



SAFETY AND TRANSPORT

Lithium-ion Batteries used in Electrified Vehicles – General Risk Assessment and Construction Guidelines from a Fire and Gas Release Perspective

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Abstract

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This report presents a general and broad risk assessment and construction guidelines for lithium-ion battery systems used in electrified vehicles, from the perspectives of fire and gas release. General types of Li-ion battery systems and electrified vehicles, ranging from light to heavy-duty vehicles, are included. The findings in the report are based on results obtained in the project “*Safer battery systems in electrified vehicles – develop knowledge, design and requirements to secure a broad introduction of electrified vehicles*”, conducted between the years 2012-2017 and lead by RISE Research Institutes of Sweden. The guidelines focus on both how to design the battery system and on how to integrate and place the battery in the vehicle in order to increase the safety in terms of fire and gas release.

Key words: Lithium-ion battery, safety, fire, gas release, toxic emissions, guidelines, battery system, electrified vehicles, design, placing

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Preface

This report have been conducted within the project “*Safer battery systems in electrified vehicles – develop knowledge, design and requirements to secure a broad introduction of electrified vehicles*”. The project was conducted from May 2012 to September 2017 and the project partners were RISE Research Institutes of Sweden AB (project leader), Atlas Copco Rock Drills, Elforsk and Chalmers University of Technology. The FFI-project was partly funded by the Swedish Energy Agency which is gratefully acknowledged. The total project budget was about 6.4 Million SEK.

Sammanfattning

I den här rapporten presenteras en allmän och bred riskanalys samt konstruktionsriktlinjer för litium-jon batterisystem i elektrifierade fordon, utifrån ett säkerhetsperspektiv med fokus på brand och gasutsläpp. Allmänna typer av Li-jon batterisystem och elektrifierade fordon, från lätta till tunga fordon, ingår. Resultaten i den här rapporten är baserad på resultat som framkommit i projektet *”Säkrare batterisystem för elektrifierade fordon – utveckla kompetens, design och krav för att säkerställa en bred introducering av elektrifierade fordon”*, som genomfördes mellan åren 2012-2017 och leddes av RISE Research Institutes of Sweden. Konstruktionsriktlinjerna fokuserar på designen av batterisystemet och hur det integreras och placeras i fordonet för att på så sätt öka säkerheten utifrån ett brand och gasutsläppsperspektiv.

1 Introduction

1.1 Scope and aim

The information found here is valid for lithium-ion (Li-ion) batteries and is derived from the findings in the project “*Safer battery systems in electrified vehicles – develop knowledge, design and requirements to secure a broad introduction of electrified vehicles*” conducted between the years 2012-2017.

This report aims to be general and to cover all types of Li-ion battery systems used in all types of electrified vehicles, ranging from light to heavy-duty vehicles. The report is based on the project findings from a perspective of fire and gas emissions and does not attempt to cover all Li-ion battery related safety aspects. Furthermore, all possible fire and gas release perspectives are probably not covered in this report. Li-ion batteries are still a relatively new technology and Li-ion battery safety is a recent research area. The importance of this report and its topics is enhanced by the consequences connected to risks of Li-ion batteries present in a vehicle, which, in case of a malfunction, may imply serious outcomes, for example if the driver is affected by smoke or by fire/explosion.

The report is focused on the risks associated with fire and gas release. Li-ion battery safety is an active research field where much is yet in early stages of investigation, e.g. failure mechanisms, failure states, probability and consequences, battery-size scaling and environmental effects. Anyhow, it is the authors’ intention that the risk assessment and the construction guidelines can serve as an important base in order to construct safer Li-ion battery systems for use in electrified vehicles. The requirements on the battery system may however vary with battery size, vehicle application and operational environment. Since this is an active field of research it is also important that the reader of this report follows new findings about Li-ion battery safety in general, including results regarding fire and gas release.

1.2 Publication list of the project

This report is based on results obtained in the project. Via the project, a number of publications have been made. The publications, sorted by publication year, are:

1. Fredrik Larsson, “[Lithium-ion Battery Safety - Assessment by Abuse Testing, Fluoride Gas Emissions and Fire Propagation](#)”, PhD Thesis, ISBN: 978-91-7597-612-9, *Chalmers University of Technology*, Göteborg, 2017.
Available online:
<http://publications.lib.chalmers.se/records/fulltext/251352/251352.pdf>
2. Fredrik Larsson, Simon Bertilsson, Maurizio Furlani, Ingvar Albinsson, Bengt-Erik Mellander, “[Gas explosions and thermal runaways during external heating abuse of commercial lithium-ion graphite-LiCoO₂ cells with different levels of ageing](#)”, *submitted manuscript*.

