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Exploration of future battery types and safety

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Contents

Summary

Since batteries are crucial to a future-proof energy transition, governments and industry are investing heavily in the development of new energy storage systems. An important part of this is the search for alternative materials to replace, for example, lithium, nickel and cobalt which are now used in lithium-ion batteries. This report outlines some key developments in the field of large-scale battery storage from a safety perspective.

The conclusion is that risks continue to exist for every new type of battery. In principle, the new generation of lithium-ion batteries has the same risks as the current lithium-ion batteries. The safety issue of thermal runaway with its associated effects of toxic clouds, battery fire and a vapour cloud explosion or a flash fire, continues to exist for all lithium-ion subtypes. Although the introduction of solid-state batteries will reduce the probability and severity of these effects, the effects listed will not be completely eliminated. As the effects are of a comparable nature and the systems are structured in the same way, we expect only limited improvement in the degree of suppressibility compared to current lithium-ion batteries.

The safety risks of sodium-ion batteries have been found to be similar in nature as those of lithium-ion batteries. Scientific experiments have shown that sodium-ion battery cells can also go into thermal runaway. However, since their energy density is lower, the speed and severity of this thermal runaway are probably slightly less than they would be with lithium-ion battery cells. Because sodium-ion battery systems also consist of carefully packed battery cells, suppressibility is also expected to be frustrated by the fact that it is hardly possible to cool the cells during an incident. The introduction of the first lithium-ion solid-state batteries will soon be followed by the introduction of sodium-ion solid-state batteries, resulting in better safety.

As for redox flow batteries, it has been found that all subtypes contain toxic substances as the system's active substance. As a result, the safety risks of redox flow batteries are mainly of a toxic nature. No evidence of thermal runaway was found for this main category of batteries and the active substances, including liquids, are not flammable (with the exception of the hydrogen in hydrogen-bromine batteries). An incident involving a redox flow battery will therefore be of a similar nature to a toxic liquid leakage or spill, in a sense. The current Dutch IBGS (hazardous materials incident response) procedures can offer a guideline for suppressing such incidents.

Introduction

Background

The first introduction of lithium-ion neighbourhood batteries in the Netherlands raised some concerns with the fire service.[1] In recent years, NIPV and the fire service in the Netherlands have learned more and more about the technology and the safety risks of lithium-ion batteries and how to respond to any incidents involving these batteries. However, technical developments and innovations in new batteries are following each other in rapid succession. The number of battery systems for stationary storage, also referred to as energy storage systems (ESS), and the number of electric vehicles will also increase dramatically in the coming years worldwide, including in the Netherlands. It is important for the fire service in the Netherlands to be prepared for this.

The times when and the locations where renewably generated energy, such as solar power and wind power, is produced or consumed are not always in sync with each other. Since energy storage systems, such as batteries, are needed to ensure security of supply, they are crucial to a future-proof energy transition. Governments and companies are investing heavily in developing new energy storage systems, partly to accelerate the development of fully-fledged alternatives to fossil fuels.

An important part of this is the search for alternative materials to replace, for example, lithium, nickel and cobalt which are now used in lithium-ion batteries. One goal of this search is to develop new materials with higher energy density, enabling more energy to be stored. On the other hand, manufacturers are looking for alternatives to the metals currently used in batteries, as they are scarce and their extraction sometimes involves poor working conditions.

In order to achieve all goals, new types of battery with new materials or new properties are being developed. This report outlines some key developments in the field of large-scale battery storage from a safety perspective.

Objective

The goal of this study is to outline the development of new batteries from a safety perspective and look ahead for their impact on companies, the fire service and the Dutch safety regions.

To achieve this goal, the study was conducted in three phases, each with their own objectives:

1. Gathering background knowledge: Mapping and obtaining a view of the main categories of new types of battery that have reached an advanced stage of development and might potentially be marketed in the Netherlands within ten years from now.

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[1] EenVandaag TV show, Fire Service worry about proliferation of neighbourhood batteries. https://eenvandaag.avrotros.nl/item/brandweer-bezorgd-over-wildgroei-buurtbatterij/.

2. Literature review: Reviewing the scientific literature on the safety of each new main category of battery type.
3. Safety analysis: Using the knowledge from the scientific literature and our own expertise to forecast the probability, severity of the effect and degree of suppressibility of an incident involving these new types of battery.

Scope

- Our focus is limited to battery chemistry. This means that we look at safety intrinsic to the type of battery and the materials used. Developments within the other components of energy storage systems, e.g. the Battery Management System (BMS) and connectors, are not part of our study.
- Several potential materials or subtypes are being developed for every new type of battery. Which potential materials will be 'winners' and will be marketed to a relatively large extent is often not known yet. Moreover, it would not work to study dozens of subtypes in detail. The types of battery discussed in this report were defined partly on the basis of external expertise. The following types of batteries were selected: lithium-ion, sodium-ion and redox flow.
- The size of battery systems will grow in the future. This report does not include any research into specific safety risks related to increases in scale.
- Our focus is on the safety of the battery types, not on the safety involved in the extraction of raw materials and the associated working conditions.

1 Research method

Thousands of research institutes, companies and universities all over the world are working on battery technologies of the future. Many news items are produced on this subject, discussing breakthroughs and introducing all kinds of new terms, from nanotechnology and solid-state to air batteries. As a result, any searches for new batteries come up with too many hits, more than can be studied. The study was therefore conducted in three phases, each with its own approach.

1.1 Phase 1: Gather background knowledge

The first phase was about gathering basic background knowledge on different approaches within new battery developments. For this purpose, two interviews were held with Professor Mark Huijben, Professor of Nanotechnology for Energy Storage at the University of Twente. The key questions for these interviews were:

1. On the basis of which grounds can developments that have reached an advanced stage be distinguished from those that still have a long way to go? In response, current battery developments were first explained and then new developments were discussed.
2. Which new types of battery are considered to be the most promising and have reached an advanced stage of development? The guideline used was that the new battery technology should have the potential to be launched into the market for energy storage systems and electric vehicles within ten years.

The main types of battery that were identified through this multi-stage analysis were the new generation of lithium-ion (lithium-silicon, solid-state lithium-ion and lithium-metal), sodium-ion and redox flow batteries. This report therefore deals with these three types.

1.2 Phase 2: Literature review

The basic information gained here was used to carry out a targeted literature review of the safety aspects of these new types of battery as the second phase of this study. We looked for scientific literature about the safety and the stage of development of new types of batteries. Many of the articles we found dealt with the microscopic issues involved in developing the materials. This is because laboratory proof of a material's stability and usability is a prerequisite for its further implementation. Although stability provides an indication for safety, it was sometimes hard to concretely verify which causes of failure and which effects were, or were not, ruled out. Since the available literature was still limited for certain aspects, partly because these are new technologies, some authors of articles and developers of batteries were consulted in order to fill in any missing knowledge. For example, there was an email correspondence with three experts from Tianjin University, China, who carefully monitor developments concerning solid-state batteries and specifically study their safety. There were also phone calls with developers in the Netherlands who produce new materials for lithium-ion batteries. Since the redox flow battery is a relatively new system for the Netherlands and involves different safety risks to lithium-ion batteries, a working visit was paid to a developer of batteries in the Netherlands, as this would offer added value. The experts contacted were particularly asked for their expectations regarding the effects in the event of an incident. A key question here was about the extent to which thermal runaway might still occur in the new types of batteries.

1.3 Phase 3: Safety analysis

The information from the orientation phase and the in-depth literature review was used to conduct a safety analysis during the third phase of the study. The key question was what the practical safety effects of the types of battery studied would be. Since this study concerns new types of battery, they have not been involved in any incidents yet, as far as we know. Therefore we based the safety analysis on our own knowledge and experience and our own interpretation (deduction) of the results from the literature review.

Phase 2 consisted of a thorough study of the operation and internal structure of all battery types and the materials in them in order to obtain a good understanding of each type of battery. This was followed by a safety analysis based on conclusions from the literature review. The scheme in table 1.1 was used for this. This was based on our findings from the literature review. This table links probability, effect and suppressibility of an incident to two criteria. For example, higher stability of materials implies lower incident probability. To be able to visualise the probability, the severity of effects and the degree of suppressibility to a certain extent, radar charts were used. The input for these charts was based on the safety analysis in the concluding section of each chapter on a main category of battery type.

Table 1.1 Safety analysis criteria

Aspect	Criteria and explanatory notes
Probability	**Stability of materials** The stability of batteries is generally divided into thermal, electrical and mechanical stability. If a material has a higher stability margin, this means that it has a tolerance for a wider temperature range or voltage difference. It is then less likely to fail or decompose in case of high temperatures or an electrical fault, for example. **Intrinsic failure mechanisms** This refers to failure mechanisms that are specific to the battery system or design and can occur autonomously while charging or discharging.
Effect	**Nature of effects** The known effects are fire, explosion and a toxic cloud. Which of these three effects are possible is identified for each new type. **Impact of effects** The severity of the effects may differ for different subtypes, depending on the materials used and the nature of the effects.
Suppressibility	**Thermal runaway** Currently, suppressibility is greatly frustrated by the fact that thermal runaway can take place in lithium-ion batteries, due to which the incident becomes self-sustaining although active incident response is taking place. **Hazards for incident responders** Suppressibility can be worsened if there is an explosion or toxic exposure hazard.

2 Lithium-ion

2.1 Introduction

The industry is bound to continue to use lithium-ion batteries for the next ten years, given the current effort to further develop lithium-ion batteries until the limits of the theoretically ideal battery have been reached. This is based on the development of new, advanced materials. A new subtype is created if a new material is discovered and made available for any of the basic components (anode, cathode or electrolyte) (Battery 2030+, 2022; Lu et al. 2019). In essence, the principle of the battery remains the same, but the battery's efficiency increases as new, advanced materials with finer and more complex structures are added. The term ‘nanotechnology’ has come up in this context; this means that materials are further optimised down to the smallest level.

2.2 System description

2.2.1 Working principle: anode (-), cathode (+) and electrolyte

The battery cell is the basic unit of a lithium-ion battery. Battery cells come in three different forms: cylindrical, pouch and prismatic cells (Figure 2.1). Figure 2.2 sketches an example of a cylindrical cell, i.e. the most common form of battery cell. Several different layers of materials rolled up within the battery cell form the active components of the battery cell.

