Fire Safety of Lithium-Ion Traction Batteries

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ABSTRACT
As the number of electric vehicles rises both in passenger cars and larger transportation vehicles, potential hazards caused by Li-Ion batteries will occur on public roads as well as underground infrastructures like road tunnels or car parks. Fire propagation due to thermal runaway differs from fire spread mechanisms known from conventional fires in these kind of infrastructures. In the course of the research project SUVEREN Real-scale fire tests have been performed and temperatures and exhaust gases caused by these fires, with and without suppression, have been investigated. It was proven that successful firefighting of uncovered Li-Ion battery fires is possible and a matter of suitable design in terms of fire suppression agent, detection system and the installation of the battery.

KEYWORDS: Li-Ion battery, water mist system, fire testing, fire suppression

INTRODUCTION

Climate change is demanding a more sustainable lifestyle, including especially the field of mobility. The need to reduce climate-wracking gases like CO2 results in new technologies and alternative propulsion systems. Electric vehicles utilizing fuel cells or Lithium-Ion (Li-Ion) batteries for traction are becoming more and more popular.
In the event of fire, the burning characteristics of Li-Ion batteries differ from those of pool fires caused by conventional ICE vehicles. Battery fires are driven by exothermic internal reactions.
In the early stages of the research project, a lack of respective experimental data about the propagation of these thermal runaways was identified. Even fewer data was published about influence of firefighting when interacting with Li-Ion batteries. In addition the available work, like [1] and [2] mostly performed tests on cell level. As cell failure caused by thermal runaway can propagate through the entire battery, knowledge and experience in dealing with this hazard is essential for the design of a fixed firefighting system.
The lack of empirical data was addressed by setting up a pair of fire test series. At first the thermal runaway propagation and burning of the battery was investigated using a specially designed calorimetry. The results about the burning characteristics investigations were then used for the design of the second test series. Here the effectiveness of different firefighting agents was investigated and compared. All fire tests were performed with Li-Ion battery packs or modules. Gas and surface temperature were analysed as well the composition of the exhaust gases.
This paper provides insight in the main observations regarding Li-Ion fire behaviour and the interaction of Li-Ion battery fires with firefighting agents.

APPROACH & BACKGROUND

A fire test program on battery fire load, consisting of two fire test series with different focus and slightly specified set-up, was conducted. The first test series focused on the burning behavior of Li-Ion batteries in general to fill the identified knowledge gap in this field. Focus of the second series were detection systems and suppression agents to minimize the risks caused be the batteries.
The first series was conducted in March and June 2019 while the second series took place in December 2019 and January 2020. Tests were carried out in northern Germany by IFAB - Institute for Applied Fire Research GmbH, a certified fire testing company, at the company's fire test facilities.

Fire load
All fire tests used original battery modules or packs provided by the automobile industry. Fire tests with whole electric vehicles had been ruled out due to budget restrictions. Further the development of electric vehicles is very dynamic, leading to many different electric vehicle models, types and batteries used. A reproducible fire test protocol, which suits all available electric vehicles, is not available. Consequently, the fire behaviour of the main new component of an electric vehicle was investigated to combine the results subsequently with experiences of passenger vehicle fires.
The batteries provided by a German manufacturer were partially split up into individual modules by the fire test team. Fire tests included two cell types, cylindrical and prismatic with slightly different cell chemistry. Details of the batteries used for fire testing are summarized in Table 1.

Table 1 Detail of batteries involved in the fire tests. Listed by the two different batteries types (Type A and Type B) that were used for the tests.

