their ignition potential is listed in Ignition Handbook [73]. This book also contains some discussion on frictional heat needed to ignite different flammable gas mixtures.

Another possible fire cause is self-ignition of the waste pile which has been initiated as friction heat, as described in Section 7.

Article 15 of the Batteries Directive (2006/66/EC) [37] concerns the safe storage of batteries before/during the recycling process, among other battery recycling topics. This document requires all fluids and acids to be removed from batteries to be treated prior to storage. The treatment/storage sites must also have impermeable surfaces, suitable weatherproof covering or clearly labelled, leak-proof containers. Notably, Article 15 does not mention external short circuit protection.

9.4 Mixing risks

A general recommendation is that it is safest not to mix different types of batteries during storage. However, no information has been found in the literature concerning what battery types should not be stored together. Based on the chemical content in different batteries some risks when mixing battery types have been identified and these are given below.

9.4.1 Mixing of lead-acid batteries that contain sulphuric acid with batteries that contain zinc metal or some other metals including metallic casings

If lead-acid batteries that contain sulphuric acid are mixed with other battery types (that contain a lot of metal in the casing) hydrogen gas evolution can occur if leaking acid comes in contact with metal. In primary batteries that have a zinc metal electrode, the casing itself can be used as an electrode, i.e. the casing is made of metallic zinc (as in, for example, zinc carbon batteries). Hence, if these batteries are stored together with batteries that leak sulphuric acid, flammable hydrogen gas can be produced.

9.4.2 Mixing of lead-acid batteries that contain sulphuric acid with organic material

If lead acid batteries that contain sulphuric acid are mixed with organic material and the batteries start to leak, a vigorous reaction can take place between concentrated sulphuric acid and many organic materials.

9.4.3 Mixing of lithium batteries and lithium-ion batteries with other batteries

Lithium batteries that contain metallic lithium should be kept separated from batteries that contain aqueous electrolytes in order to prevent contact between metallic lithium and water that will produce hydrogen gas. It is difficult to say if scenarios where metallic lithium comes in contact with water are likely to occur in practice. Some lithium batteries also contain thionyl chloride that reacts with water (forming hydrogen chloride and sulphur dioxide that are not flammable).

Since lithium batteries contain metallic lithium and (highly) flammable organic solvents, and one lithium battery type contains thionyl chloride that reacts with water, special fire-fighting tactics may be necessary for these batteries compared to other batteries.

Similarly, since lithium-ion batteries contain flammable organic solvents and often lithium hexafluorophosphate, special fire-fighting tactics may be necessary for these batteries compared to other batteries.

9.4.4 Mixing of batteries that contain hydroxide solutions with metallic aluminium

Mixing of batteries that contain potassium hydroxide solutions as electrolyte with metallic aluminium can produce hydrogen gas if leakage of electrolyte occurs, since hydroxide solutions can produce hydrogen gas when the solution comes into contact with metallic aluminium. It is difficult to say if scenarios where metallic aluminium comes in contact with hydroxide solution are likely to occur in practice.

10 Outlooks for the future

The amount of batteries in different consumer applications will most likely continue to increase. In addition, battery development is extremely rapid and one would expect an increasing number of battery types to match the increasing number of applications being developed. Clearly, this has a high potential to increase the number of fires caused by batteries. It is therefore of key importance to develop collection systems that minimise the fire risks. In a perfect world one would have systems for automatic discharge of the batteries (that would also restore energy) and a means to automatically identify batteries in any equipment during the recycling chain (this would save a lot of material used in batteries). The former would not be technologically difficult but no system presently exists. The latter is presently not solved, or easily solvable, given that batteries have no simple identifying characteristic that makes them stand out relative to other fractions.

Another possibility, that would encourage an increased consumer motivation to recycle would be to include a deposit tariff on existing batteries. If consumers were given a return on their deposit when disposing of the battery this would motivate a higher collection percentage. In the case of aluminium cans the recycling rate is over 60% largely due to

the deposit system with extensive collection facilities available in most grocery stores. This would solve some of the problems associated with batteries being left in the fraction sent to grinding and defrag but would not solve the risks associated with mixed storage of batteries waiting for destruction or recycling.

Battery technology is evolving quickly nowadays and large amounts of research money is spent on finding batteries that have higher power, longer lifetime and reliability together with increased safety. The rapidly increasing use of batteries also results in development of new safety devices and safer chemistries which will eventually also have a beneficial impact on mitigating the fires in the recycling chain.

General advice for storage and handling of batteries include: store in a cool, dry and well-ventilated area; do not mix batteries; do not short circuit them; and protect them from mechanical damage. In Sweden the WEEE recycling chain advice has not been rigorously implemented. It is, however, difficult to judge which of the factors has a larger impact on the fire risk- if it is the weather exposure or the mechanical treatment from the trucks for unsorted batteries.

The battery directive [6] includes advice for safe storage of batteries before/during the battery recycling process. This includes e.g. requirements for all fluids and acids to be removed before storage, weatherproof covering or clearly labelled leak-proof containers. This directive does not apply for the WEEE recycling chain but the batteries collected in this chain will hopefully end up in the battery-recycling chain and it could be useful to implement some of these measures also for the storage and transportation of batteries in the WEEE chain.

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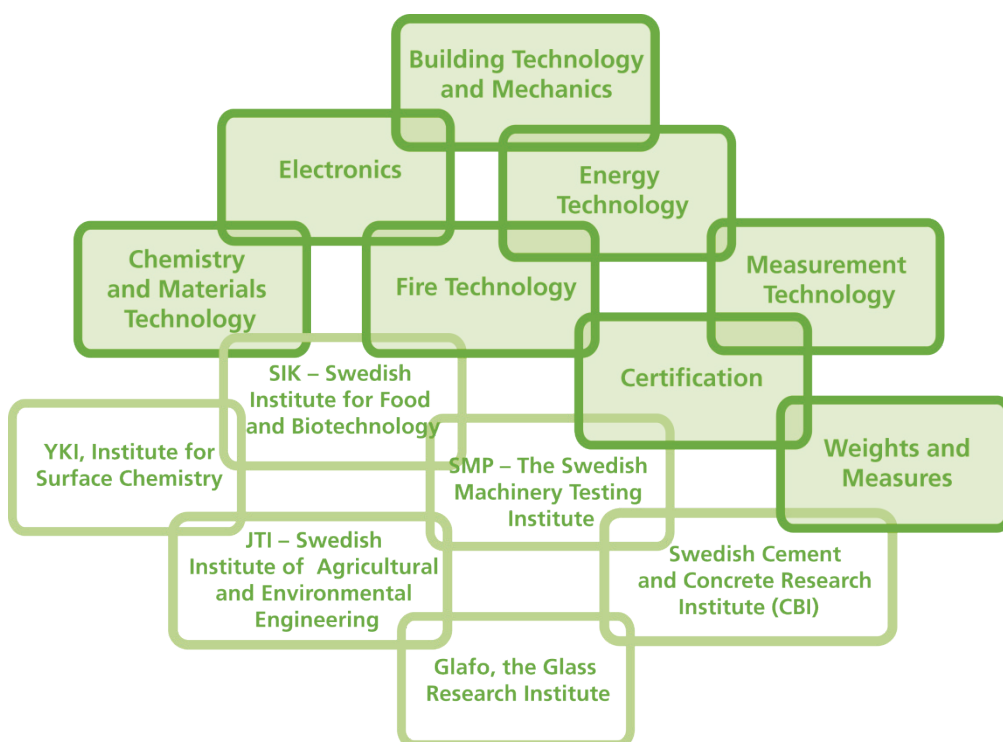
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