3. Fredrik Larsson, Petra Andersson, Bengt-Erik Mellander, “[Are electric vehicles safer than combustion engine vehicles?](#)”, in: Systems perspectives on Electromobility, edited by Björn Sandén, Pontus Wallgren, *Chalmers University of Technology*, Göteborg, Sweden, updated chapter, in press.
4. Fredrik Larsson, Petra Andersson, Per Blomqvist, Bengt-Erik Mellander, “[Toxic fluoride gas emissions from lithium-ion battery fires](#)”, *Scientific Reports* 7, article number 10018 (2017).
Available online: <https://www.nature.com/articles/s41598-017-09784-z>
5. Simon Bertilsson, Fredrik Larsson, Maurizio Furlani, Ingvar Albinsson, Bengt-Erik Mellander, “[Lithium-ion battery electrolyte emissions analyzed by coupled thermogravimetric/Fourier-transform infrared spectroscopy](#)”, *Journal of Power Sources*, 365, 446-455 (2017).
6. Fredrik Larsson, Antti Rytinki, Istaq Ahmed, Ingvar Albinsson, Bengt-Erik Mellander, “[Overcurrent abuse of primary prismatic zinc-air battery cells studying air supply effects on performance and safety shut-down](#)”, *Batteries*, 3, 1 (2017).
7. Fredrik Larsson, Johan Andersson, Petra Andersson, Bengt-Erik Mellander, “[Thermal modelling of cell-to-cell fire propagation and cascading thermal runaway failure effects for lithium-ion battery cells and modules using fire walls](#)”, *Journal of The Electrochemical Society*, 163 (14), A2854-2865 (2016).
8. Fredrik Larsson, Petra Andersson, Per Blomqvist, Bengt-Erik Mellander, “[Gas emissions from lithium-ion battery cells undergoing abuse from external fire](#)”, Conference proceedings of Fires in vehicles (FIVE) 2016, Baltimore, USA, 5-6 October 2016, edited by Petra Andersson, Björn Sundström, *SP Technical Research Institute of Sweden*, Borås, Sweden, p. 253-256 (2016).
9. Petra Andersson, Per Blomqvist, Anders Lorén, Fredrik Larsson, “[Using Fourier transform infrared spectroscopy to determine toxic gases in fires with lithium-ion batteries](#)”, *Fire and Materials*, 40 (8), 999-1015 (2016).
10. Fredrik Larsson, Petra Andersson, Bengt-Erik Mellander, “[Lithium-ion battery aspects on fires in electrified vehicles on the basis of experimental abuse tests](#)”, *Batteries*, 2, 9 (2016).
11. Fredrik Larsson, Johan Anderson, Petra Andersson, Bengt-Erik Mellander, “[Safer battery systems in electrified vehicles – an electrified bus perspective](#)”, *Eurotransport*, June edition 2016, Russell Publishing Ltd, Kent, United Kingdom, 3, 50-53 (2016).
12. Petra Andersson, Per Blomqvist, Fredrik Larsson, Anders Lorén, “[Fire risks with lithium-ion batteries - measurements of gas emissions](#)”, *2nd IAFSS European Symposium of Fire Safety Science (ESFSS)*, Nicosia, Cyprus (2015).
13. Petra Andersson, Johan Anderson, Fredrik Larsson, Bengt-Erik Mellander, “[Modelling of thermal events in lithium-ion batteries](#)”, *2nd IAFSS European Symposium of Fire Safety Science (ESFSS)*, Nicosia, Cyprus (2015).
14. Johan Anderson, Fredrik Larsson, Petra Andersson, Bengt-Erik Mellander, “[Thermal modeling of fire propagation in lithium-ion batteries](#)”, *24th International Technical Conference on the Enhanced Safety of Vehicles (ESV)* 2015, Paper Number 15-0073, Gothenburg, Sweden (2015).
15. Fredrik Larsson, “[Assessment of safety characteristics for Li-ion battery cells by abuse testing](#)”, Licentiate thesis, *Chalmers University of Technology*, Göteborg, 2014. Available online:

<http://publications.lib.chalmers.se/records/fulltext/202184/202184.pdf>

16. Fredrik Larsson, Petra Andersson, Bengt-Erik Mellander, “[Battery aspects on fires in electrified vehicles](#)”, Conference proceedings of Fires in vehicles (FIVE) 2014, Berlin, Germany, 1–2 October 2014, edited by Petra Andersson, Björn Sundström, *SP Technical Research Institute of Sweden*, Borås, Sweden, p. 209–220 (2014).
17. Johan Anderson, Fredrik Larsson, Petra Andersson and Bengt-Erik Mellander, “[Fire spread due to thermal runaway in a lithium-ion battery cell](#)”, Conference proceedings of Fires in vehicles (FIVE) 2014, Berlin, Germany, 1–2 October 2014, edited by Petra Andersson, Björn Sundström, *SP Technical Research Institute of Sweden*, Borås, Sweden, p. 268-271 (2014).
18. Fredrik Larsson, Petra Andersson, Per Blomqvist, Anders Lorén, Bengt-Erik Mellander, “[Characteristics of lithium-ion batteries during fire tests](#)”, *Journal of Power Sources*, 271, 414-420 (2014).
19. Fredrik Larsson, Bengt-Erik Mellander, “[Abuse by external heating, overcharge and short circuiting of commercial lithium-ion battery cells](#)”, *Journal of The Electrochemical Society*, 161 (10), A1611-A1617 (2014).
20. Fredrik Larsson, Petra Andersson, Bengt-Erik Mellander, “[Are electric vehicles safer than combustion engine vehicles?](#)”, in: Systems perspectives on Electromobility, edited by Björn Sandén, Pontus Wallgren, *Chalmers University of Technology*, Göteborg, Sweden, ISBN 978-91-980973-9-9, p. 33-44 (2014).
21. Petra Andersson, Per Blomqvist, Anders Lorén, Fredrik Larsson, “[Investigation of fire emissions from Li-ion batteries](#)”, *SP Technical Research Institute of Sweden*, Borås, Sweden, SP Report 2013:15, ISBN 978-91-87461-00-2 (2013).
22. Fredrik Larsson, Bengt-Erik Mellander, “[Energy storage system safety in electrified vehicles](#)”, Conference proceedings of Fires in vehicles (FIVE) 2012, Chicago, USA, 27-28 September 2012, edited by Petra Andersson, Björn Sundström, *SP Technical Research Institute of Sweden*, Borås, Sweden, p. 303-306 (2012).
23. Fredrik Larsson, Jesper Martaeng, Bengt-Erik Mellander, “[Design for safety](#)”, *Proceedings of Advanced Automotive Battery Conference (AABC) 2012*, Orlando, USA (2012).

