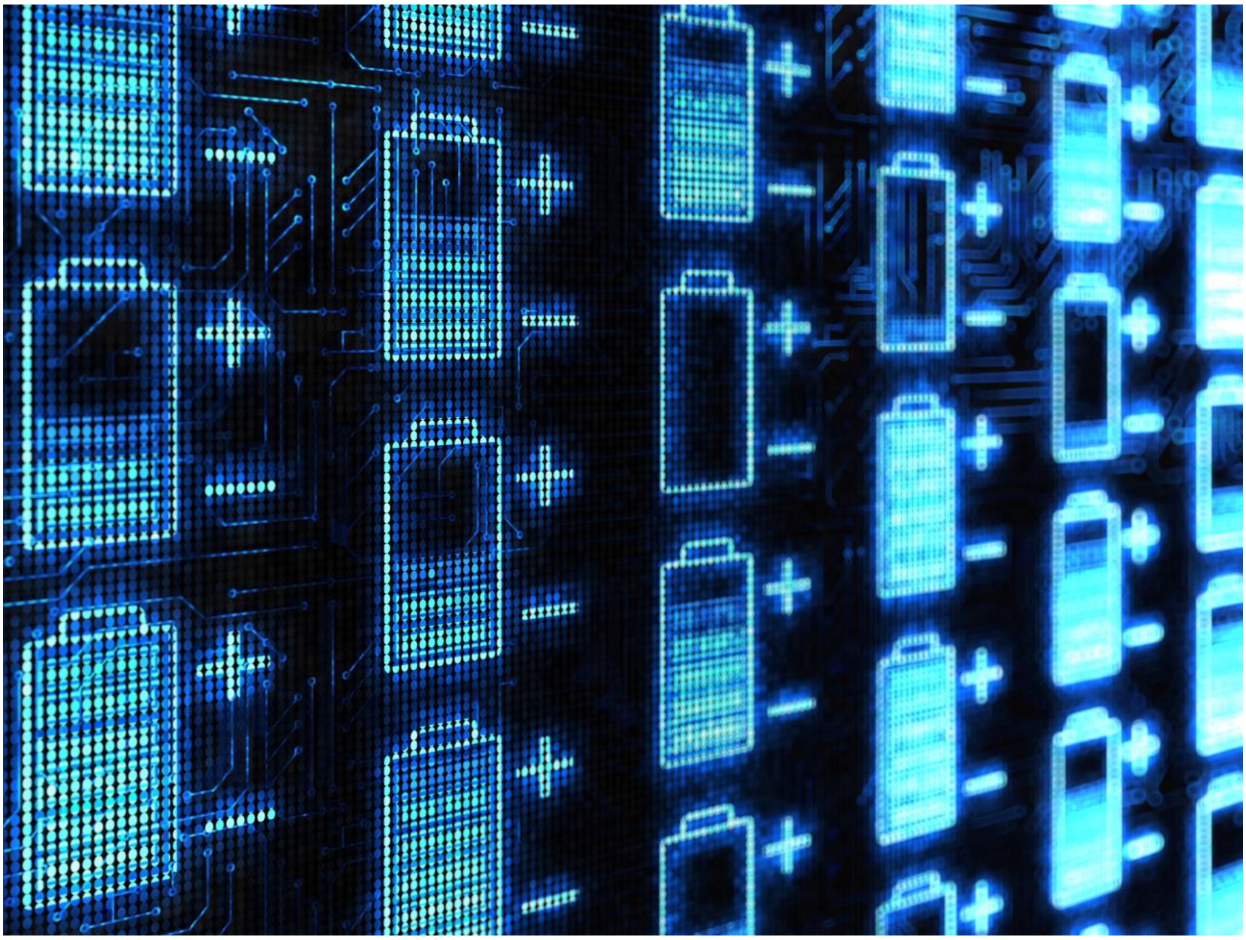
MARITIME BATTERY SAFETY JOINT DEVELOPMENT PROJECT