	Type A	Type B
Designed purpose	Vehicle traction	Vehicle traction
Operating Voltage [V]	259.2 – 398.4	260.0 – 436.8
Cell type	cylindrical	prismatic
No cells per module	12	132
Cell dimensions	173 mm x 45 mm x 125 mm	65.0 mm (height), 18.4 mm (diameter)
Weight per cell	2.05 kg	0.048 kg

Based on the results of the first tests a reference battery fire load was defined for the follow-up fire testing. A similar and well defined fire load is necessary to compare the effectiveness of different firefighting agents and strategies among themselves. The selected fire load during the entire second series consisted of two modules with cells from Type A. Module 1 became the initial module while the second one was labelled as the target module. In previous tests, under freeburn conditions, thermal runaway has spread across both modules. The success of the different firefighting strategies was assessed by the fact and the extent of containing the propagation.
Fire testing during the SUVEREN project did further include investigations about CNG jet fires and the suppression of vehicle fires as well, but results have been published separately [3]. Only the fire tests including Li-Ion batteries will be part of this work.
The first series was conducted in March and June 2019 while the second series took place in December 2019 and January 2020.

EXPERIMENTAL SET-UP
All fire testing was performed inside the IFAB fire test hall. The compartments used for the fire testing were temporary and mobile installations designed and built exclusively for the research project to keep comparable conditions throughout all tests. The fire stands were constructed with dimensions best suited for the research purpose, a footprint of 4.0 m x 4.0 m and a height of 2.0 m. A roof was added to this for some of the tests in order to collect the exhaust gases. Both freeburn and suppression fire tests could be handled inside the compartment. The compartment as primary set-up further provided safety for both staff and equipment.
Fire test stands
Two variations of the compartment were used during the fire tests and the fire test stands have been adapted due to the aims of each fire test series in order to match the specific needs.
The calorimeter built for the fire test batteries was mainly shaped by the needs of the methods used to determine the heat release rate and the gas measurement systems. Determination of the heat release is a major factor in fire protection and important to know when describing the fire behavior of Li-Ion batteries and comparing its influence to known kinds of hazard.
The use of a compartment as primary set-up added some safety for both staff and equipment. Dealing with a, at that time, relatively unknown fire load led to additional and safety measures. Figure 1 and Figure 2 provide some insight showing a photo and one of the drawings.

Figure 1 Photo of calorimeter- Series 1

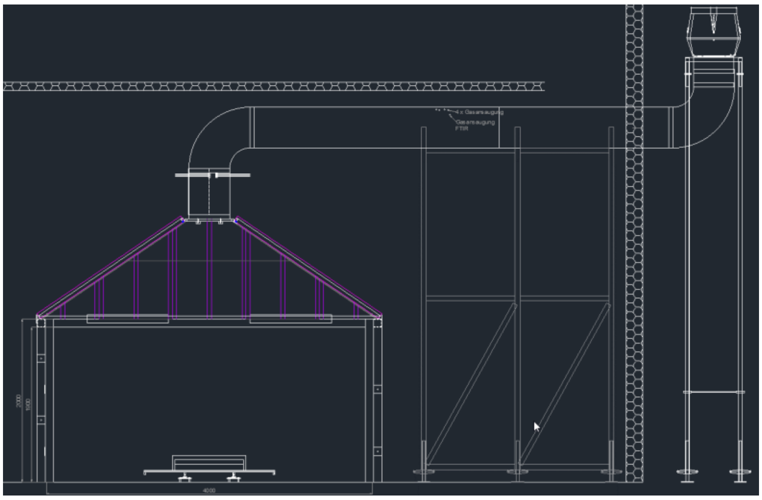


Figure 2 Drawing of calorimeter - Series 1

As displayed in Figure 2 the exhaust duct connected the inside of the calorimeter with the outside via a fire-proof ventilator which was positioned right outside the hall. The exhaust duct's connection was located at the top of the roof. The power of the ventilator (max 1.5 kW) was adjusted to control the volume flow from the inside of the calorimeter. A gap of 20 cm between the floor of the fire test hall and the lower parts of the walls of the calorimeter allowed fresh air to flow, preventing the ventilator from failing and delivering a steady oxygen supply during the fire tests.

Several measurement devices, thermocouple, velocity probes as well as single and multi-gas sensors had been installed inside the exhaust duct. The collection of the exhaust gases from the battery was used to analyse the composition and the amount of the exhaust gases.

For the second test series the fire test stand was adapted due to the focus of the investigation. The main differences were a flat roof which was better suited for the installation of firefighting and detection systems. No forced mechanical ventilation was attached during these tests, as the fire test stand could be operated in two ventilation modes: sealed and open. Figure 3 shows that fire test stand.