1.3 Lithium-ion battery safety

Lithium-ion batteries offer many excellent properties such as high energy density, high power density, long life time and high efficiency. However, compared to other battery technologies Li-ion has some drawbacks in terms of safety, e.g. a narrower stable operational window (both in the voltage and temperature ranges) and the cells contain reactive and flammable materials. If the Li-ion cell/battery is exposed to abuse, the battery temperature can increase that may result in a gas release or in a thermal runaway with heat and gas release and eventual fire and/or explosion. A thermal runaway is a rapid self-heating (exothermic) process within the Li-ion cell itself. Figure 1 shows an overview of different abuse types on the cell level and their potential spreading/propagation to adjacent cells and to the complete battery system.

Regarding the term explosion, there are different types. In case extreme pressures are formed inside a battery cell, the cell can explode, e.g. emitting ballistic fragments in the surroundings. This is generally referred to as a “cell case explosion” or “cell explosion”. This can happen if the cell construction allows the build-up of very high pressures, e.g. in cylindrical and hard prismatic cells, but since these types of cells have a built-in safety vent they have protection against this type of event if designed properly and provided there are no malfunctions.

Another type of explosion can occur if flammable gases from a cell/battery are accumulated and mixed with air in a confined/semi-confined space to form a flammable gas mixture and later ignited (delayed ignition). This is here referred to as accumulated gas ignition; in many cases it is also called a gas explosion as an ignition of a flammable gas mixture results in a very rapid expansion of the gases due to the rapidly increased temperature and a subsequent pressure increase. The battery cells can vent (release gases) at temperatures significantly lower than those of the thermal runaway, consequently, if these gases are ignited, there is a risk for this type of event even if a thermal runaway has not occurred. The consequences of a delayed ignition of released gases can be much more severe than those in the case of a cell case explosion.

For a more comprehensive introduction to Li-ion battery safety, see Larsson [1].

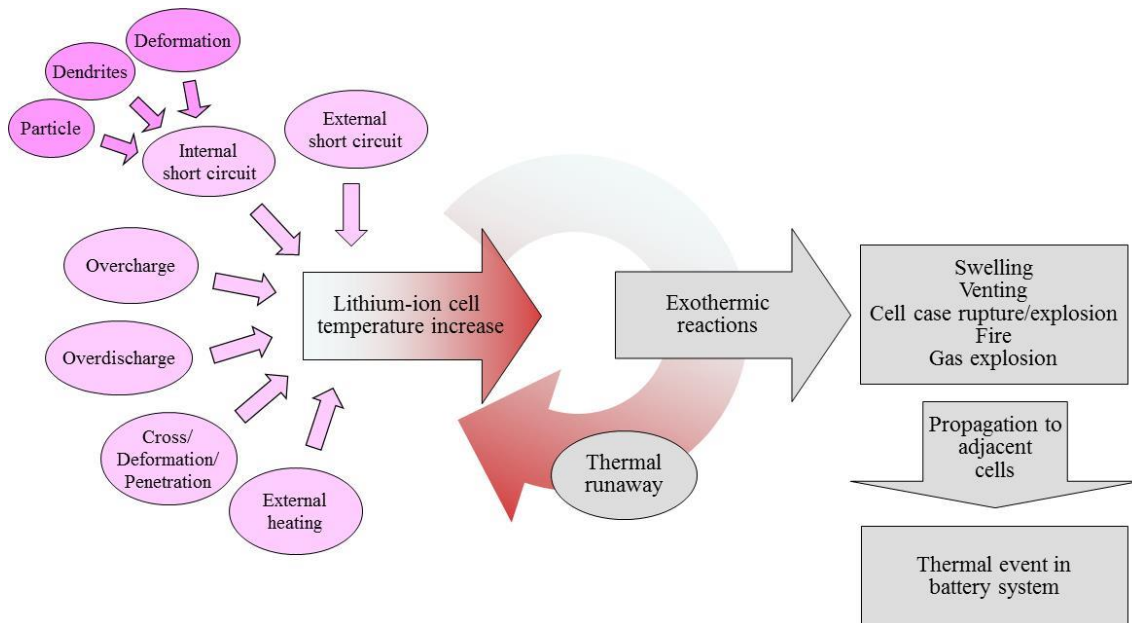


Figure 1 Thermal runaway in a single cell and its potential propagation to complete battery system level. Reprinted with permission from Larsson [1].

1.4 Protection provided by the Battery Management System

The Battery Management System (BMS) is very important in order to protect the battery system from various failure modes but the BMS cannot protect from all types of abuse conditions, see Table 1. It is therefore important to assess and handle consequences on a larger system scale, especially for those situations where the BMS cannot protect but also for situations which can occur when there is a BMS and/or sensor failure.

Table 1. A simplified general overview of abuse situations where the BMS can/cannot protect the battery system.

Abuse type	BMS protection?	Protection strategy
External battery pack short circuit	YES	Disconnect the battery by using fuse or possibly contactors
External cell short circuit	POSSIBLE*	The BMS can protect if the short circuit current is possible to interrupt by a circuit breaker.
Internal cell short circuit	NO**	-
Overcharge	YES***	Disconnect the battery by using contactors
Overdischarge	YES***	Disconnect the battery by using contactors
Mechanical cross / deformation / penetration	NO	-
External heating, mild	YES	Cooling by using thermal management system
External heating, strong	NO	-
External fire	NO	-

* This case refers to a situation with an external short circuit of one or multiple cells inside the battery pack. Theoretically, many short circuit paths are possible, and if the short circuit happens to be within a current path involving a fuse or possibly contactors then it is possible to stop the short circuit.

** Spontaneously starting on micrometer scale inside the cell battery due to e.g. particle contamination or dendrite formation.

*** The detection and the consequent actions until current shutdown must be rapid enough to ensure that the battery is not exposed to over/under voltages.