Technical Reference for Li-ion Battery Explosion Risk and Fire Suppression

Partner Group

Report No.: 2019-1025, Rev. 4
Document No.: 1144K9G7-12
Date: 2019-11-01



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Project name: Maritime Battery Safety Joint Development project
Report title: Technical Reference for Li-ion Battery Explosion Risk and Fire Suppression
Customer: Partner Group

Customer contact:
Date of issue: 2019-11-01
Project No.: PP180028
Organisation unit: Environment Advisory
Report No.: 2019-1025, Rev. 4
Document No.: 1144K9G7-12
Applicable contract(s) governing the provision of this Report:

Objective: This report is intended for persons assessing energy storage installations, from a design, engineering or regulatory perspective, to better evaluate risks and solutions with regard to lithium-ion battery fire, off-gassing and explosion.

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Keywords:
Fire, Suppression, Battery, Safety, Ventilation, CFD analyses, Lithium-Ion, Off-gas, explosion, Quantitative Risk Assessment, Qualitative Risk Assessment, Thermal Runaway, Toxicity, Temperature Class, Gas Group

Rev. No.	Date	Reason for Issue	Prepared by	Verified by	Approved by
1	2019-04-29	First JDP Committee Draft Review	Ben Gully	Gerd Petra Haugom	Terje Sverud
2	2019-09-06	Second JDP Committee Draft Review	Henrik Helgesen	Nathaniel Frithiof	Terje Sverud
3	2019-09-30	Third JDP Committee Draft Review	Henrik Helgesen	Nathaniel Frithiof	Terje Sverud
4	2019-11-01	Final Report	Henrik Helgesen	Nathaniel Frithiof	Terje Sverud

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The following report presents the findings from a joint development project incorporating expert input and perspective from the following key industry organizations and authorities:

Sjøfartsdirektoratet
Norwegian Maritime Authority

DANISH MARITIME AUTHORITY

Scandlines

Stena Line

DAMEN

Maritime Administration 1950 United States of America

ABB

KONGSBERG

Leclanché

DNV·GL

Corvus Energy

SUPER B
lithium battery

FIFI4MARINE

NEXCERIS
where energy meets environment

Marioff

FFI Forsvarets forskningsinstitutt
Norwegian Defence Research Establishment

With additional funding provided by:

Forskningsrådet

1 EXECUTIVE SUMMARY

This report is intended to enable persons assessing energy storage installations, whether from a design, engineering or regulatory perspective, to better evaluate risks, capabilities and solutions with regard to safety. The focus and context are on installations in the maritime environment although most findings will apply similarly to other applications and industries.

Like any energy source, lithium-ion batteries pose significant hazards with regard to fire and safety risk. Systems and tools are available which are fully capable of handling these risks, but it is necessary to better understand both these risks as well as the tools available so that they may be appropriately selected and implemented. It is important that the protection systems match the failure modes and consequences of a particular battery system.

Thus, the primary objective of this report is to provide information which enables:

1. The regulative authorities to write clearer and more prescriptive rules and guidelines.
2. An easier and more thorough approval process.
3. Engineers to better understand the risks and ensure that effective protection systems and barriers are implemented.

Two key areas were prioritized to provide information.

The first key focus was quantifying off-gas content and explosion risks. Different test setups can give different results and it was needed both to normalize these inputs and provide characterization of gas contents and quantity that can be used for consistent evaluation of explosion risks. Testing was performed at both the cell and multi-cell level, for different chemistries and form factors, and under different failure modes. Cell and rack/module testing results were used as input to calibrate Computational Fluid Dynamics (CFD) models which were then used to evaluate a wider range of configurations. These results provide reference and guidance on the amount of ventilation and the effectiveness. In general, the magnitude of potential consequence depends heavily on the number and size of the battery cells expected to be involved in an incident, and guidance is provided such that this can be assessed for a given system and used as input for evaluating explosion consequences.

The second primary objective was evaluation of the capabilities of various fire suppression and extinguishing media with respect to lithium-ion battery fires. Each of the systems available has different strengths and weaknesses, and thus different systems may be more effective or necessary depending on the key risks posed by a particular battery arrangement or installation. In general, fire suppression is more effective when detected and deployed early and if it can be released into the module. Key factors to evaluate as far as requirements are short term cooling, long term cooling, and gas absorption.