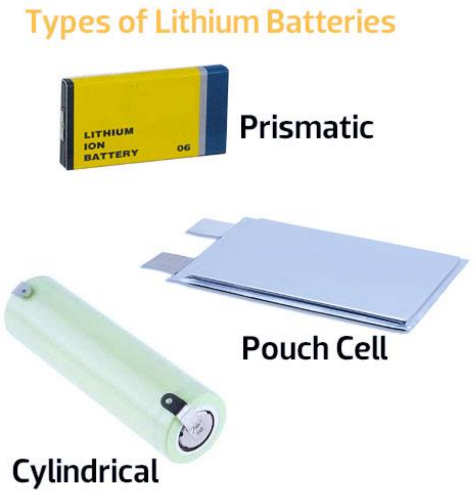


Figure 2.1 Prismatic, pouch and cylindrical battery cells (source: https://www.hylasermachine.com/news-battery-welding.html)

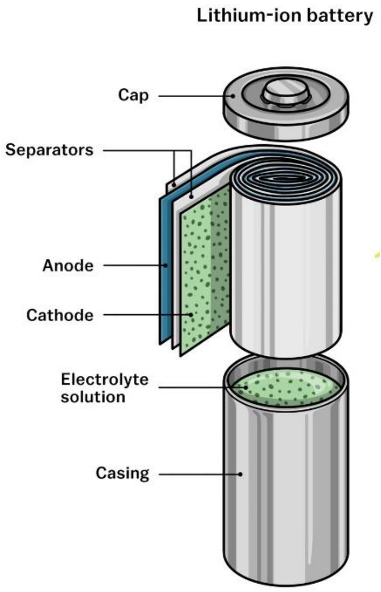


Figure 2.2 The interior of a cylindrical lithium-ion battery cell (source: Eliana Rodgers for vox.com)

The three active components of a battery cell are the anode, cathode and the electrolyte. Since the electrolyte of current battery cells is a liquid, it is necessary to provide a separator to physically separate the anode and cathode. The anode is connected to the battery's negative pole and the cathode to the positive pole. The electrolyte is located in between. Different materials can be chosen for all three components, creating different subtypes. Figure 2.2 shows a lithium-ion battery cell. The anode in today's battery cells is made of graphite and the cathode is made of material consisting of lithium compounds. The electrolyte is liquid and consists of a mixture of lithium salts, solvents and additives.

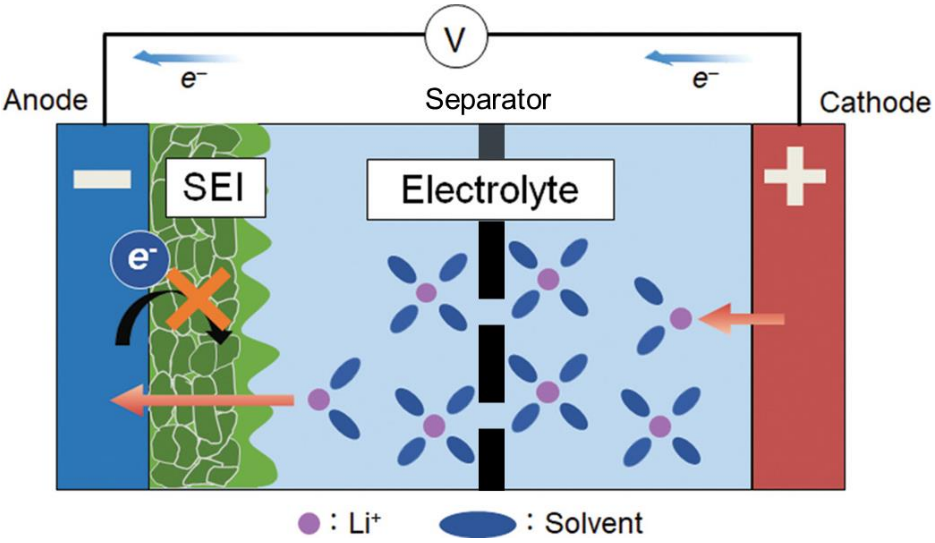


Figure 2.3 Schematic view of a lithium-ion battery (source: Takenaka et al. 2021)

Figure 2.3 gives a schematic view of the three basic components (anode, cathode and electrolyte), the separator and the Solid Electrolyte Interphase (SEI) and illustrates their operation. The figure shows how the charging process works with lithium ions (Li+) and electrons (e-). This link gives an animated presentation of this process.

During use, lithium ions move back and forth through the electrolyte, from the cathode to the anode and vice versa. At the same time, electrons leave the battery cell and flow through the electrical circuit to form an electric current. This reveals the primary property of the electrolyte: it allows ions to pass through, but not electrons. Figure 2.3 gives a schematic presentation of the direction when charging. When charging, the process direction is from cathode (+) to anode (-) until all the lithium ions and electrons come together again in the anode and the battery is fully charged. An external power supply (V) such as a wind turbine or solar panel is needed to provide the energy while charging. This process is reversed when discharging, i.e. the process direction is from anode (-) to cathode (+), and the power supply can be replaced by a motor that consumes the energy.

Formally speaking, batteries are electrochemical cells. This means that electrochemical reactions take place while they are being charged or discharged. For lithium-ion batteries, the electrochemical reaction takes place between the lithium ions and electrons. Whenever a neutral lithium atom (Li) departs from the anode or cathode, it is split into a positive lithium ion (Li+) and a negative electron (e-). On arrival, the electron and ion unite into a lithium atom. What is important for this process is that the electrochemical reactions take place in a controlled manner. This requires the battery cell to be stable, i.e. no unwanted effects or reactions are allowed to take place.

The Solid Electrolyte Interphase (SEI) acts as a protective layer here. The SEI is not a factory-attached layer of material, but it is a microscopic deposit layer that is formed, and attaches to the anode, during the first few charging cycles. This is because there is a voltage difference between the anode (negative pole) and the cathode (positive pole). A carefully compounded electrolyte with the right properties is necessary to ensure that the battery cell remains stable. The SEI serves to reinforce this. Among other things, the SEI prevents uncontrolled jumping of electrons when the battery cell is full, which is also shown schematically in the figure, making it an important factor for the stability of battery cells.

Finally, there is also a separator in the electrolyte of all current battery cells with liquid electrolytes. Since the electrolyte is liquid, the separator prevents physical contact between the anode and the cathode. The separator's function is thus to prevent internal short circuits. It does not play any further role in charging and discharging or in the electrochemical reaction. Batteries with a solid-state electrolyte will also become available in the future, doing away with the need for the separator.

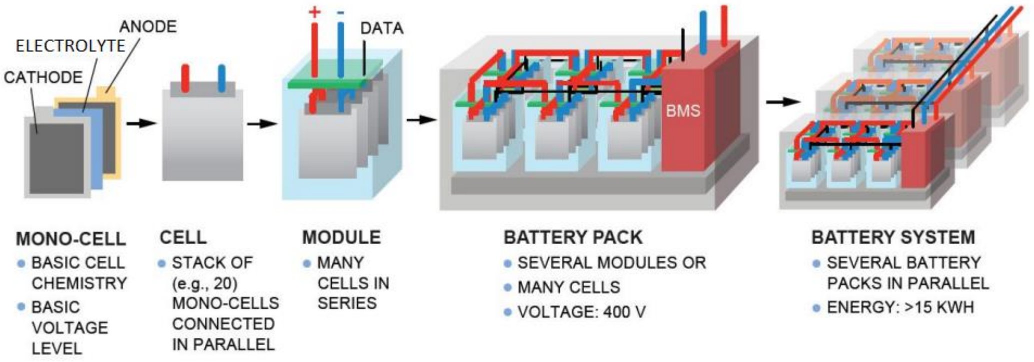
Table 2.1 summarises the functions of the three basic components (anode, cathode and electrolyte) and the SEI.

Table 2.1 Active components of battery cell and SEI

Anode (-)	SEI	Electrolyte and separator	Cathode (+)
Negative pole and place where all lithium particles are when the battery is fully charged.	Microscopic deposit layer on the anode and necessary in order to assure the stability of the battery cell.	The electrolyte is the medium through which lithium ions move back and forth. In the case of liquid electrolytes, there is also a separator in the electrolyte. The separator is an ion-permeable membrane that prevents physical contact between the anode and the cathode.	Positive pole and place where all lithium particles are when the battery is fully discharged.

2.2.2 Composition of the energy storage system

An energy storage system can be built by combining several battery cells. Figure 2.4 sketches the composition of a lithium-ion energy storage system. Here, the battery cell forms the basic unit; it consists of an anode, cathode and electrolyte. Several battery cells together form a battery module. These battery modules are assembled into a battery pack and connected to a Battery Management System (BMS). The BMS is responsible for the battery's operation within operational limits and hence for safety. At present, the BMS mainly regulates and controls at module level. In an ideal situation, it should regulate and control at the individual cell level, as this enables an anomalous battery cell to be detected at an early stage and switched off immediately. In line with this, there are developments with 'smart batteries’ that can monitor themselves as it were (Battery 2030+). A larger battery system can consist of several interconnected battery packs.



Source: Alexander Otto, Fraunhofer Institute for Electronic Nano Systems ENAS, presentation of May 30, 2012, "Battery Management Network for Fully Electrical Vehicles Featuring Smart Systems at Cell and Pack Level."

Figure 2.4 Composition of a lithium-ion energy storage system

2.3 Types of system

2.3.1 Current systems: variations to the cathode

Table 2.2 shows the current lithium-ion subtypes. The names of current lithium-ion subtypes refer to the cathode material. This is shown in Table 2.2. So far, most innovations to the lithium-ion battery concerned the cathode. The main challenge for the cathode is essentially that it should achieve the highest possible energy density with abundantly available elements. Attempts are also being made to give the powder particles that make up the cathode the optimum size. Currently, nickel, manganese and cobalt are mainly used in lithium-ion battery cathodes. Since manufacturers want to reduce the amounts of nickel and cobalt used because of price fluctuations and the unethical aspects of mining, LFP (Lithium Iron Phosphate) is being used more and more; it is associated with less scarcity of materials and ethical extraction issues (Huijben, 2022).

Table 2.2 Current subtypes of lithium-ion: variations to the cathode

Subtype	Anode (-)	Electrolyte	Cathode (+)
NMC	Graphite	Liquid, consists of a mixture of: > Lithium salts > Solvents > Additives	Lithium nickel manganese cobalt oxide
NCA			Lithium nickel cobalt oxide
LMO			Lithium manganese oxide
LTO			Lithium titanate
LFP			Lithium iron phosphate

New materials for the anode and electrolyte will also be added in the future. Variations of this will then become possible and, as a consequence, the names will no longer always be linked to the cathode material. Therefore, the following paragraphs clearly indicate what the expected new subtypes – identified by their basic components – will involve.