2 General and Broad Lithium-ion Battery Risk Assessment

The contents in this text and the risk assessment tables are reprinted with permission of Larsson [1].

A risk assessment is a well-established important method in order to determine risks. There are various types of risk assessment procedures and all of them need adequate reference data (input-data). The input-data, i.e. the existing knowledge, is crucial for the robustness of the assessment. With poor input-data the risk assessment will generate unreliable output-data and not the desired adequate risk determination. At present, major parts of the input-data, particularly for large battery systems, are missing or have too low quality.

A general simplified risk assessment for Li-ion batteries is presented below. The risk assessment aims to be broad and general, covering Li-ion batteries from small size to large size Li-ion battery systems, for various applications and environments, and the method therefore needs to be simplified. The Li-ion battery hazards are identified and listed and the risk assessment is presented in two tables, Table 2 and Table 3. Table 2 presents the hazards and its sources and how the sources typically can be mitigated or hindered (protection strategy). All hazards in Table 2 can potentially come from any of the sources. In Table 3 the same hazards are presented together with their consequences as well as with possible mitigation strategies.

The probability and the severity of each hazard are not quantified in detail, since there are not enough data available to determine that. Consequently it is not possible to present the rating, i.e. probability multiplied by severity. The ultimate goal of a risk assessment is to present the real-world risks. In order to do that probability, severity and ratings are needed for each hazard and for each battery type/size and application/environment conditions. Today, some values might be estimated for small sized Li-ion batteries in consumer products, e.g. a general cell failure rate of about 1 ppm, anyhow it is difficult to apply such data to the detailed hazards in the presented general risk assessment.

The data from field failures in large Li-ion battery systems are very limited since there are yet too few systems and incident statistics available. The risks are also depending on the battery use, the environmental conditions and the battery applications. That is, unfortunately not all risk numbers are known. Therefore, it is not possible today to conduct a full covering real-world risk assessment and it is particularly difficult for large Li-ion systems. Anyhow, risk assessments have to be conducted and are important, however, the risk assessment, if done properly, can only be as good as the available reference data. Statistical data from incidents in the field and investigations of such incidents will obviously be important input-data to improve future Li-ion battery risk assessments.

The risks typically have a strong dependence of battery size and application as well as the application environment. The focus has for some time been on reducing the risk of fire for Li-ion cells by several approaches, e.g. by increased onset temperatures, more

stable and less reactive cell materials, use of flame retardants etc. For consumer Li-ion batteries a fire is typically a worst case scenario that should be avoided. However, for large Li-ion battery systems, things become much more complex and the risk analysis is significantly more challenging to conduct because the technology is new and e.g. statistics, failure distribution, consequences and mechanisms of the risks are still not well known. Especially for large battery systems, risks associated with flammable and toxic gases can induce dangerous situations in terms of accumulated gas ignition and lethal gas concentrations in the battery vicinity.

If in the future it is found that fire should by all means be avoided, the gas threat must anyhow be removed by changing the cell chemistry or by other means, e.g. ventilation, minimization of the size of the cell(s) involved etc. A fire is a potential source of further fire spreading within vehicles/buildings/etc and should of course be avoided (or handled, e.g. by firefighting), however, not to the cost of a much more severe accumulated gas ignition or toxic gas emission release. However, there are no publicly available studies about these complex aspects and the authors are not aware of any studies/reports that even mention/discuss this matter. Consequently, there is a need for future studies about this.

Table 2. General simplified risk assessment of Li-ion batteries for all battery sizes/applications; hazard, its sources and mitigation/protection.

Hazard	Source	Mitigation/protection strategy	Probability	Severity	Rating
1. Swelling (but no gas release) 2. Gas release / venting: 2.1 Toxic gas emissions 2.2 Corrosive acid / gas 2.3 Accumulated gas ignition* 3. Electrolyte leakage 4. High cell pressure 4.1 Cell case rupture 4.2 Cell case explosion 5. High temperatures 6. Accumulated gas ignition ** 7. Fire*** 7.1 Fire in battery cell 7.2 Fire in battery pack material	External heating	If minor, BMS by cooling via thermal management system	Lack of data to conduct an assessment		
	External fire	Fire barriers, fire fighting			
	Mechanical cross / deformation / penetration	Battery protected box, reinforced deformation structure, placing of the battery.			
	Short circuit, external cell	Circuit breakers, e.g. fuse			
	Short circuit, internal cell	Not possible for cell, propagation protection by system			
	Overcharge	BMS, possible cell internal cell safety mechanisms			
	Overdischarge	BMS			
	BMS fault	Electrical insulation, correct personal handling technique and equipment.			
	Mechanical cross / deformation / penetration				
	8. Electrical voltage hazards				

* Ignition of accumulated battery vented gases, at relatively low temperature without a thermal runaway, can generate a flammable gas mixture and in case of ignition a pressure increase.

** Ignition of accumulated battery vented gases, in case of thermal runaway having its own ignition source (e.g. cell temperature higher than autoignition temperature, spark) in case of within the flammability limit.

*** Fire from the battery cell and/or from fire of non-cell material, e.g. plastics, cables, electronics, within the battery system.

Table 3. General simplified risk assessment of Li-ion batteries for all battery sizes/applications; hazard, its consequence and mitigation/protection.