Figure 3 Fire test stand "Detection & Firefighting"

Measurement systems
In addition to several scientific measurement devices to observe the fire tests common commercial detection systems, based on different markers, were installed as well. This allowed to compare and calibrate the results of the commercial detection systems with scientific measurements. Thermocouples were placed all over the calorimeter, the inside of the exhaust duct and atop the fire load. The heat release rate was measured using oxygen consumption calorimetry (OCC) which is widely used to experimentally determine the heat release rate of all kinds and sizes of fires. The OCC is mainly depending on the amount of oxygen consumed by a fire, but may include corrections based on the concentrations of CO_2 and CO. All three gases were measured during the fire tests. Heat release results from these fire tests have been published in [4]. In addition to the OCC the heat release rate was determined by the SERA (Sensible Enthalpy Rise Approach) which is based on energy balances. A description and an assessment by simulations is published separately [5].
The design of the calorimeter was mainly shaped to fit the requirements of the heat release rate methods mentioned above. While the OCC requires the collection and dilution of all exhaust gases the determination of volume flow is required by the SERA.


Figure 4 Measurements system

Fixed-firefighting system
Major objective of the second fire test series was the testing of firefighting systems and agents. Consequently, different firefighting systems available on the market were installed. The early suppression tests were performed using a high-pressure water mist system that was in standby as safety backup during all tests and could be activated manually from the outside.

FIRE TEST SET-UP
In addition to freeburn tests fire tests with a water mist system were performed as well. Similar fire load and boundaries allowed for a direct comparison with suppression tests. Suppression tests were performed with both cell types.

Specifications of first series
The main objective was to achieve a better understanding of the processes involved during thermal runaway and battery fire. The main focus was on the identification of methods and techniques that would be helpful in dealing with Li-Ion battery fires in real-case scenarios. Accordingly, the exhaust gases have been analysed in order to know the risks coming from battery off-gases for potential evacuees. Also there is a possibility to use the gas data to identify good strategies for detecting a failing battery as early as possible.
The thermal runaway process was triggered by mechanical drilling of one cell. After the ignition started, the drilling device was removed from the calorimeter waiting for the start of the thermal runaway and its propagation. The water mist systems was mobilized for safety reasons and activated manually based on pre-set conditions. As long as the threshold values were not exceeded no interaction was taken in the freeburn tests.
Specifications of second series
The second fire test series focused on the capabilities of dealing with the fire risks caused by Li-Ion batteries. The details of this test series were developed based on the findings from series 1. The reference battery fire load described above was used as a fire load in all tests. Thermal runaway was initiated by forced electrical overcharging, a less invasive ignition method. Several commercial detection systems were installed to work during the fire test. These commercial detection and suppression concepts and technologies were investigated in order to find efficient ways of dealing with these fire risks in application scenarios.
Before SUVEREN, very little data was available about the firefighting of Li-Ion batteries and most publications do not compare different firefighting agents. This was addressed by fire tests with both water- and gas-based agents. The agents were chosen as they were identified to be mentioned in terms of suppression of battery fires lately.

Table 2 Overview firefighting agents

Fire suppression agent	Category	Specification
High Pressure Water Mist	Water-based	Different nozzles, pressure > 60 bar
Low Pressure Water Mist	Water-based	Pressure below 10 bar
Sprinkler	Water-based	Operating pressure 3 bar
F500	Water-based	Added to water mist
FOAM	Water-based	VdS approved firefighting foam
Aerosol	Gas-based	Multiple generators according to the required application density
Nitrogen	Gas-based	Supposed to fill the entire room in less than 60 s
Carbon Dioxide	Gas-based	Keep the oxygen concentration below 14 Vol% for at least 10 minutes
NOVEC	Gas-based	VdS 2381 [6]

As water- and gas-based firefighting agents require different conditions for normal operating, the fire test stand was equipped with adjustable ventilation openings. These allowed fresh air to flow in and out of the compartment during the suppression test with water-based agents. As leakage would significantly affect the gas-based firefighting agents and might very well place them beyond their application conditions, the fire test stand was sealed during those tests.