2.3.2 Lithium-silicon: new material for the anode

The anodes of lithium-ion batteries originally consist of graphite, and only slight improvements have been made to this over the years. Switching over to a new material is needed in order to significantly improve energy density. Silicon has reached an advanced stage of development (Table 2.3).

Table 2.3 Lithium-silicon: new material for the anode

Subtype	Anode (-)	Electrolyte	Cathode (+)
Lithium-silicon	> Graphite-silicon nanoparticles > Pure silicon	Current liquid electrolytes	Current cathode materials

Lithium-silicon is the term for the first new subtype of lithium-ion. In the case of lithium-silicon, nanoparticles of silicon are added to the anode or the entire anode is made of silicon. The main problem regarding the application of silicon is that silicon expands and contracts during use. Therefore, it is expected that a small amount of silicon will be added to the graphite in these anodes. These anodes are already being made. Once a suitable solution to the expansion and contraction has been found, they will be replaced by pure silicon anodes (Sun et al. 2022).

2.3.3 Solid-state lithium-ion

Solid-state lithium-ion

In solid-state batteries, the liquid electrolyte has been replaced by a solid-state electrolyte. ‘Inorganic solid electrolytes’ (ISE) are considered to be a promising candidate material, since this type of material has a high ionic conductivity (allows lithium ions to easily pass through) and is non-flammable. Currently, much is expected of garnet- (a group of minerals) and sulphide-based ISE (Guo et al. 2022).

Furthermore, a solid takes up less space. This reduces the amount of packaging material needed whilst increasing energy density in terms of kWh per kilogram of battery cells. Lots of experiments are being undertaken with all kinds of potential materials and composites. Which of these materials will be ‘winners’ is not yet known, but many companies are claiming that they have reached an advanced stage of development of solid-state batteries (Huijben, 2022).

Table 2.4 Solid-state: new solids for the electrolyte

Subtype	Anode (-)	Electrolyte	Cathode (+)
Hybrid solid-state lithium-ion	Current and new anode materials	Combination of liquid and solid electrolytes, as a precursor to a fully solid electrolyte.	Current and new cathode materials
Solid-state lithium-ion		Solid-state electrolyte > Inorganic solid electrolytes > Garnet-based > Sulphide-based > Polymer-based	

Hybrid solid-state

Often ‘hybrid solid-state’ batteries are classified as a type of solid-state batteries too. To a certain extent, hybrid solid-state, quasi solid-state or liquid-solid batteries are a kind of intermediate step towards batteries with a fully solid electrolyte. The use of a hybrid electrolyte means that less liquid electrolyte has been used, possibly in combination with a solid-state electrolyte. Some manufacturers have already managed to set up production of hybrid solid-state batteries (Yu et al. 2022).

2.3.4 Lithium-metal (all-solid-state lithium-ion)

The anodes of lithium-metal batteries are made of pure lithium metal. This maximises anode capacity. However, the problem is that lithium ions settle unevenly on the surface of the anode when a pure lithium-metal anode is being used, forming unwanted and protruding branching, i.e. dendrites. Dendrites can grow through the interior of the battery cell from the anode and cause internal shorting. Dendrite formation is also a problem encountered in current lithium-ion batteries, and anodes of pure lithium metal actually show the strongest dendrite formation. A solution to this problem is sought by developing all kinds of interlayers and coating layers (Huijben, 2022). In addition to this, a modified electrolyte is also being looked into (Zhang et al. 2021).

Expectations are high for the combination of a solid-state electrolyte and a pure lithium-metal anode (Huo et al. 2021), since this combination would improve both energy density and stability. This also means that it will not be until after the introduction of solid-state batteries that the first (solid-state) lithium-metal batteries are expected, also referred to in the scientific literature as all-solid-state. Lithium-sulphur has been mentioned on some occasions as well. Lithium-sulphur usually refers to a future lithium-metal subtype where sulphur is used as a new cathode material.

Table 2.5 Lithium metal: anodes of pure lithium metal

Subtype	Anode (-)	Electrolyte	Cathode (+)
Lithium metal All-solid-state	Pure lithium metal	Solid-state electrolyte > Inorganic solid electrolytes > Garnet-based > Sulphide-based	Current and new cathode materials
Lithium-air	Pure lithium metal	As yet unknown	Air

Lithium-air
The anode of the theoretically ideal battery is made of pure lithium metal and its cathode is made of air. That is why lithium-air is listed at the end of the end of the timeline of new subtypes of lithium-ion batteries. This theoretical concept has been studied for quite some time, but so far there is no stable design suitable for production (Matsuda et al. 2022). Therefore, no concrete statements can be made about this theoretically ideal subtype at this point in time.

2.4 Literature review of safety: current situation

Thermal runaway is considered to be the main safety risk of current lithium-ion batteries (Zhang et al. 2021). This section explains the concept of thermal runaway based on our current knowledge of lithium-ion batteries.

2.4.1 Thermal runaway

The interior of the battery cell is designed to remain stable under normal operating conditions. This is important because electrochemical reactions take place all the time when charging and/or discharging the battery cell. However, if the internal components or the protective coating layer (SEI) are damaged, the electrochemical process is disrupted. This can have several thermal, electrical or mechanical causes. Examples of thermal causes include overheating or an external fire. Electrical causes may be overcharging, deep discharge or forced charging with excessively high currents. Piercing and crushing are examples of mechanical causes. An important note here is that the development of thermal runaway and the nature of the effects can be the same for all three causes (Christensen, 2022).

Ageing or degradation of the battery cell may also be of influence. Plating and dendrite formation are examples of this. Plating means that lithium ions are forced when charged with an excessively high charge current or at low temperatures. This means they are not absorbed into the anode but form a lithium metal deposit layer on the anode instead. In the long run, plating can promote dendrite formation.

In the initial stages before thermal runaway occurs, the battery cell heats up, disrupting the normal electrochemical process in the cell. The normal process is replaced by unwanted chemical reactions. These unwanted processes can start from a temperature as low as 60 °C. They are exothermic reactions in which heat and large amounts of toxic and flammable gases are released. This causes increasing damage to the interior of the battery, and the battery cell heats up (Wu, 2021). Generally, the SEI decomposes first, after which the electrolyte, the anode and finally the cathode decompose. Once a temperature of approx. 200 °C is reached – depending on the subtype – the exothermic reactions and heat generation self-reinforce until the situation becomes catastrophic. This is the tipping point where a situation of thermal runaway is reached**.**

In essence, the unwanted process is a self-sustained process from then on and the unwanted reactions (with heat and pressure build-up due to the gases formed) steadily increase. The consequences are that the heated battery cell bursts open and the flammable and toxic gases formed are released (Figure 2.5). In addition, the electrolyte will evaporate, leading to more gas being formed (Jin et al. 2021).

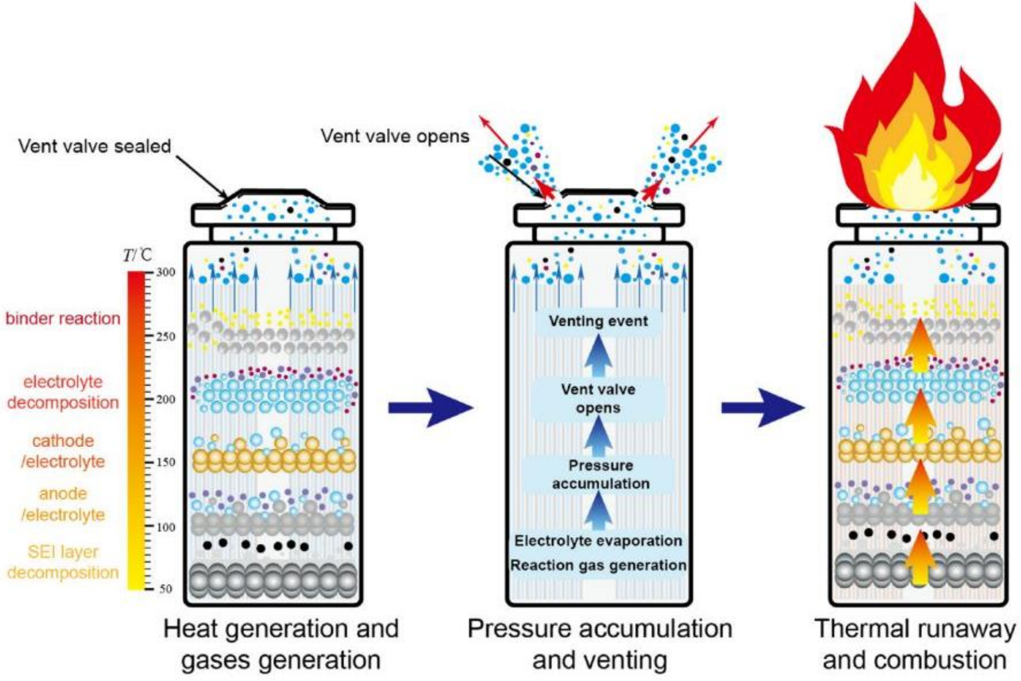


Figure 2.5 Thermal runaway (Kong et al. 2022)

Thermal propagation (neighbouring battery cells being exposed to heat radiation) enables the process to spread to other battery cells, causing them to successively reach a state of thermal runaway as well (Figure 2.6).

Figure 2.6 Thermal propagation (source: evservice.eu)

2.4.2 The effects of thermal runaway

The effects of thermal runaway can be:

- a toxic and flammable gas mixture being released
- battery fire
- vapour cloud explosion / flash fire

A toxic and flammable gas mixture being released

Flammable and toxic gases are released during thermal runaway. When battery cells burst open, a popping sound is produced, and when the gases are released a hissing sound can be heard.

Some of the gases and vapours released are listed in Figure 2.7 on the next page. The size of the letters here indicates the volume released of each gas. THC here is short for Total Hydrocarbon Content. Both the gas volumes and the gas percentages vary strongly depending on the type of battery and, consequently, the incident in question (Baird et al. 2019; Christensen 2022). Furthermore, only a limited amount of scientific research has been conducted on the exact composition, ratio and volume of the actual gas mixture. In addition, it is difficult to analyse the entire gas cloud in an experimental setup and the cloud ignites during most incidents. Since only part of the gas mixture was analysed in each of the papers and experiments reviewed, the results of different scientific papers were combined to compile this figure. The gas composition also depends on the subtype and the State of Charge.