Hazard	Consequence (worst case)	Possible mitigation / protection strategy	Probability	Severity	Rating
1. Swelling (but no gas release)	Acute safety typical ok, a balloon of flammable gases have increased fire risks.	<ul style="list-style-type: none"> • BMS • Detection and remove/replace cell probably important. 	Lack of data to conduct an assessment		
2. Gas release/venting: 2.1 Toxic gas emissions 2.2 Corrosive acid / gas 2.3 Accumulated gas ignition *	Acute toxicity <i>See point 6.</i>	<ul style="list-style-type: none"> • Early detection – warning and personal evacuation • Propagation mitigation (limit problem size/severity) • Battery placing • Ventilation • Detox (anti-dote) gas filters <i>See point 6.</i>			
3. Electrolyte leakage	Increased risk of fire (flammable vapours) and toxicity (of decomposition products).	<ul style="list-style-type: none"> • Ventilation • No heat/ignition sources 			
4. High cell pressure 4.1 Cell case rupture 4.2 Cell case explosion	Spreading out of combustible material, increased fire risk. Ballistic projectile hazards for persons/vehicles/etc.	<ul style="list-style-type: none"> • Cell designed to release gas before extreme internal pressure is reached • Ballistic projectile protection 			
5. High temperatures	Burn hazards for persons, ignition source	<ul style="list-style-type: none"> • Cooling by thermal management system (if still operational) 			
6. Accumulated gas ignition **	Damage to building and persons, potentially severe (life threatening).	<ul style="list-style-type: none"> • Pressure release in battery pack • Propagation mitigation (lower amount of gas) • Ventilation (dilution) • Pilot flame / controlled ignition 			
7. Fire*** 7.1 Fire in battery cell 7.2 Fire in battery pack material	Heat release Fire source to spread to adjacent structures.	<ul style="list-style-type: none"> • Propagation mitigation • Fire fighting 			
8. Electrical voltage hazards	From small burn to potential lethal injury.	<ul style="list-style-type: none"> • Insulation • Floating ground • BMS • Adequate personnel training on electrical hazards and equipment 			

*, **, *** See notes in Table 2.

3 General Construction Guidelines

3.1 Scope

The information found here is valid for Li-ion batteries and is derived from findings in the project “*Safer battery systems in electrified vehicles – develop knowledge, design and requirements to secure a broad introduction of electrified vehicles*”. The guidelines are presented from the perspective of the findings in the project regarding fire and gas emissions, consequently the guidelines are not necessarily covering all aspects regarding fire and gas emissions and all aspects of Li-ion battery safety are thus not covered. The guidelines can rather be seen as important examples of the consequences of fire and gas emissions and are presented in a compact and hopefully useful way for Li-ion battery systems used in electrified vehicle applications.

3.2 Holistic perspective

The Li-ion battery safety topic is complex and a holistic perspective is needed. The battery design, battery size, implementation and design on the vehicle, the application and its environment determine the overall safety. In order to achieve a high battery safety and minimize the occurrence of battery failure incidents, it is essential to use high quality Li-ion battery cells, a high quality Battery Management System (BMS), adequate safety mechanisms and to implement layer-by-layer safety, as illustrated by the “safety-onion” in Figure 2.

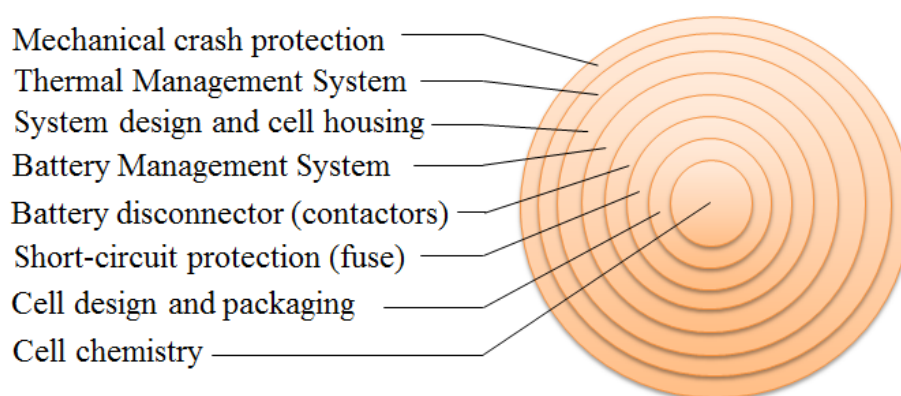


Figure 2 The safety onion illustrates that high safety is achieved by using many layer-by-layer. Reprinted with permission from Larsson [1].

The BMS cannot protect from all abuse situations, as described in section 1.4, and it is important to assess and handle those situations with adequate strategies. There can be failures in the function of the BMS and its sensors and it is equally important to assess and handle the consequences of such failures. Furthermore, it is essential that the

number of sensors and the response times in the BMS system are determined so that detection and counter-actions can be performed in time relative to the severity/consequences of the risks. Redundancy and adequate sensing are important parts of a high quality BMS.

3.3 Fire and heat

All commercial Li-ion battery cells today use electrolytes containing flammable organic solvents. The Li-ion cell, even without contact with the outside environment, in itself contains all three parts of the fire triangle in case of overheating; heat, combustible material and released oxygen. Upon abuse or failure the Li-ion battery can undergo a thermal runaway, which is a rapid self-heated cell temperature increase typically accompanied by one or several of the following events; strong venting (smoke and gas release), cell case rupture/explosion, accumulated gas ignition and fire.

For smaller Li-ion batteries used in consumer products the consequences of a fire, accumulated gas ignition and/or toxic gas release can be relatively limited compared to that for large Li-ion battery systems, nevertheless the battery can e.g. act as an ignition source of other flammable materials, it can e.g. start a building fire. To lower the heat and fire risks new electrode materials and additives such as flame retardants and electrode coatings have been developed. For larger batteries it is not known to which extent this development is in response to a holistic evaluation or to a consideration of the risk for delayed ignition and increased toxicity of gas emissions.

The Li-ion cell emits toxic gases upon abuse, in particular hydrogen fluoride (HF) but also other toxic or potentially toxic fluorine and non-fluorine gases. For the overall safety it might be favorable not to use e.g. fluoride containing flame retardants and other electrode additives because although, in case of an occasional fire, there will be an increased heat release rate, the toxic gas emissions and the risks for accumulated gas ignition will be lowered. Anyhow, the occurrence and consequence of the fire should be assessed and counter-actions be implemented, e.g. by firefighting.