In addition, a Quantitative Risk Assessment (QRA) has been performed to present a framework quantifying the risks involved to an acceptance criterion. Frequencies of failures has been calculated with and without common safeguards to highlight the importance of the protection systems. Finally, a comparison of the probability of a conventional engine room fire has been made.

This report consists first of a summary of all main findings in Section A, followed by a Section B containing a detailed account of those findings from the standpoint of test setup, analysis methodologies, key assumptions and more.

Project work was initiated and managed by DNV GL, as a Joint Development Project; a collaborative effort from many essential partners representing the entire maritime battery value chain. Funding was contributed by all members and by the Research Council of Norway, and all members provided input to approaches and technical objectives as well as review and assessment of results.

1.1 Main conclusions

This section summarizes the main conclusions for the safety aspects of Li-ion batteries investigated. Note that the conclusions are based on tests performed at Li-ion batteries containing liquid electrolyte with Nickel Manganese Cobalt Oxide (NMC) and Lithium Iron Phosphate (LFP) cathode chemistries. These batteries are the most common for maritime applications at the publication time of this report. Battery technology is in rapid development, and new advancements might influence the presented results.

Limited tests were also performed, and the conclusions are only drawn where clear patterns between the different test results could be found. Calculations and evaluations are also made with conservative assumptions, compensating for the lack of parallel tests.

1.1.1 Fire suppression systems

Tested fire suppression systems provide different benefits, with unique strengths and drawbacks, providing no ‘silver bullet’ solution. The different properties are presented in a comparison table.

Direct injection of foam shows the best heat mitigating performance compared with all tested methods. This method had the highest potential for module-to-module fire mitigation, especially when designed for sufficient capacity to flood the modules/racks over longer time periods. In cases where alternative ship integration concepts are to be evaluated - such as a battery installed without a dedicated battery room - this may be a particularly attractive approach to evaluate the equal level of safety. The gas temperature and gas absorption are not evaluated.

High pressure water mist protection provides good heat mitigation at module level in addition to providing full battery space protection from external fires. It also has good gas absorption and gas temperature reduction capabilities.

NOVEC extinguish the battery fire flames, but performs poorer regards to heat mitigation, gas temperature reduction and gas absorption compared to water mist. Room ventilation needs to be closed for this suppression method to be functional. This can increase the toxic and explosive battery gas concentration in the room until ventilation can start again.

Sprinklers do not extinguish the visible flames but records similar heat mitigation capabilities at module level as high-pressure water mist. Since water can displace the gas into pockets with high concentrations, the explosion risk is considered to become more severe with sprinklers.

Each battery installation will have to assess necessary barriers in consultation with the battery manufacturer to identify the application most suited for that project. Due to limited amount of available suppression media onboard a vessel, the actual volumes and release rates needs to be calculated and are dependent on the battery system.

A methodology for comparative tests between different battery fire suppression systems available in the maritime market is proposed. Both heat and gas mitigation performance are evaluated.

1.1.2 Heat and gas generation

The cell level and module level tests presented in this report provided evidence that visual combustion produced more heat, but less gas compared to tests without visual combustion. Tradeoffs in the risk evaluation needs to be done between extensive heat generation vs extensive explosive and toxic gas generation.

The NMC cell which released significantly more volume was the one test that did not induce visible combustion external to the cell. It seems that the gas production is halved when there is visible combustion. However, further tests are needed to quantify the exact number.

The amount of oxygen released is not sufficient to affect combustibility external to the cell. It is considered more likely that O2 is released internal to the cell and play a very central role in the onset of thermal runaway. This will also result in more aggressive heat development and increased CO or CO2 production.

It is also seen that limiting the oxygen supply will suppress the battery fire, but not be sufficient to cool down the battery. In these cases, the off-gassing is increased compared to fires where oxygen is fueled to the fire.