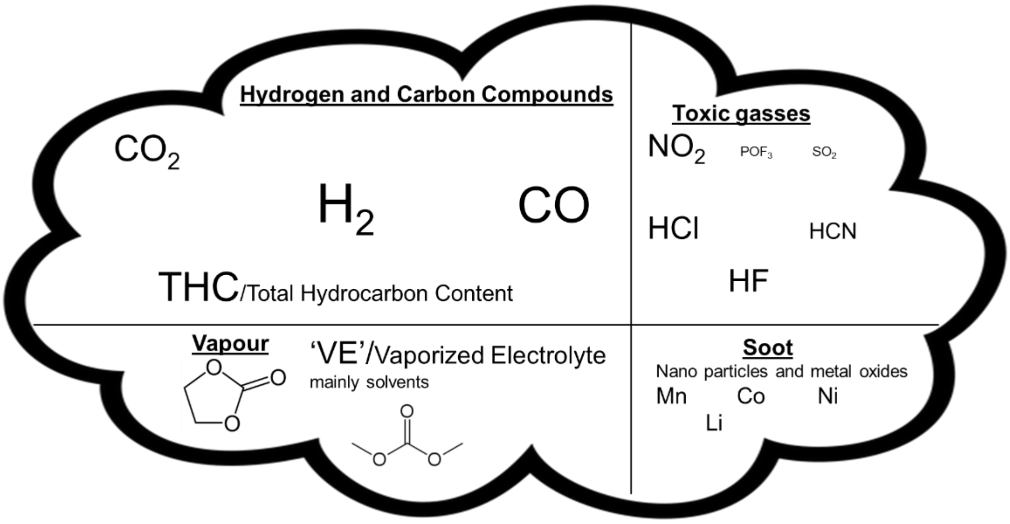


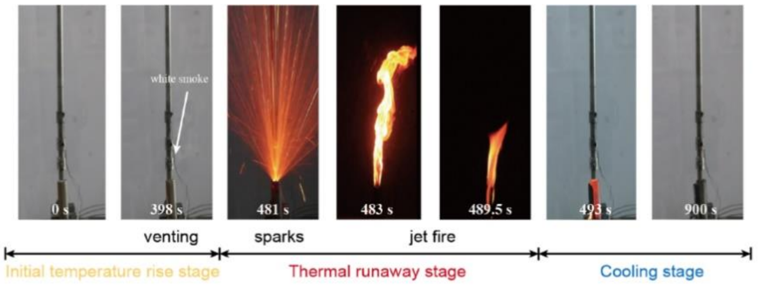
Figure 2.7 Lithium-ion thermal runaway - toxic and flammable gas mixture

Battery fire

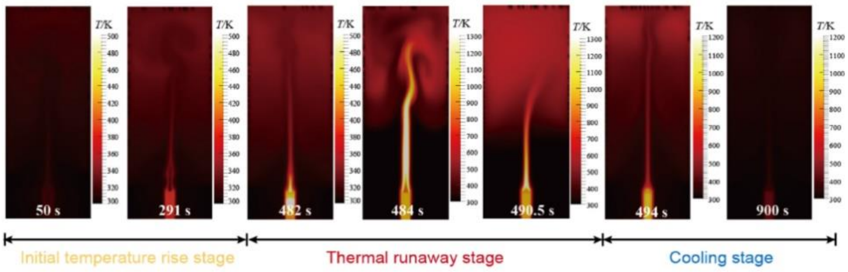
In most cases, the flammable gases ignite immediately, causing a fire in a battery pack. During a battery fire, flares and explosions occur intermittently. This is explained by the fact that the individual battery cells burst open or explode in succession. The fire behaviour of a single battery cell because of thermal runaway can be described in three phases as shown below in Figure 2.8 (Kong et al. 2022):

1. the battery cell heats up until the point where ignition takes place
2. the battery cell bursts open; this is accompanied by an intense flare
3. a decreasing phase.

As the heat spreads to other battery cells (thermal propagation) during the fire, new battery cells and subsequently battery modules reach a state of thermal runaway over and over again. As a result, an incipient fire of one or a few cells can quickly grow.



(a) Experimen results of the overall evolution for the cell under thermal abuse



(b) Simulation results of the overall evolution for the cell under thermal abuse

Figure 2.8 Fire development of a single battery cell during thermal runaway (source: Kong et al. 2022)

Vapour cloud explosion / flash fire
There may be situations where ignition does not take place immediately during a thermal runaway. If ignition is delayed, the accumulated gases may then lead to an intense vapour cloud explosion. The possibility of an explosion must be taken into consideration particularly in situations where the gas concentration cannot be reduced in time or if emergency ventilation fails. The latest findings indicate that evaporated electrolytes also contribute to the explosion hazard (Jin et al. 2021).

Suppressibility
The fact that a thermal runaway is self-sustaining makes it difficult to suppress. Add to this the fact that battery cells are usually well packed, making them hard to cool from the outside. The consequence of this is that a fire caused by a thermal runaway will burn for a long time. It should be noted that thermal runaway does not stop immediately once the fire has been extinguished. For as long as gas is being produced because of the thermal runaway or the battery is still unstable, the risk of re-ignition and explosion will continue (Christensen, 2022).

2.4.3 Relationship between battery chemistry and the severity of thermal runaway

At present, the flammability of current liquid electrolytes is considered to be the main intrinsic safety problem (Zhang et al. 2021). This means that the electrolyte is an important factor for the stability of the battery cell and therefore safety. Several strategies, including adding all kinds of additives such as flame retardants, have been devised to reduce this problem with current battery types. What is relevant here is that the composition and stability of the electrolyte exert the greatest influence on both the probability and effects of thermal runaway.

Incident data has shown that, besides the influence of the electrolyte, the severity of the effects in incidents involving NMC batteries is greater than in incidents involving LFP batteries. Since the energy density of an NMC cathode is higher than that of an LFP cathode, this indicates a statistical correlation between the energy density of the cathode and the extent of the effects of an incident (Yu et al. 2022).

2.5 Literature review of safety: future subtypes

2.5.1 Lithium-silicon

On the one hand, thermal tests by producers of silicon anodes have shown that their new materials are thermally stable, so there are no indications that the material itself is a fire hazard. On the other hand, these producers have said that it is still unknown to them how adding silicon to the anode affects the behaviour of battery cells during incidents. The reason for this is that the producers of silicon anodes only supply the material for the anodes, which the manufacturers of batteries incorporate into the current batteries (Huijben, 2022; Spreafico, 2022).

An important source of the safety risks continues to exist for as long as liquid electrolytes continue to be used. This then means that the possibility of thermal runaway definitely continues to exist as well. Manufacturers of silicon anodes expect that safety gains will be achieved once their silicon anodes are incorporated into solid-state lithium batteries (see the next section). Initially, lithium-silicon is expected to improve performance, but it is not expected to bring any improvements regarding safety yet (Huijben, 2022; Spreafico, 2022; Li et al. 2022; Wang et al. 2022).

2.5.2 Solid-state lithium-ion

Major safety gains are expected from solid-state batteries. There is agreement in the scientific literature on the prospect of solid-state lithium increasing the safety of lithium-ion batteries, as it is generally expected to increase the mechanical, electrical and thermal stability of battery cells. A solid material is stronger and, additionally, some important potential materials are not flammable. Furthermore, the probability of dendrite formation is reduced, because a solid suppresses this. As a consequence, the safety of this battery type is almost taken for granted (Guo et al. 2022).

However, it might still be a bit early to take this for granted, since safety risks cannot be completely ruled out. For instance, it is not clear whether dendrite formation will still be an issue in the case of a failing battery management system or extreme overcharging. The fire behaviour of a failing battery cell during an incident is not yet known either and knowledge about the possible or actual process of thermal runaway in solid-state lithium is lacking (Guo et al. 2022).

And a solid-state electrolyte is not unbreakable. A collision or external pressure caused by battery cells being stacked on top of each other in large systems may still present a risk of bursting, cracks and short circuits. Experiments have shown that a short circuit or damage can still cause toxic and flammable gases to be released. These gases can ignite if temperatures are high (Huo et al. 2022; Chen et al. 2020; Chung et al. 2017; Guo et al. 2022; Wu et al. 2022).

The probability of unwanted chemical reactions and subsequent release of toxic and flammable gases continues to exist in all these cases (Huo et al. 2022; Chen et al. 2020; Chung et al. 2017; Guo et al. 2022; Wu et al. 2022). However, it is known that the heat released on ignition is less than would be the case with batteries with liquid electrolytes. Furthermore, the risk of explosion is reduced because fewer flammable gases and vapours are released (Huijben 2022; Wu et al. 2022).

Finally, it is important to highlight that a large number of potential materials are under development, each with their own different properties. It is possible that the safety advantage offered by one material does not apply to another material. However, solid-state is generally expected to bring considerable safety advantages and to reduce the probability and effect of thermal runaway.

Thermal runaway in solid-state batteries

The above shows that the properties of solid-state batteries are more favourable than those of current batteries. An important question is whether thermal runaway can still occur with solid-state batteries, since it is often claimed that the probability of thermal runaway is ruled out with solid-state batteries. To shed more light on this, three experts affiliated with Tianjin University who researched this specific subject were contacted (Wu et al. 2022).

Firstly, it is important to emphasise that the thermal runaway process of hybrid solid-state batteries is similar to that of current lithium-ion batteries. Essentially, we still do not know enough about the actual or possible process of thermal runaway for new solid-state batteries with a solid-state electrolyte. However, based on multiple studies (Wu et al. 2021, Wu et al. 2022, Huang et al. 2022 en Bates et al. 2022) it can be concluded that thermal runaway in solid-state batteries will take place at higher temperatures than is the case in current lithium-ion batteries with a liquid electrolyte. This matches Figure 2.9 (Wu et al. 2021). This shows the decomposition temperatures of several different candidate materials for the solid state electrolyte, and, to enable comparisons, the decomposition temperatures of liquid electrolytes in blue. These are the temperatures at which the material melts, enters a phase transition or is decomposed, which is also what happens in case of thermal runaway. It is immediately apparent from the figure that the decomposition temperatures for solid-state electrolytes are higher than for liquid electrolytes, which implies higher thermal stability because the stable operating temperature is higher.