Firefighting of Li-ion batteries is at the moment not well-studied. The access to the battery fire can be difficult since the battery packs are compactly designed with high tightness level (e.g. IP67). The Li-ion battery fire needs to be cooled at its source, the cell/cells. Water is a common firefighting medium, it offers excellent cooling capability, it is environmentally friendly and it is thus likely to be suitable for Li-ion battery fires, however more studies are needed. Perhaps an inlet and an outlet in the battery system/box(es) allowing flooding with water might be a solution, even though it might cause some negative effects, e.g. short circuits. Additionally, the run-off water from firefighting can be toxic, e.g. HF easily dissolves in water to form toxic hydrofluoric acid.

3.4 Ignition sources

In order to minimize fire and delayed ignition of released gases it is essential to minimize the ignition sources. Ignition sources can for example be the electronics and the BMS system, e.g. a failed and hot circuit component, a hot electrical cable or connection, the cell itself or external sources onboard the vehicle or outside the vehicle.

3.5 Propagation mitigation

Depending on the abuse and failure conditions one or multiple cells can fail, e.g. undergo gas release, thermal runaway and fire. The heat can spread to adjacent battery cells/modules and it is in general important to mitigate propagation effects. Figure 3 illustrates four different interfaces between levels where propagation protection can be implemented. The design and installation of the battery system determine to a high degree the propagation protection.

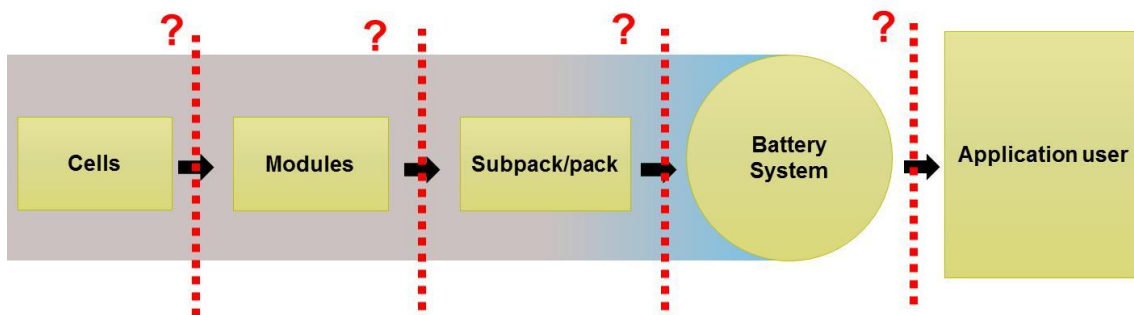


Figure 3 Propagation can occur between many levels within the battery system and the application user (e.g. the electrified vehicle). The thermal event can be initiated at many different levels by different failures/abuse. What will the consequences of various initiation scenarios be? Can they be stopped? At what level can the propagation be stopped? Reprinted with permission from Larsson [1].

It can be difficult to completely stop the propagation for all cases without having a heavy, bulky and expensive battery system. Instead of completely stopping the propagation it might be more commercially viable to delay the propagation, this could still be very valuable since it could give additional time for detection, warning, evacuation of personnel, counter-actions and firefighting actions as well as increased time for firefighters to arrive. For example, the evacuation time for all passengers in a fully occupied bus can be rather long, several minutes, thus the time for detection as well as a delay of propagation might be essential to achieve complete evacuation.

Today there are no commercially useful, intrinsically safe Li-ion cells. This means that a single cell failure can and will occur with some (low) probability. Protection from cell-to-cell propagation can therefore be needed and it can be essential to handle the consequences of such a failure. For other abuse situations, e.g. external heat, overcharge, short circuit or mechanical deformation more than one cell can

simultaneously be affected. Consequently, mitigation of cell-to-cell propagation might not be enough, and module-to-module or subpack-to-subpack propagation mitigation might be needed.

Dividing a large battery system into multiple battery packs, placing the packs with appropriate physical separation, for example in different locations in the vehicle, might offer a significantly increased propagation safety. In general, propagation can be delayed or hindered by the use of fire walls, increased battery cell spacing or a high-cooling-rated cooling system (e.g. close to ideal heat sinks) [2].

Note also that for a large battery system, to stop or delay propagation results in less heat release but also less amounts of flammable and toxic gases.

3.6 Gas release and ventilation

The Li-ion battery electrolyte contains volatile organic solvents and the cells are therefore in many cases designed to release gases at overtemperatures. By releasing the gas at a pre-designed state, the cells are protected from cell case explosion. Unfortunately the gases are flammable and toxic which results in other risks.

A gas release can occur well before and without the occurrence of a thermal runaway, for example at temperatures of about 100 °C, thus at considerably lower temperatures than that of the thermal runaway. Larsson et al. [3] studied hard prismatic Li-ion cells during abuse by external heating and identified three different vents, two well before thermal runaway and the third at the thermal runaway. If the emitted gases are mixed with air in a confined or semi-confined (e.g. the battery box itself) environment a gas explosion can occur if the gas mixture is ignited, which can result in severe damage.

In order to prevent the release of gases it is important to design the battery system so that the probability for this is as low as possible. Today there is limited knowledge of the gas composition released and when and how the different complex gases are emitted. For example, more knowledge is needed about when flammable gases and toxic gases are emitted, e.g. if they are emitted at the same time. Consequently, it is complex and difficult to determine a general strategy.