FIRE TEST RESULTS
A total number of 13 fire tests with identical fire loads were performed, including two complete freeburn tests. Before the activation of the suppression systems the conditions in all battery fire tests have been equal to those in the freeburn test. The ignition and early fire stage of the battery modules were observed. The bar in Figure 5 represents the time from the start of the overcharging until the failure of the first cell, which was recognized by the cell bursting. All measured times are within a

range of 45 s and just below 80 s, proving that the ignition method is working reproducibly.

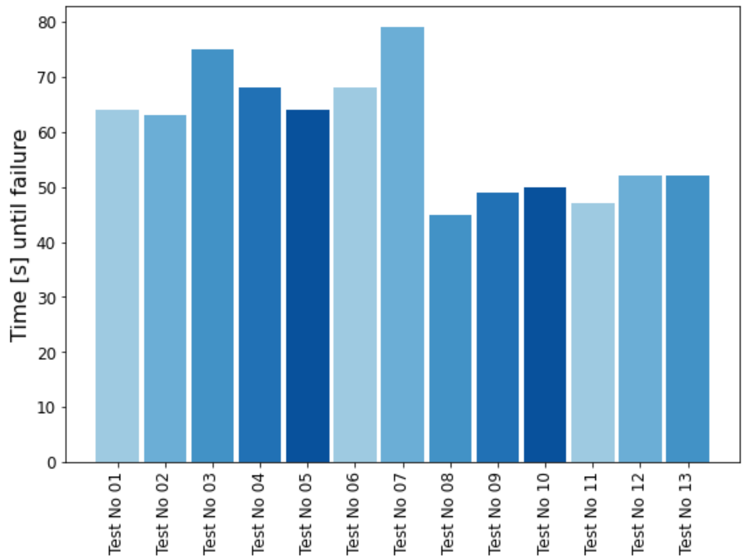


Figure 5 Duration of charging until ignition / failure of first battery cell

The times displayed in Figure 6 represent the instance when a mean temperature of 50 °C was reached inside the fire test stand. In all tests this threshold value was reached after multiple cells had bursted due to the pressure caused by thermal runaway. The time range is larger than those of the ignition times. After the burst of the first cell, the charging was stopped and while charging was performed with a constant amperage, it led to the very similar conditions during the heat up of the cell. Even though the time until 50 °C was reached differs, the propagation did happen in all 13 fire tests. The time ranges from around 150 s to almost 500 s. At that criterion the suppression systems were activated and the free burn process was stopped for all but two battery modules.

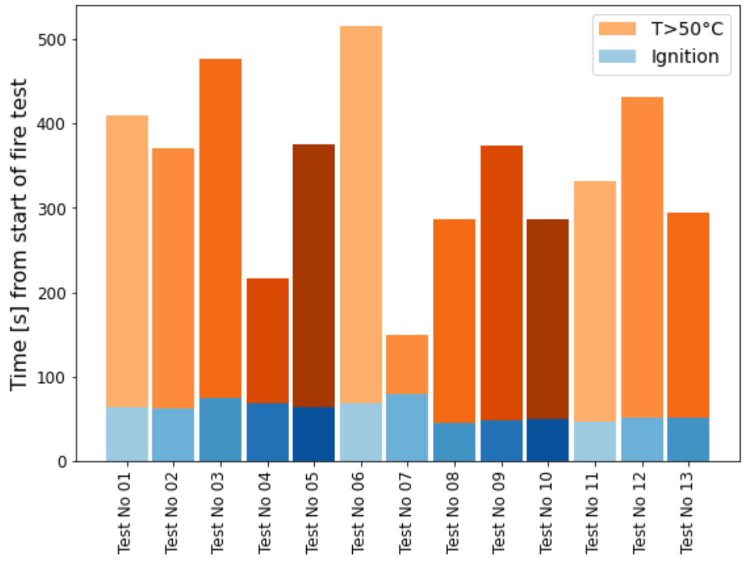
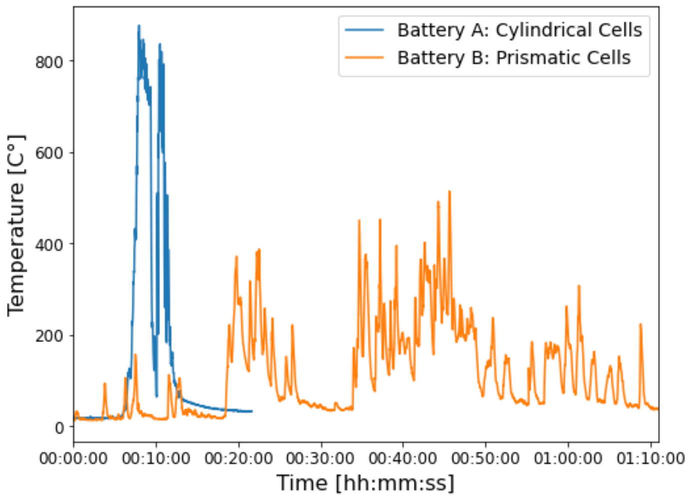