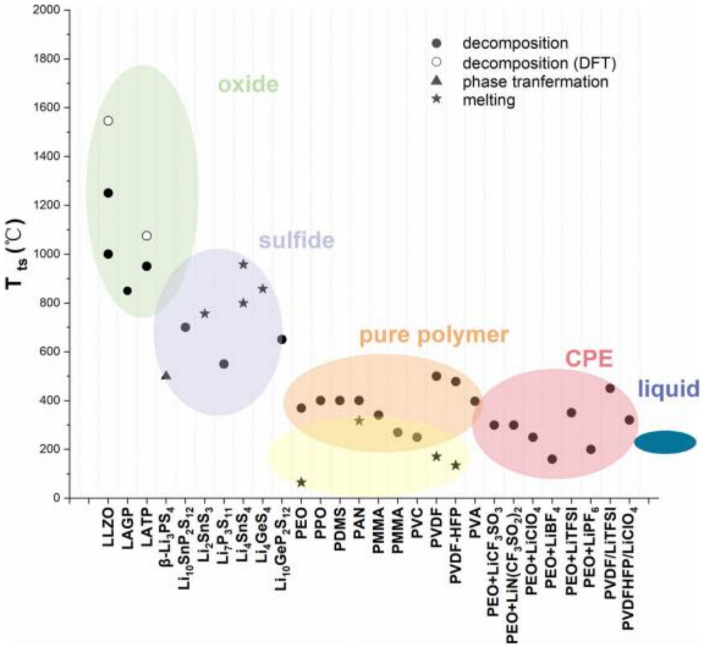


Figure 2.9 Decomposition temperatures of solid-state electrolyte candidate materials (source: Wu et al. 2021)

An important note should be made here. Even if the solid-state electrolyte itself is non-flammable or is more stable, lithium metal can still ignite at temperatures of 180 °C or higher. This was also demonstrated in laboratory tests as shown in Figure 2.10. And the cathode can also go into thermal runaway at temperatures of 250 °C or higher (Wu et al. 2022; Guo et al. 2022; Wu et al. 2021).

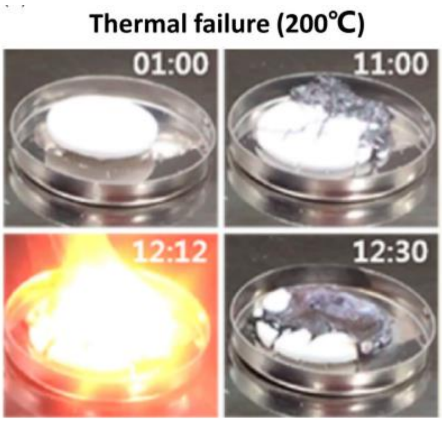


Figure 2.10 Pure lithium metal and thermal failure (source: Wu et al. 2021)

Although thermal runaway cannot be completely ruled out, scientific studies have shown that less energy is released and because of this the expected effects are less intense (Yu et al. 2022). This means that the safety prospects for solid-state batteries are favourable, but that incidents are not completely ruled out.

2.5.3 Lithium-metal (all-solid-state)

The term ‘lithium-metal’ is used also for existing non-rechargeable lithium-metal batteries, also called ‘primary cells’. This section focuses on yet to be developed rechargeable lithium-metal batteries.

The strong formation of dendrites in pure lithium-metal anodes is a major stability issue in the development of lithium-metal batteries (Jiang et al. 2022). A consequence of this is that there is still a considerable probability of internal short-circuiting and this means that a lithium-metal battery will not by definition be safer than current lithium-ion batteries as far as the internal short-circuiting aspect is concerned (Bates et al. 2022).

An additional safety issue here is that lithium metal is highly reactive with oxygen and can ignite. Therefore, if an incident involving pure lithium metal occurs, all the lithium metal must have burned out completely or have been secured (Guo et al. 2022). For these reasons, it is argued that a non-flammable electrolyte is desirable or even necessary (Zhang et al. 2021). As described, a solid-state electrolyte is a possible and popular candidate for this because combining it with a pure lithium-metal anode seems to provide a stable solution. This makes solid-state lithium-metal batteries the logical successors to the first generations of solid-state batteries.

So, several steps will still have to be taken to solve the stability problems associated with pure lithium metal and produce the first lithium-metal batteries. This makes it difficult to make any concrete statements about safety at this point. However, studies have shown that it is also true for pure lithium-metal anodes that their safety is better if a solid-state electrolyte is used instead of a liquid electrolyte (Yu et al. 2022). Regarding lithium-sulphur batteries it has been found, similar to the experiments with solid-state batteries, that thermal runaway can occur at higher temperatures compared to current subtypes (Huang et al. 2022).

2.6 Safety analysis

The diagram below (Table 2.6) shows our safety analysis based on the literature review of new-generation lithium-ion batteries. It shows us what to expect in terms of the probability, effects and suppressibility of incidents involving the new types of battery based on the criteria identified in the research method. The current Li-ion NMC subtype served as the basis and the new subtypes were compared to this subtype.

Table 2.6 Safety analysis of lithium-ion

	Probability	**Effect**	**Suppressibility**
Li-ion NMC	Mechanical, thermal or electrical failure can cause a thermal runaway. A flammable liquid electrolyte with a **low stability margin** is used.	Fire, explosion and a toxic cloud are three realistic effects of thermal runaway. These effects are **severe.**	Suppressing the incident will be **problematic** due to the thermal runaway. In addition, a large amount of toxic and flammable gases is released, jeopardising bystanders.
Li-ion LFP	The probability of thermal runaway is primarily related to the stability of the electrolyte. Since the **composition** of the electrolyte is **the same** as that of NMC batteries the probability of an incident is comparable.	The nature of the effects is the same as for Li-ion NMC. However, its **severity** can be **lower** because of LFP's lower energy density.	**Comparable** to NMC.
Lithium-silicon	**Comparable** to Li-ion NMC and LFP.	**Comparable** to Li-ion NMC.	**Comparable** to Li-ion NMC and LFP.
Hybrid Solid-State	The thermal runaway process is comparable, but stability should be slightly better since there is less liquid electrolyte in the battery. The probability of an incident is expected to be **slightly lower**.	The nature of the effects is **the same** as with Li-ion NMC. However, the effects can be less severe because the electrolyte in these batteries is not as flammable.	**Comparable** to Li-ion NMC and LFP.
Solid-state lithium-ion	Mechanical, thermal and electrical stability will all increase. The stability margin of the electrolyte will increase significantly. This will **significantly lower** the probability of an incident.	**Less heat** will be released in the event of thermal runaway and the probability of an explosion will be less Effects (fire, explosion and toxic cloud) are **still possible.**	Because less heat is released, the **thermal propagation speed** should be **lower**. This means that it should be easier to contain any thermal runaway to a single module.

Lithium-metal / all-solid-state	The application of the solid-state electrolyte significantly increases stability. However, **pure lithium metal** can be a problem and no sound solution has been found.	**Less heat** will be released in the event of thermal runaway and the probability of an explosion will be less	In principle, this should be better since the probability and effect of thermal runaway have decreased. A new problem is that pure lithium metal has to be made safe since it is **highly reactive** with oxygen and water.

3 Sodium-ion

3.1 Introduction

The same operating principles that apply to lithium-ion batteries also apply to sodium-ion batteries; the systems are also constructed in the same way. (The chemical symbol Na is used for sodium) However, lithium-ion batteries have been on the market for quite some time, whereas sodium-ion batteries are new. This can be explained by the fact that lithium particles are smaller than sodium particles, increasing the ability of lithium particles to move through a battery's interior. Lithium-ion battery cells are also comparatively lighter, resulting in a higher energy density (kWh per kg). However, sodium has the advantage that it is globally available in much larger amounts, making it easier to extract. This makes the new type of sodium-ion batteries particularly interesting for stationary storage, such as home and neighbourhood batteries, since weight considerations play a less important role there than, for example, for batteries for electric vehicles. Inventions resulting from the development of lithium-ion batteries may eventually be applied to sodium-ion batteries as well.

This chapter is about the new sodium-ion battery ion, which should not be confused with the Molten Salt battery, another type of battery that already exists. Other terms to indicate the Molten Salt battery are SMC (Sodium Metal Chloride), ZEBRA or salt battery. The Molten Salt battery is not the same type as the sodium-ion battery. They both have sodium as a raw material, but in the case of the Molten Salt battery this is sodium in the form of molten salt, requiring a temperature of about 250 °C.

3.2 System description

As described above, the operating principle of sodium-ion batteries is essentially the same as that of lithium-ion batteries (see Section 2.2). The exterior of sodium-ion batteries resembles that of lithium-ion batteries (Figure 11). The difference is inside the batteries, at a microscopic level. In sodium-ion batteries, sodium ions move back and forth instead of lithium ions and the corresponding electrochemical reaction involves sodium ions (Na^+) and electrons (e^-) instead of lithium ions.

Knowledge previously gathered with lithium-ion batteries is commonly used in the development of sodium-ion batteries. The challenge is that sodium ions are larger than lithium ions, making it more difficult for them to move through the battery material. It is therefore expected that the first generations of sodium-ion batteries will use known materials and technologies that are also used in current lithium-ion generations, since, as a rule, these materials allow particles to pass through more easily than more advanced materials do. Hard carbon is an example of a possible material that is being developed for the anode. In the longer term, it will become possible to apply innovations developed for lithium-ion to sodium-ion batteries as well (Kallitsis et al. 2022; Huijben, 2022).

Figure 11 Sodium-ion cylindrical cell, pouch cell and module (source: Faradion)

3.3 Types of system

As is the case for lithium-ion batteries, different active materials can be used for the anode, cathode and electrolyte in Na-ion batteries. The development of subtypes of Na-ion is expected to progress along a similar chain as lithium-ion (Lu et al. 2019; Huijben, 2022). This development is broadly sketched in Table 3.1. The first sodium-ion batteries marketed will have a liquid electrolyte and an anode of carbon-based materials. The initial cathodes may consist of nickel and manganese, i.e. transition metals. Improved anodes and cathodes and the first solid-state electrolytes are expected to become available in due course, and this will lead to solid-state sodium-ion batteries.

Table 3.1 Possible materials for sodium-ion batteries

Subtype	Anode (-)	Electrolyte	Cathode (+)
Sodium-ion	Several anode materials are being developed. This will result in several different subtypes: > Cold Based Carbon > Hard Carbon > Titanium nitride	Liquid, consisting of a mixture of: > Sodium salts > Solvents > Additives	Several cathode materials are being developed. This will result in several different subtypes: > Sodium transition metal oxides > Polyanion
Hybrid solid-state		Combination of liquid and solid electrolytes, as a precursor to a fully solid electrolyte.	
Solid-state sodium-ion		Future solid-state electrolyte	

3.4 Literature review of safety

There is not a lot of scientific literature on the safety of sodium-ion available yet. The available studies suggest that, for the time being, the safety issues are similar to those of lithium-ion batteries (Wang et al. 2019). For example, one experiment consisted of putting a lithium-ion and a sodium-ion pouch cell into thermal runaway under identical conditions (Robinson et al. 2017). The conclusion of this experiment was that, during a thermal runaway, comparable unwanted reactions take place in both battery cells, i.e. exothermic reactions that produce heat and toxic and flammable gases. An experimental analysis showed that the composition of the gases and vapours released was comparable to that of current lithium-ion batteries (Bordes et al. 2022).