From a toxic gas perspective, to contain toxic gas emissions inside the battery box instead of releasing them can provide a safety enhancement since it may protect the surrounding environment where people might be present. Anyhow, it would require a gas-tight battery box and the available free air volume in a battery box is typically relatively small and can only contain a limited amount of gas before leaking/bursting. Containing toxic gases can also be a risk for service personal at a later stage. Balancing risks with toxic gases and accumulated gas ignition, it might be better to ventilate and detox/filter the released gases, to protect for both risks.

An important safety enhancement can be obtained keeping the gas emission concentrations out of the flammability limit thereby prohibiting ignition. The lower flammability limits (LFL) for common electrolyte solvents is about 3% [1]. In the small free volume typically found inside a battery box the LFL levels can be reached with relatively small amounts of evaporated/vented electrolyte materials from e.g. a part of a

single cell. Removing vented gases using ventilation can be an important method in order to lower the concentration of flammable gases and thereby lowering the risk for a fire and/or an accumulated gas ignition to occur.

The venting/bursting location(s) on the cell and the venting direction should be known. The cell integration, module design and overall battery system design should be constructed so that the gases are allowed to be ventilated out, i.e. not locally trapped in a part of the battery pack. One or several predesigned locations in the battery system box(es) should have ventilation outlets. The location where the gases are released to the outside ambient air should be chosen wisely to lower risks for fire and toxic exposure to driver, passenger and other humans.

In order to control the spot(s) where the gases are released it is recommended that the outlets on the battery box(es) are connected to an outside ventilation system using piping, see section 3.12.2. If a ventilation fan is used (inside or outside the battery box) it should be EX-classed to not introduce an ignition source. A further improvement of the gas ventilation system could include internal battery system piping connecting to individual battery modules, cell safety vents or known venting positions. Before releasing the gases to open air a filter/pre-treatment could be used, see next section.

3.7 Filtration of released gases

The released gases could be filtered either inside the battery pack/system or in the vehicle system (outside the battery system) before releasing them to the outside ambient air. The filtration can be done with different cleaning methods and filters (e.g. carbon filters), to treat (detox) toxic gas emissions or handle flammable gases.

Gas filtration can be essential for large Li-ion batteries and/or operation in confined or semi-confined spaces. Without filtration, lethal levels of toxic gases might be present.

3.8 Release of toxic gases

Toxic gases released from Li-ion batteries have been studied to a very limited degree. “Traditional fire gases” such as CO and CO₂, have been most studied while only few studies are available regarding emissions of hydrogen fluoride (HF) and other toxic fluorine as well as non-fluorine compounds. In a recent study by Larsson et al. [4] seven different types of commercial Li-ion batteries were investigated in fire tests and it was found that the released amounts of HF ranged from 20 to 200 mg/Wh, where Wh denotes the nominal energy capacity of the battery. This means that a fire that consumes a 100 kWh Li-ion battery will release 2-20 kg HF. HF is known to be very toxic, having an IDLH (Immediately Dangerous to Life or Health) value of 25 mg/m³ (30 ppm) [5] and a 10-min lethal value (AEGL-3) of 139 mg/m³ (170 ppm) [6]. The maximum allowed exposure level to workers in Sweden at any time is 1.7 mg/m³ (2 ppm) [7]. HF gas is also corrosive and might attach to walls/surfaces. Furthermore, HF easily dissolves in water forming toxic hydrofluoric acid.

3.9 Protection against accumulated gas ignition

Ventilation of released and accumulated non-combusted flammable gases is of paramount importance to prevent accumulated gas ignition, see section 3.6. Furthermore, the battery and its installation space onboard the vehicle should be designed with adequate pressure release devices and protection strategies to minimize the consequence of an accumulated gas ignition, mitigating the pressure build-up and damage level. In other terms, it is recommended to develop pressure release strategies in order to properly equip and design the battery box(es), but also to consider the placing (location) of the battery in the vehicle as well as to consider pressure release/mitigation/protection designs for the battery integration.

For some situations a fire is less severe than an accumulated gas ignition. Consequently, a controlled ignition, via e.g. a pilot flame, might be favorable. However it is difficult to state in which situations this would be an improvement to safety. The design/integration of such a device could also be challenge, e.g. not to act as the ignition source of an accumulated gas ignition. The overall safety should be assessed by holistic perspectives in which the risk for an accumulated gas ignition has to be weighed against other risks. However, other means than a controlled ignition should however first be attempted.

3.10 Protection from ballistics projectiles

Cylindrical and hard prismatic cells can build a high internal pressure and are therefore equipped with a cell safety vent designed to release gases before extreme cell pressures are reached. However, in case of bad design or malfunctions, a cell case explosion can still occur. In a cell case explosion as well as in an accumulated gas ignition, hazardous projectiles might be ejected and the battery system should thus be designed to offer protection to humans from such projectiles. The risk of a cell case explosion for pouch cells is however estimated to be low since pouch cells typically cannot build high pressures.

3.11 Detection

Failure detection is important and should typically be done by the BMS. For some failure scenarios detection is anyhow more difficult. For example, a cell can overheat and release gases, but without temperature sensors on the cell surface, the excessive heat might not be detected or detected too late if the temperature sensor is placed at a distance from the malfunctioning cell. The cell voltage is normally detected for each cell by the BMS. Detection of a voltage deviation is thus in principle easy but a cell voltage drop to 0 V can be due to a numbers of reasons, e.g. broken sensor, BMS failure, activation of current interrupt device (CID) (if present, not functional in battery system with voltage above around 50 V) as well as from a thermal runaway/fire. The detection

of a low voltage may thus show that there is a malfunction but not supply much information on the character of the event.