Figure 6 Duration until a mean value of 50 °C was measured inside calorimeter

Fire behavior Li-Ion batteries

Regardless of the method of ignition in case of a thermal runaway initiated inside a single cell of the module, the thermal runaway tends to propagate to all cells of the module and very likely to adjacent modules. In all fire tests without suppression, every cell of the ignited module did react and consequently burst due to overpressure. Differences in speed of propagation have been identified depending on both battery-related and exterior boundary conditions. In SUVEREN fire tests the cell type had a significant influence on the propagation of thermal runaway inside and across modules.

The resulting temperature inside the exhaust duct during the complete reaction and burning of two large battery packs is displayed in Figure 7. Battery A consists of cylindrical cells and battery B consists of fewer and larger prismatic cells. The cell chemistry is similar as both batteries originate from the same manufacturer and were designed for the same purpose. Details about the cell chemistry



are summarized in Table 1.

Figure 7 Temperature in exhaust duct during battery fire tests

Battery pack A reaches a high temperature within in a very short time. This fast and intense reaction ends up with a completely burnt battery pack in which all cells have already reacted in less than 20 minutes after ignition. The fire development from battery B significantly differs from that. Lower temperatures are reached but their duration is much longer. It takes over 70 minutes until the whole battery, respectively its cells, have completely reacted. The exothermal reactions inside the cells keep firing up themselves and off-gases burn in shape of up to 1.5 m jet fires over that span. Battery B burns with several temperature peaks and contains phases of low temperatures until the whole battery is burnt. These phases are caused by the burning of plastic parts, i.e. the coverage of the pack or other parts of the battery compartment.

Batteries A and B were burnt with their original cover, which was made of plastic. The fire test series included battery tests without a coverage and it was observed, that the coverage has an influence at least on the early fire spread. The heat released by the first bursting cells was kept inside the battery pack as the cover was still in place at that time, though it started to burn by itself.

The development of Li-Ion battery fire depends on the ventilation condition, especially regarding its speed of propagation. Both the reaction rate inside a module and the spread to adjacent modules is affected. Figure 8 displays the time-dependent temperature of battery module fire tests with three different ventilation conditions: closed room, natural ventilation and mechanical ventilation. The temperature indicates that the initial module and the second module reacted one after another, as temperatures lowered after the complete reaction of a module. While the reactions based on the temperature analysis are similar in all three cases, the time needed for a complete reaction is longer in the case without ventilation. The influence is more significant when looking at the reaction of the second module. The time between the finish of the reaction in module 1 and the start of the reaction in module 2 is longer and the temperatures reached are over a 100 °C lower than those measured during the reaction of the first module. The opposite is true for the better ventilated cases. If enough oxygen is available the reaction rate and the resulting temperature tend to rise. The time-dependent temperatures of three free burning Li-Ion modules under different ventilation conditions are displayed in Figure 8. The fire tests shared the same fire load, two modules with cylindrical cells arranged next to each other, but had different ventilation conditions. During the sealed test all openings from the compartment to the outside were closed, while these were opened during the natural ventilation test. The fire test using mechanical ventilation was performed inside the calorimeter as described in Figure

2.