However, the thermal runaway in the sodium-ion battery cell seemed to develop more slowly. Another experiment showed that the cathode material of a sodium-ion battery went into thermal runaway at 254 °C. This temperature compares to the temperature where a cathode in a lithium-ion battery goes into thermal runaway (Cui et al. 2022).

The electrolyte is also identified as an important factor for the stability of sodium-ion batteries. Since there are no suitable solid-state electrolytes at present, we will first get sodium-ion batteries with a liquid electrolyte while suitable additives to improve safety will be looked for. The tricky thing here is that tests have shown that a minute change in the mixing ratio of the electrolyte directly affects electrochemical performance (Mosallanejad et al. 2021).

Solid-state sodium-ion

The safety gains that solid-state electrolytes offer for lithium-ion batteries are also expected to be achieved for sodium-ion batteries. Our literature review showed that the ionic conductivity of most candidate materials is lower, which would currently mean a lower performance compared to the less safe liquid electrolytes. This is a field in which developers can still make many improvements (Wang et al. 2019).

3.5 Safety analysis

The diagram below (Table 3.2) shows our safety analysis based on the literature review of sodium-ion batteries. Since our literature review showed that the safety issues are comparable to those involved in lithium-ion batteries, the probability, effects and suppressibility of incidents involving sodium-ion batteries have been compared to those involving lithium-ion batteries.

Table 3.2 Sodium-ion safety analysis

	Probability	Effect	Suppressibility
Sodium-ion	Mechanical, thermal or electrical failure can cause a thermal runaway. A flammable liquid electrolyte with a low stability margin is used. Therefore, the probability of an incident is **comparable** to current Li-ion batteries.	Fire, explosion and a toxic cloud are three realistic effects of thermal runaway.	Assuming the same bottlenecks as exist for Li-ion, suppressing these situations will be **problematic** for the time being. An experiment has shown that the thermal runaway process develops more slowly.
Solid-state sodium-ion	The probability of an incident **decreases**. Mechanical, thermal and electrical stability will all increase. The stability margin of the electrolyte will increase significantly.	**Less heat** will be released in the event of thermal runaway and the probability of an explosion will be lessened. It should be taken into account that all effects (fire, explosion and toxic cloud) are still possible.	Because less heat is released, the thermal propagation speed is expected to be lower. This means that it will be **easier to contain** any thermal runaway to a single module.

4 Redox flow

4.1 Introduction

The redox flow battery is an energy storage system in which the energy is stored in liquids or in a liquid and gas. Since redox flow batteries are relatively large installations, they are mainly relevant for large-scale stationary energy storage. An important aspect of this is that it will be possible to considerably increase the storage tanks for the liquids in the future, enabling the battery to provide energy at maximum power for a longer period, i.e. days rather than hours. This gives this system the potential to store a large dynamic supply of energy as produced by solar and wind farms (Wittman et al. 2022).

4.2 System description

4.2.1 System operation

Redox flow batteries do not consist of individual battery cells, but consist of arrangements of stacks and storage tanks. Stacks are electrochemical cells in which electrochemical reactions take place while charging and discharging. Liquid or gaseous electrolytes from storage tanks are circulated through these stacks. The electrolytes flow past each other in the stacks, creating the electrochemical reaction that charges and discharges the battery. The concept of redox flow batteries enables both energy content and power to be increased separately. The energy content can be increased by enlarging the storage tanks and the power can be increased by adding more stacks.

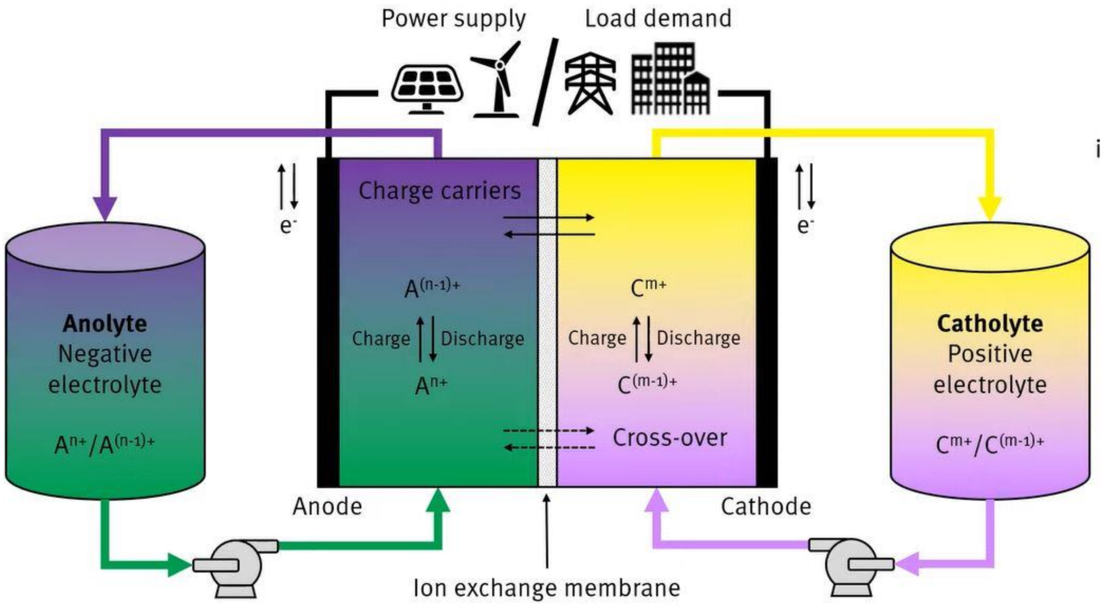


Figure 4.1 Operation of a redox flow battery (source: Wu, 2022)

Table 4.1 Active components of a redox flow battery

Anode electrolyte ‘Anolyte’ (-)	**Membrane**	**Cathode electrolyte ‘Catholyte’ (+)**
Liquid connected to the negative pole of the battery.	Ion-permeable membrane separating the anolyte and catholyte liquids from each other. The membrane allows hydrogen ions to pass through when charging and discharging, but has to prevent cross-over, i.e. mixing, of the liquids.	Liquid connected to the positive pole of the battery.

Table 4.1 shows the active components of a redox flow battery. Several combinations of electrolytes, i.e. ‘anolyte-catholyte pairs’ are being developed. Most of them consist of a liquid-liquid pair. Other subtypes are a liquid-gas pair and a liquid-metal pair, sometimes referred to as hybrid variants. We have decided to study the safety aspects of all-vanadium and hydrogen-bromine batteries in this report (Table 4.2). The reason for this is that all-vanadium batteries are already sold in the Netherlands and hydrogen-bromine batteries are currently being developed in the Netherlands. The all-vanadium battery serves as an example of a battery with two liquid electrolytes; the hydrogen-bromine battery serves as an example of a battery with a liquid and a gas. Moreover, apart from the zinc-bromine hybrid with a liquid-metal pair, most of the other variants (i.e. electrolyte pairs) have not reached a similar stage of development yet.

Table 4.2 Redox flow subtypes

Subtype	**Anode electrolyte ‘Anolyte’ (-)**	**Cathode electrolyte ‘Catholyte’ (+)**
All-V (liquid-liquid)	Vanadium ($V^{2+} \rightleftarrows V^{3+}$)	Vanadium ($V^{4+} \rightleftarrows V^{5+}$)
H-Br (gas-liquid)	Hydrogen	Bromine

4.2.2 Configuration of the energy storage system

An example of a stack (electrochemical cell) is shown in Figure 4.2 for illustrative purposes. These stacks are connected to the storage tanks and a pump is used to circulate the two electrolytes.

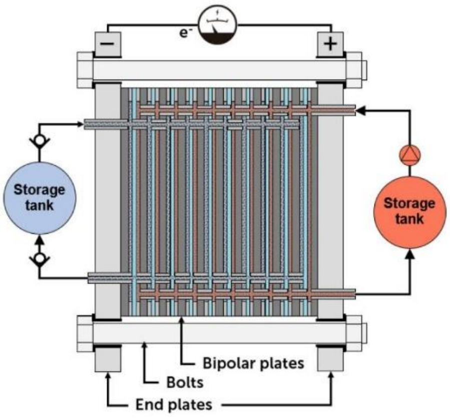


Figure 4.2 Schematic representation of a stack and photo of a prototype (source: Elestor)

A schematic representation of the entire system is shown in Figure 4.3. This figure shows two storage tanks connected to four stacks. The active components, i.e. the stacks and storage tanks are shown, as well as support systems, such as a Battery Management System (BMS) and ventilation.

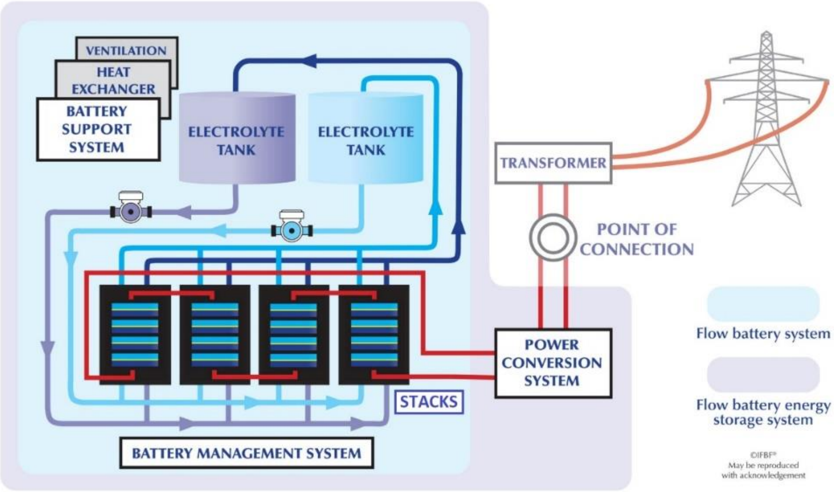


Figure 4.3 Configuration of a redox flow energy storage system (source: IFBF)

4.3 Types of system

4.3.1 All-vanadium

An all-vanadium (all-V) system works with vanadium in a negatively and positively electrically charged state. The vanadium has been dissolved in water and is stored in liquid tanks. Vanadium is extracted in various ways, including as a residual product of steel production. The system consists of stackable shipping containers containing the stacks (Figure 4.4).