Without the use of gas sensor(s) it might be difficult/impossible to detect the release of toxic and flammable gases. Without detection there can be a situation where the battery pack is filled with flammable gas from vented cell(s) mixed with oxygen (present from the start and/or released from the cell(s)) and thus only an ignition stands between a non-event and a potentially severe incident. Actually, without detection of vented gases, it may be impossible to eliminate a situation in which an accumulated flammable gas mixture is formed. Situations like this could be detected via gas sensors installed in the battery system box(es). The response time using a gas sensor can be short offering early detection. A battery which has been well-categorized in terms of thermal response to various abuse conditions with a strategically planned temperature detection system might also provide a secondary indication of a gas release [3].

Suitable sensors can for example be detecting hydrocarbons (electrolyte solvents, e.g. dimethyl carbonate (DMC) and ethylene carbonate (EC)) as well as toxic gases, e.g. hydrogen fluoride. Thus, two sensor types can be useful; one for flammability protection detecting hydrocarbons and a second for identification of toxic gases. More studies are needed of gas emissions and when different gases are emitted and/or produced. The battery size, application and environment determine the needs. For a large battery system, multiple gas sensors could be needed.

3.12 Placing and packaging of battery system in electrified vehicles

3.12.1 Ignition sources

To minimize the risks of fire and accumulated gas ignition, it is essential to minimize potential ignition sources in the vicinity of the battery system and particularly at the location(s) where gases can be released.

3.12.2 Gas release, ventilation and filtration

In case of gas release, detection, ventilation and filtration are essential to handle flammable and toxic gases. Ventilation can be achieved by connecting the ventilation outlet(s) from the battery system to an onboard vehicle ventilation system having e.g., tubing, “chimney” and/or using a fan (EX-classed in order not to introduce an ignition source for the flammable gases). The flammable and toxic gases are thereby diluted to lower fire and accumulated gas ignition risks inside the battery pack. It is important to consider where/at what environment (e.g. the presence of humans) the ventilated gases are released outside the battery pack/vehicle, including e.g. toxicity on walls/surfaces.

Filtration of gases before releasing can be essential, e.g. to detox gases such as hydrogen fluoride. For some scenarios it might be possible to contain toxic gases in the battery or on the vehicle instead of releasing them to the open air.

The largest toxic threat is estimated to be the emission of battery gases in confined/semi-confined spaces, e.g. garages, tunnels, inside buildings and underground structures. The risks increase with increasing Li-ion battery size. For example, EV-buses provide an opportunity for indoor driving lanes and bus stops due to their zero-tail-emissions. Anyhow, having large Li-ion battery packs in an indoor environment with limited air space may be hazardous in case of a major battery malfunction. Such hazards might be considered also for outdoor environments, e.g. in tight/compact city centers.

3.12.3 Fire propagation

Fire walls or fire barriers between the battery system and other parts of the vehicle, e.g. the passenger compartment are important to hinder spreading of heat, fire, gas and smoke. A thermal event or fire can start inside the battery but an external adjacent fire (e.g. a building fire, a fire in another vehicle) can also occur. The case of an external fire might actually be more probable than fires starting inside the battery, however there are yet insufficient statistics to determine the risk levels. Protection from external fire involves the use of fire barriers/walls and possibly the battery cooling system. It may be difficult, however important, to delay/stop/mitigate toxic gas release as well as fire and heat spreading.

It is important to place the battery so that it is protected both from heat/fire propagation from an internal battery heat/fire source as well as protection from an external heat/fire source. This influences the release of toxic gases, heat and fire.

3.12.4 Placing

The placing of the battery system in electrified vehicles should be done in order to protect the battery system from external abuse, such as external heating/fire and mechanical damage, but also to protect it from failures originating from the battery system. The placing can affect the direction of vented gases and smoke as well as the angles of fire flames and heat. It is difficult to give recommendations on a general placement strategy since different environments and vehicle types have different properties.

4 References

- [1] Fredrik Larsson, “Lithium-ion Battery Safety - Assessment by Abuse Testing, Fluoride Gas Emissions and Fire Propagation”, PhD Thesis, ISBN: 978-91-7597-612-9, *Chalmers University of Technology*, Göteborg, Sweden (2017).
Available online:
<http://publications.lib.chalmers.se/records/fulltext/251352/251352.pdf>
- [2] Fredrik Larsson, Johan Andersson, Petra Andersson, Bengt-Erik Mellander, “Thermal modelling of cell-to-cell fire propagation and cascading thermal runaway failure effects for lithium-ion battery cells and modules using fire walls”, *Journal of The Electrochemical Society*, 163 (14), A2854-2865 (2016).
- [3] Fredrik Larsson, Simon Bertilsson, Maurizio Furlani, Ingvar Albinsson, Bengt-Erik Mellander, “Gas explosions and thermal runaways during external heating abuse of commercial lithium-ion graphite-LiCoO₂ cells with different levels of ageing”, *submitted manuscript*.
- [4] Fredrik Larsson, Petra Andersson, Per Blomqvist, Bengt-Erik Mellander, “Toxic fluoride gas emissions from lithium-ion battery fires”, *Scientific Reports*, 7, article number 10018 (2017).
Available online: <https://www.nature.com/articles/s41598-017-09784-z>
- [5] “Documentation for immediately dangerous to life or health concentrations (IDLHs) for hydrogen fluoride (as F)”, *The National Institute for Occupational Safety and Health (NIOSH)* (1994).
- [6] “Acute exposure guideline levels for selected airborne chemicals: volume 4, subcommittee on acute exposure guideline levels”, ISBN: 0-309-53013-X, Committee on Toxicology, *National Research Council* (2004).
- [7] A. Middelman, “Hygiensiska gränsvärden AFS 2015:7, Hygieniska gränsvärden”, Arbetsmiljöverkets föreskrifter om hygieniska gränsvärden och allmänna råd om tillämpningen av föreskrifterna, ISBN 978-91-7930-628-1, ISSN 1650-3163, *Swedish Work Environment Authority* (2015).

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