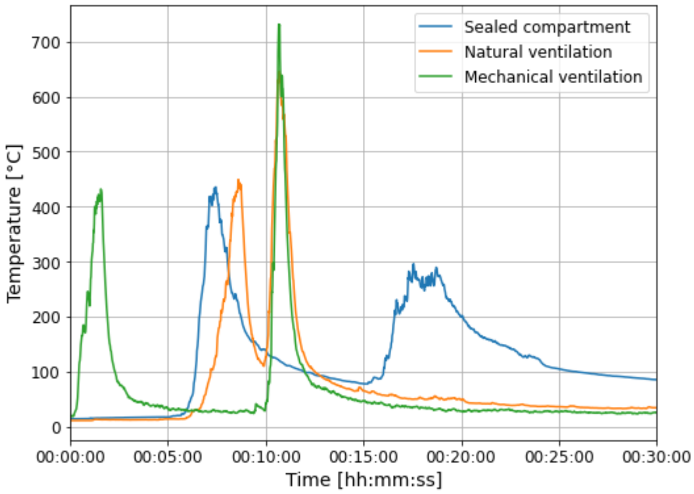


Figure 8 Time dependent-temperature resulting from Li-Ion module free burning tests with different ventilation conditions

FIREFIGHTING & DETECTION

In Figure 9 the time-dependent temperature during a suppression test is displayed. Fire load and other boundaries are similar to the ones used in the fire test of Battery B, as in Figure 7.

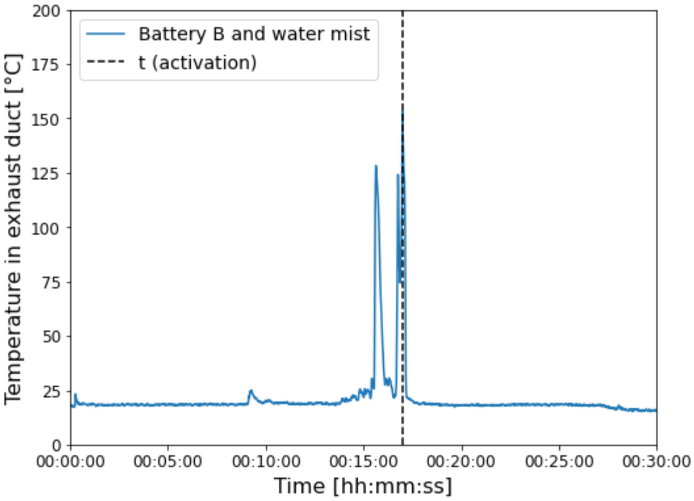


Figure 9 Temperature of battery fire test with active suppression by water mist

The prismatic cells show a similar behavior as small peaks in temperature are measured right after the penetration of the first cell and again around 9 minutes after ignition. Both of these off-gases do not ignite, thus temperatures are still low. Around 15 minutes after ignition temperature rises as multiple cells burst and lead to jet-fires. The suppression system was activated manually after the criterion of reaction of multiple cells and ignition of the off-gases was matched. The activated water mist system was able to end the propagation quickly. No more heating up was recorded after the uncovered battery was extinguished.

While the fire test described above was a proof-of-concept that the propagation could be stopped, the follow up suppression tests did include multiple different firefighting agents. The firefighting agents summarized in Table 2 were tested facing the same fire load, 2 modules of fast reacting cylindrical cells. The criterion for activation was the same in all tests, as the firefighting systems were activated after the mean air temperature of 50 °C was reached inside the fire test stand. Both water and gas-based firefighting agents were able to protect the second module.