It is seen that modules with IP4X produces less heat and more gas compared to modules of IP2X. This is due to the limitation of oxygen in the IP4X modules.

1.1.3 Toxicity

If the room is to be entered after an event, all the identified toxic gases needs to be considered. The gasses identified in this project are carbon monoxide, nitrogen dioxide, hydrogen chloride, hydrogen fluoride, hydrogen cyanide, benzene, toluene.

Very small gas concentrations will make the atmosphere toxic, and the gas will dilute fast. Hence the sensor detecting the toxic gases can be placed in the normal breathing zone for people, 1-1.8 meters from the floor.

Personal Protection Equipment should be used when re-entering the battery space after a battery fire, also after deployment of fire suppression material.

The properties of a battery fire can be compared to burning plastics.

When weighting the Immediately Dangerous to Life or Health (IDLH) values with the released gas amounts, CO, NO2 and HCL will first reach its IDLH values.

1.1.4 Off-gas detection

Gas release profile - CO is the main component present for the longest period of time and is considered especially important for early stage detection.

Off-gas in the early stages of thermal runaway events will be colder than off-gas release in the later stages. The early off-gas can therefore become heavier than the air, collecting at floor level. It should therefore be considered if gas-detection related to room explosion risks should be applied at both levels, close to the floor and close to the ceiling.

Tests conducted in this project indicate that solely relying on Lower Explosion Limit sensor(s) and cell voltage levels to detect early stages of a thermal runway event is insufficient.

Both the Li-ion Tamer sensor® and smoke detector, when placed close to or inside the affected module, proved the most reliable means of pre-thermal runaway warning. The early detection of thermal runaway has also proven that a cell can be disconnected, effectively stopping the overheating process.

1.1.5 Ventilation

In order to realize the most potential of a forced extraction duct, a high extraction point in the room has proven to be the key factor. This ensures that the required air changes per hour stays low while still providing the necessary dilution of explosive gases in the space.

The explosion pressure limit is set to 0.5 barg. Above this pressure the bulkheads will be damaged. With a ventilation rate of 6 ACH it should be sufficient to avoid such pressure if 350 liters of battery gas released in the room is considered as a worst case. This corresponds to a cell or module of 115-175Ah. If cells of total 250Ah is failing, this requires 10 ACH, while failing 500Ah requires 22 ACH in a room of 25m3 of free space. The ventilation can be turned on demand based at early off-gas detection with sensors close to or inside the modules.

If batteries of 4000 Ah is failing, it will not be sufficient with 100 ACH to avoid an explosion magnitude of 0.5 barg.

A ventilation formula for a battery room is proposed. The formula calculates the air changes per hour (ACH) with the size of the failed batteries, the design bulkhead pressure, the room volume and the vent distance from the ceiling as input variables.

1.1.6 Temperature class and gas group

The key requirements when designing explosion proof equipment are temperature class and gas group.

Based at the tests performed, the temperature class for battery off-gas explosion proof equipment is recommended to be T2 according to the IEC 60079 standard.

The gas group is identified as Group IIC according to the IEC 60079-20-1 standard.

1.1.7 Thermal runaway identification

Based at the tests performed, significant difference was observed between the Nickel Manganese Cadmium (NMC) and Lithium Iron Phosphate (LFP) cells. The LFP cylindrical cells were much harder to force into thermal runaway compared to the NMC pouch cells.

For the NMC pouch cells, a temperature increase rate above 10 °C/sec together with a max temperature above 450°C seems to be sufficient to identify the onset point for a thermal runaway with visual combustion.

For the LFP cells, a temperature increase of 4 °C/sec seems to be sufficient to identify the onset point for the thermal runaway. The chance of achieving this increase with increased state of charge, and it might be necessary to charge the LFP battery cells beyond 100% SOC to provoke visual combustion.

1.1.8 Quantitative Risk Assessment

Key findings based on a Quantitative Risk Assessment (QRA) for the battery system, are that fire propagation protection and the Current Interruptive Device are two of the most important safeguards to be installed in the battery system.