Figure 4.4 Stacks of an all-vanadium system (source: CellCube)

4.3.2 Hydrogen-bromine

The hydrogen-bromine (H-Br) battery works with bromine dissolved in water and hydrogen gas. The advantages of hydrogen and bromine are that they are amply available, relatively inexpensive and suitable for recycling, since bromine can be extracted from seawater. The hydrogen is stored in gas tanks. Several options are possible for this. It can be stored under atmospheric pressure in a gas dome, i.e. a kind of double-walled balloon, or it can be stored under pressure in gas tanks. The bromine is dissolved in water and stored in liquid tanks. Figure 4.5 shows the current prototype. The purple-pink liquid in the transparent tubes is the bromine solution. An interesting aspect is that the colour of the liquid shows whether the battery is charged or empty: the more purple the colour, the higher the battery charge.

Figure 4.5 Prototype of a hydrogen-bromine system (source: Elestor)

4.4 Literature review of safety

4.4.1 General safety risks

Leakage or spillage from storage tanks – toxic cloud

The large storage tanks with toxic liquids or gases in them pose a safety risk. Vanadium and bromine are toxic and harmful to the environment. Manufacturers take safety measures to prevent leakage and spillage and to mitigate the consequences of any leakage or spillage. Examples of preventive measures are double-walled storage tanks, or underground or underwater storage tanks. Examples of mitigating measures are the use of drip trays or tarpaulins, neutralising agents, oil as a protective layer in the drip trays (to prevent leaked fluid from vapouring), covering with water or the use of so-called 'binding agents'. Binding agents adhere to the leaking liquid, preventing it from evaporating (Lauret, 2022).

However, the risk remains that the installation may be damaged by external heat radiation, e.g. from a fire. If the storage tanks are also damaged, this might cause electrolyte leakage or spillage.

All the redox flow batteries studied require a large amount of toxic substances for their operation. If the storage tanks are involved in an accident or if there is an electrolyte leakage or spillage, these toxic substances can be released. Exceeding certain limits, these agents are harmful to health and can cause all kinds of health problems, including respiratory problems. In the event of an unexpected release, these substances can cause damage to the environment (Hadatsch, 2022; Lauret, 2022). Leakage or spillage of the entire content of a storage tank, or a significant amount, will lead to a toxic cloud. Depending on where the tanks are placed, this will also contaminate the soil.

Hydrogen gas formation due to potential difference
In the event of a failure or disturbance in the battery, an (abnormal) potential difference may occur between the anode and cathode, where hydrogen gas may be formed from the liquids used. This potentially applies to all subtypes of Redox-Flow batteries. Under normal operating conditions, this will not occur; nevertheless, this failure mechanism deserves further investigation. Ideally, the voltage across the different stacks should be equal and balanced, otherwise incomplete reactions may take place that could cause hydrogen gas and oxygen to be released (Gundlapalli and Jayanti, 2021). These unwanted reactions can also damage the battery (Fetyan et al. 2019). In the case of redox flow batteries, hydrogen is not burnt, but is an unwanted residual product. Hydrogen is an active substance only in the hydrogen-bromine variant, not in a combustion reaction but in an electrochemical reaction.

Electrical short circuit
The electrical installation in and around the redox flow battery will generally be designed with an eye to eliminate electrical short circuits to the fullest extent possible. Human error or other mistakes when installing, operating or maintaining the installation can cause an external short circuit, but this is unlikely. An internal short circuit can occur due to degradation of the ion-permeable membrane between the two electrodes. This can enable dendrites to form in hybrid variants where a metal plate is part of the active substances. This can eventually cause an internal short circuit (Whitehead et al. 2017).

Thermal runaway is not applicable
Regarding Redox-Flow batteries, the safety risk of a thermal runaway basically does not play a role, as no evidence has been found that mixing electrolytes leads to a thermal runaway (Hadatsch, 2022; Lauret, 2022). It has also been investigated whether within Redox-Flow batteries a spontaneous reaction can occur between the active substances used, but no such mechanism has ever been found. Moreover, the vast majority of actives are stored separately.

In addition, the potential consequences of thermal failure causes are considered harmless. Should a thermal failure situation in the active part of the battery (the stack) lead to the release of energy or heat, only a small fraction of the total volume of substances will be affected, as the rest of the substances are stored in the storage tanks. Experiments also show that the high heat capacity and large volume of the liquid electrolyte can easily absorb any released heat (Wittman et al. 2020). As the substances are pumped around, the heat will be absorbed quickly and heat up the plant only to a limited extent. In addition, the liquid electrolytes are a solution in water and are not flammable (Wittman et al. 2020).

4.4.2 All-vanadium

Short-circuit experiments with an all-vanadium battery did not cause any hazardous situations (Whitehead et al. 2017). Although the temperature of the electrolyte in the stack was found to increase by approx. 25 °C, this temperature increase was compensated as soon as the liquid re-entered the liquid tank. The explanation given for this was that only about one per cent of the vanadium is in the stack during use and the vast majority is in the storage tanks.

Some fire experiments were also conducted with components of redox flow batteries. They showed that, indeed, the electrolytes were not flammable and that only an electrode frame was flammable (Chen et al. 2022).

Vanadium is a corrosive liquid that can cause severe burns and eye damage on contact with skin and eyes. If inhaled, it can cause respiratory problems or harm to an unborn child (CellCube, 2022).

4.4.3 Hydrogen-bromine

The hydrogen-bromine battery is still in its prototype phase and, in regard to safety, the focus is mainly on preventive measures. In addition to the measures aimed at electrolyte leakage or spillage mentioned above, hydrogen storage is also paid attention to for this subtype. Hydrogen is a highly flammable gas. Since it is already widely used as a form of energy, any safety risks involved are largely known. Theoretically, hydrogen can ignite at concentrations as low as 4 to 75 vol% in air. If circumstances are highly unfavourable, released hydrogen gas can lead to an explosion (Wittman et al. 2020). In a real-life situation, if the concentration is approx. 15 vol% or higher, explosions can occur.

Hydrogen can be stored under pressure or under atmospheric pressure. Currently, there are several prototypes operating at various pressures (from atmospheric to a design pressure of currently up to 8 bar), but with a goal of reaching 80 bar for the purpose of connecting to the hydrogen network. One of the current prototype uses a double-walled gas dome under atmospheric pressure. The advantage of storage under atmospheric pressure is that the known safety risks related to high-pressure storage (such as an explosion or flare) are ruled out. Since the gas dome is outside, it may be subject to external influences. An example is the dome being struck by lightning. A special lightning rod has been designed for this.

Bromine is an aggressive acidic and corrosive liquid that produces toxic bromine vapours when released. Bromine vapours are already toxic in low concentrations and lead to respiratory tract irritation and suffocation. At the same time, even at concentrations as low as a few parts per million (ppm), they can be detected by the strong odour, so that bystanders are automatically alerted by the unpleasant smell or, in more serious cases, an orange-coloured cloud. Self-reliant people can thus flee in time. Moreover, (intrinsic) mitigating measures are in place to prevent evaporation. Measures can also be taken to limit evaporation if it does occur. However, it is important that installations are designed for this purpose and that good processes and resources exist to minimise adverse effects in the event of a disaster. Suppression of bromine vapours requires proper personal protective equipment and an upwind approach.

4.5 Safety analysis

The diagram on the next page (Table 4.3) shows our safety analysis based on the literature review of redox flow batteries. It shows what we expect in terms of the probability, effects and suppressibility of incidents involving the new types of battery.

Table 4.3 Redox flow safety analysis

	Probability	Effect	Suppressibility
All-vanadium / All-V	The only possible cause of incident seems to be a leakage or spillage from a storage tank. Maximum preventive measures have been provided for this. Short circuiting was not found to have any serious consequences. This means that the probability of an incident seems to be **low**.	The fire risk is low because the liquids are not flammable. There is nothing to suggest explosion hazard. If toxic substances are released this is **rather serious**, as they are toxic.	**Suppressible according to the existing Dutch IBGS (hazardous materials incident response) protocol.** In principle, any leakage or spillage of liquids should be able to be handled with existing procedures and personal protective equipment. However, suppressibility is time-intensive because this is a substance that should be approached in accordance with the gas suit procedure.
Hydrogen-bromine / H-Br	Since there is a storage tank with flammable gas here, the probability of an incident may be **somewhat higher** than would be the case for all-V batteries.	In case of complete failure of the hydrogen and bromine storage tank, the effects could be **severe**. Both an explosion and the release of toxic substances are possible. Bromine vapours are harmful even at low ppm and disperse with the wind.	**Suppressible according to the existing Dutch IBGS protocol.** In principle, a leak should be manageable with existing procedures and personal protective equipment. However, containment is time-intensive, as bromine is a substance that must be approached in accordance with the procedure developed for gas suits. In addition, soil contamination as a consequence should also be avoided. Furthermore, hydrogen should be taken into account during suppression.

5 Discussion

This chapter summarises the safety analyses from the previous chapters and visualises them using radar charts. This provides a better understanding of how the probability, effects and suppressibility of incidents involving the new types of batteries are expected to compare. The safety analyses from the concluding sections of chapters 2, 3 and 4 were used as input for the radar charts. The probability of an incident, the severity of effects and the degree of suppressibility are presented by the axes. The centre of the chart represents the minimum value; a point at the edge represents the maximum value.

5.1 New lithium-ion generations

Current situation

The difference between different subtypes of current lithium-ion batteries is in the cathode material. Thermal runaway can occur in all of these subtypes. The probability and severity of thermal runaway is primarily determined by the stability and composition of the electrolyte. At present, the electrolyte is still completely or partly liquid for all current subtypes, which means that the main factor is basically the same. The energy density of the cathode is the secondary factor that influences the severity of thermal runaway; this differs from subtype to subtype. The best-known example here is the distinction between NMC Li-ion and LFP Li-ion. LFP has a lower energy density than NMC and therefore the probability and effect are slightly lower, as shown in the radar chart in Figure 5.1.