HF is widely known to be emitted during thermal runaway as part of the reaction products. Serious amounts of HF were measured during SUVEREN fire tests as well. The concentration of HF along with fellow acid gas species HCl and HCN is displayed in Figure 10. The species data results from the fire test of battery B. Comparison of Figure 7 and Figure 9 reveals that the peaks in heat release rate and HF concentration match, as the fire behavior of battery pack B is determined by sudden and intense jet fires and relatively quiet breaks in-between. The analysis of HCN indicated that it does not origin from the battery cells but rather is a product of the plastic cover burning. HCN peaks at around 20 minutes and very little of it is emitted in the late stage of the fire. In contrast HCl while not reaching the peaks of HF is measured throughout the fire test and its peaks indicate that the HCl is a product of the battery reaction as well.

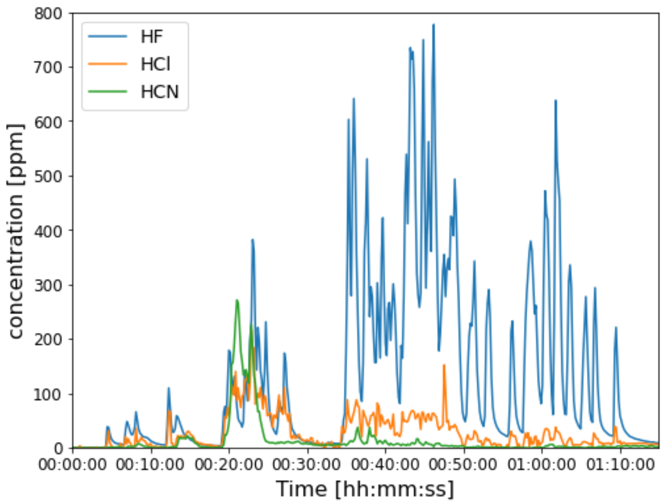


Figure 10 Acid measurement

A detailed gas analysis showed that these three species are not the only toxic substances during a battery fire. The three mentioned do have the largest peak values, besides usual fire products carbon monoxide and carbon dioxide, but in total more than ten other toxic species have been detected in significant amounts between15 ppm to over 100 ppm. These have been summarized and categorized in Table 3.

Table 3 Gas concentration range measured in Li-Ion battery off-gas

Gas species	**Value range**	**category**
Acrolein	15 ppm – 50 ppm	1
Benzol	50 ppm – 100 ppm	2
Acetylen	>150 ppm	4
Acetaldehyd	15 ppm – 50 ppm	1
Toluol	15 ppm – 50 ppm	1
Ethylmethylcarbonat	50 ppm – 100 ppm	2
Dimethylcarbonat	100 ppm – 150 ppm	3
Ethylencarbonat	50 ppm – 100 ppm	3

CONCLUSIONS

Large scale fire tests have been performed by the Research project SUVEREN investigating the burning characteristics of real Li-Ion batteries from automobile industry, detection systems and suppression agents. Li-Ion batteries can lead to serious fire incidents caused by thermal runaway impacting the entire battery. The fire behavior from Li-Ion batteries differs from conventional fuels

used in the mobility sector. Accordingly, existing firefighting strategies have to be reviewed in order to keep an acceptable safety level. The SUVEREN project contributed to this review process.
The following findings can be stated about the specific burning behavior of Li-Ion batteries:

- Different Li-Ion batteries can burn differently. The type of the cells and their arrangement have large influence on the reaction rate and how quickly a thermal runaway propagates.
- Depending on its design and cell type, the burning behaviour of different kinds of lithium-ion batteries highly differ in terms of burning rate, heat release and appropriate firefighting techniques.
- Lithium-ion battery release combustible gases due to cell failure. These gases are not ignited in every case, depending on the local situation.
- Li-Ion Batteries emit a mix of toxic and reactive/aggressive gases, HF is a prominent part, but it is accompanied by several other toxic species.
- The burning rate of lithium-ion batteries depends on the oxygen concentration and thus on the ventilation conditions. A reduced oxygen concentration leads to a lower burning rate of a lithium-ion battery fire.
- Water based firefighting agents provided good cooling ability during the fire tests, though gas based agent were able to stop the propagation as well. The firefighting systems best suited for a specific application has to be determined from case to case based on requirements and the capability of the firefighting system.
- A water mist system was able to stop the propagation of thermal runaway within an uncovered battery module. External cooling was needed to stop the propagation.

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