When comparing the battery fire risks with data registered in the HIS Fairplay database for fires in a diesel engine room, it seems that the likelihood of a battery fire is lower compared to a diesel fire. However, engine room fires registered in the HIS Fairplay database include fires of many different magnitudes not necessarily correlating to the fire scenario established in battery system QRA. This means that better data would be necessary to fully evaluate if a battery system is safer than a conventional combustion engine.

1.1.9 Battery system design

The required ventilation rate and the amount of fire suppression material depends on the number and the size of the battery cells involved in the fire. If the complete battery system catches fire, the suppression and ventilation will not be able to mitigate the fire and explosion risks. It is of most importance to design a battery system with fire propagation protection and Current Interruptive Devices to limit the fire to one part of the battery system, and to install a well-tested Battery Management System capable of preventing several modules being overcharged at the same time.

SECTION A: MAIN REPORT

A discussion and summary of findings from the project, aimed as useful reference for assessment of the primary factors with regard to lithium-ion battery safety. This is based on the test results presented in detail in Section B.

2 INTRODUCTION

The main safety concern when installing a lithium-ion battery system is that the battery will start to burn and the development of explosive and toxic gasses. When a battery is heated up, it can start an internal exothermic reaction called thermal runaway. Figure 2-1 summarizes the causes and consequences of thermal runaway. It often starts from an abuse mechanism that causes the internal temperature to rise such that the electrolyte is gasified, released and ignited. This fire might then ignite the electrodes, thus producing high temperature fires involving both liquids and gases. These fires are hard to extinguish and to cool down.

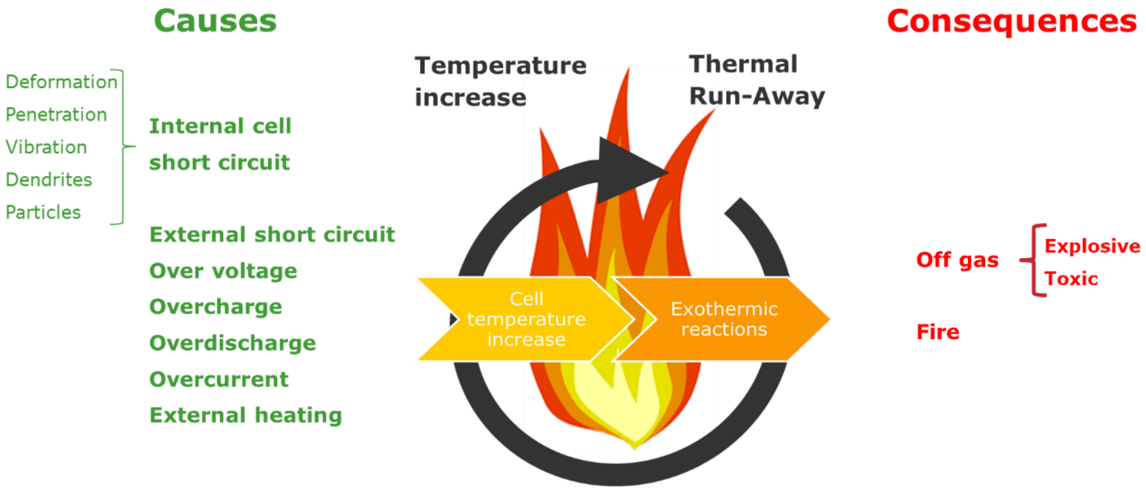


Figure 2-1: Causes and consequences of a thermal runaway in a battery system.

This report is intended to enable persons assessing energy storage installations, whether from a design, engineering or regulatory perspective, to better evaluate risks, capabilities and solutions regarding safety. The focus and context are on installations in the maritime environment although the vast majority of findings apply similarly to other applications and industries. The focus has been to give guidance regards the mitigating safeguards, addressing the battery fire and off-gassing.

2.1 Background

Lithium-ion batteries are a disruptive technology that has already significantly altered almost every industry sector, including maritime. They are a crucial, if not the central, component in the next generation of power systems and green or renewable technologies; a fact that is most immediately apparent in transportation and maritime. However, this utilization and deployment must be built upon a basis of safety.