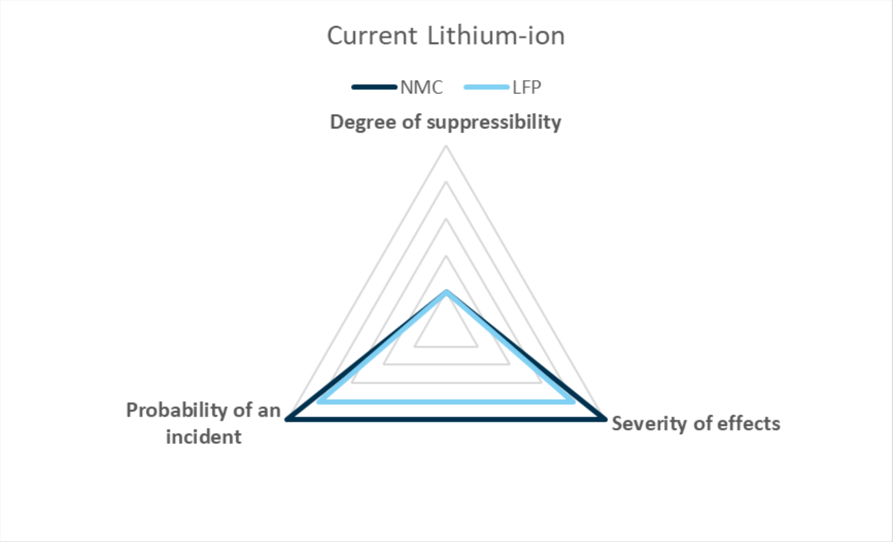


Figure 5.1 Radar chart of current lithium-ion

New lithium-ion subtypes

Solid-state batteries are the new subtypes of lithium-ion batteries that are expected to bring the greatest safety improvements. Scientific research has indeed shown that both probability and effects decrease if a solid-state electrolyte is applied. However, this does not completely rule out all safety risks. The main lesson from our study is that the risk of thermal runaway also remains in solid-state batteries, but that such thermal runaway will occur at higher temperatures than in current lithium-ion batteries because of the higher stability of the solid-state electrolyte. The radar chart below shows that the arrival of solid-state batteries will decrease probability and effect. The degree of suppressibility should also improve somewhat, since incidents will grow less fast. At the same time, the factors that complicate suppressibility, i.e. the fact that battery cells are properly packed and that thermal runaway can occur, remain unchanged. We therefore expect that the degree of suppressibility will improve only to a limited extent. The corresponding radar chart is shown in Figure 5.2.

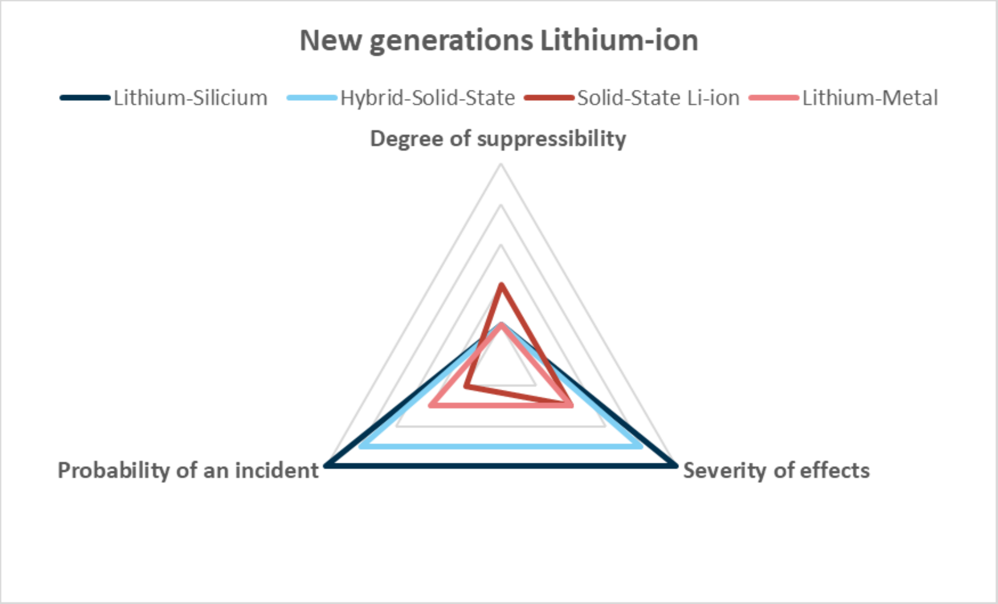


Figure 5.2 Radar chart of safety analysis of new generation of lithium-ion

In regard to suppressibility, current knowledge and expertise on how to respond to incidents involving lithium-ion batteries can also be applied to the new subtypes, since the effects that can be expected are the same.

5.2 Sodium-ion

The safety study showed that the safety and stability issues encountered with sodium-ion and lithium-ion are basically the same. Moreover, some experiments were carried out to find out whether thermal runaway can also occur in sodium-ion batteries. These experiments showed that this is indeed the case, but there is evidence to suggest that slightly less heat is released and that the process takes place at a somewhat slower pace. This can be explained by the lower energy density. The radar chart below shows that we expect the safety of the first generations of sodium-ion batteries to be comparable to that of today's lithium-ion batteries. If a solid-state electrolyte is also made available for sodium-ion batteries, safety will increase. This has resulted in the radar chart in Figure 5.3

Since the safety risks of sodium-ion are comparable to those of lithium-ion, it may be considered to initially apply the action guidelines for lithium-ion batteries to any future incidents involving sodium-ion batteries as well.

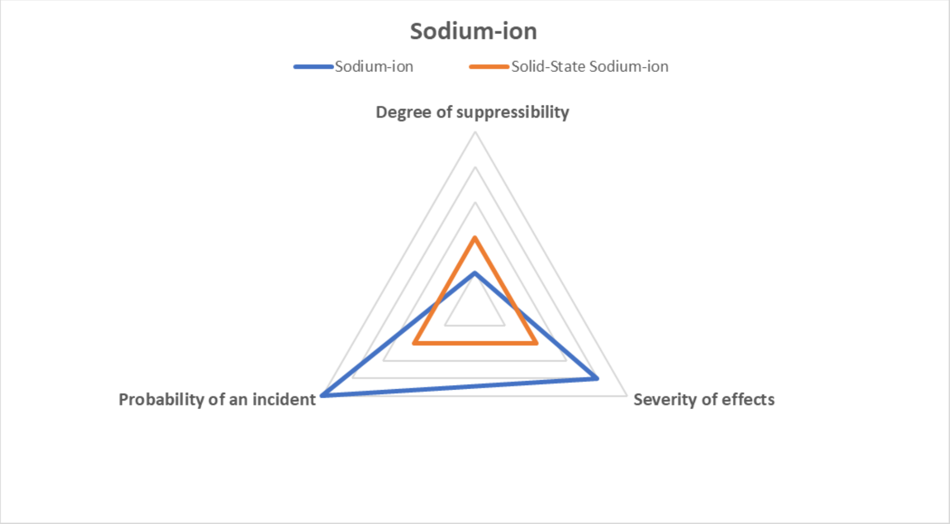


Figure 5.3 Radar chart for the safety analysis for sodium-ion

5.3 Redox flow

The study has shown that toxic liquids are the active substance of all redox flow batteries studied. As a consequence, manufacturers' safety measures tend to focus on preventing leakage and spillage, and limiting their effects. No evidence to suggest a possible thermal runaway process was found. However, in the case of redox flow batteries, an electrical failure can cause a small amount of unwanted hydrogen to form. Nevertheless, the risk of fire and explosion associated with redox flow batteries was found to be generally low, partly because the liquids used are not flammable. These effects should only be taken into account for the hydrogen-bromine variant as this is the only subtype where a flammable gas, i.e. hydrogen, is part of the active substances. This is shown in the radar chart (Figure 5.4).

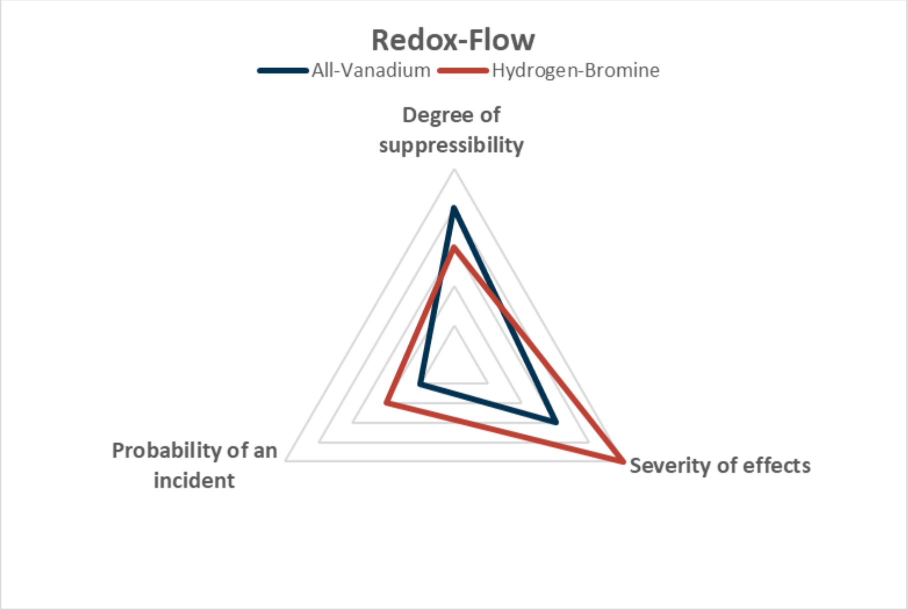


Figure 5.4 Radar chart for the safety analysis for redox flow

Since leakage or spillage of toxic liquids is an existing incident that incident responders are familiar with, the regular Dutch IBGS procedures can serve as a starting point to respond to a leakage or spillage from the storage tank.

6 Conclusion

Several important developments concerning new battery types have been studied from a safety aspect and this is summarised in this report. This study has shown that risks continue to exist for every new type of battery.

In principle, the new generation of lithium-ion batteries has the same risks as the current lithium-ion batteries. The safety issue of thermal runaway with its associated effects of toxic clouds, battery fire and a vapour cloud explosion or a flash fire, continues to exist for all lithium-ion subtypes. Although the introduction of solid-state batteries will reduce the probability of an incident and severity of these effects, the effects listed will not be completely eliminated. As the effects are of a comparable nature and the systems are structured in the same way, we expect only limited improvement in the degree of suppressibility compared to current lithium-ion batteries.

The safety risks of sodium-ion batteries have been found to be similar in nature as those of lithium-ion batteries. Scientific experiments have shown that sodium-ion battery cells can also reach thermal runaway. However, since their energy density is lower, the speed and severity of this thermal runaway are probably less than they would be with lithium-ion battery cells. Because sodium-ion battery systems also consist of carefully packed battery cells, suppressibility is also expected to be frustrated by the fact that it is hardly possible to cool the cells during an incident. The introduction of the first lithium-ion solid-state batteries will soon be followed by the introduction of sodium-ion solid-state batteries, resulting in better safety.

As for redox flow batteries, it has been found that all subtypes contain toxic substances as the system's active substance. As a result, the safety risks of redox flow batteries are mainly of a toxic nature. No evidence of thermal runaway was found for this main category of batteries and the active substances, including liquids, are not flammable (with the exception of the hydrogen in hydrogen-bromine batteries). An incident involving a redox flow battery will therefore be of a similar nature to a toxic liquid leakage or spill, in a sense. The current Dutch IBGS (hazardous materials incident response) procedures can offer a guideline for suppressing such incidents.

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