Batteries are a complex technology comprising of many interrelated scientific phenomena – and this holds true for their fundamental internal operation, their application and usage in power systems, and absolutely regarding safety. Rules and requirements have evolved to cover the full spectrum of risk, but the complexity of safety aspects mean that additional learning and understanding provide an opportunity for both improving the total level of safety as well as the efficiency of the approval process. More public knowledge on key threats and technical aspects means more consistent and focused engineering solutions. Better understanding of the total risk picture means more consistent and effective regulations and requirements. Thus, the focus of this Joint Development Project (JDP) was to bring together members of the entire value chain to identify these key issues as a team. Testing and analysis would then be performed to provide technical input for results that would then be discussed and reviewed as a team in order to provide recommendations that had been reviewed from all perspectives.

There are many different battery system designs or engineering approaches that may focus on mitigating certain challenges. In addition, there are many different tools that may be used for mitigating certain risks. Understanding the risks of a given battery design is the key and ensuring sufficient systems are in place to produce an acceptable level of risk. This document seeks to provide information that can be used as reference in assessing these risks.

3 BATTERY OFFGAS CONTENTS AND DETECTION

The off-gases in a lithium-ion battery is known to be flammable as well as toxic. This presents an explosion risk in enclosed spaces. Accurate understanding of the constituents of this gas is difficult as it depends on many variables. Often the test procedure can involve practices for measurement that may not be relevant for use as input to an evaluation of explosion potential.

3.1 Off-gas contents

Table 3-1 shows the off-gas quantities that were found in the cell level testing conducted in this project. Tests are conducted in a steel chamber with air flow through, and gas measured by FTIR; setup details can be found in Section B 13.1. Cells are charged to specific SOC values as indicated in the table and then heated using radiant and band heaters, except in the cases indicated as OC (overcharge), in which case a constant current of 50A is applied until failure.

NMC cells tested were a pouch type while both LFP cells were cylindrical. Notably, the NMC cell which released significantly more volume was the one test that did not induce visible combustion external to the cell – such that nominally the other NMC tests thus indicate how much gas may be consumed when there is combustion. This is an important phenomenon that is revisited in the module testing, Section A 7 and Section B 14.2.

Table 3-1 – Off-gas values as measured in project testing - from different chemistries, heating at different SOC, overcharge (OC) and external short circuit (SC) when possible

Value	**NMC, 63Ah**					**LFP1, 2.5Ah**				**LFP2, 1.5Ah**		
SOC	**50**	**75**	**100**	**OC**	**SC**	**50**	**75**	**100**	**OC**	**50**	**75**	**100**
CO2	19,6	25,7	40,3	38,8	65,9	44,3	20,2	63,4	20,9	22,5	23,0	35,1
CO	29,2	38,1	11,4	34,4	19	7,6	15,9	15,1	26,1	12,0	13,9	11,3
NO2	-	-	-	-	-	4,9	9,7	5,9	1,3	4,8	5,6	4,9
CH4 (methane)	12,6	9,4	19,4	12,5	2,7	4,3	5,6	3,0	3,7	5,9	5,9	5,6
C2H6 (ethane)	10,6	10,5	11,7	4,8	7,6	15,6	23,0	7,7	15,4	21,0	23,1	20,0
C2H4 (ethylene)	10,5	4,4	9,6	4,9	1,6	7,3	11,4	1,9	13,7	12,0	8,8	5,8
C3H8 (propane)	-	-	-	-	-	3,9	5,8	0,6	4,2	5,8	3,7	4,5
HCL	9,7	0,8	1,9	0,2	0,2	1,1	0,8	0,2	0,3	2,1	1,9	1,0
HF	0,7	0,3	0,3	0,1	0,1	1,6	1,6	0,4	0,1	1,9	3,7	3,6

HCN	0,0	0,0	0,0	0,0	0,0	0,1	0,1	0,0	0,1	0,4	0,7	0,6
C6H6 (benzene)	4,1	5,2	1,1	4,3	1,9	0,0	0,7	0,0	13,6	0,6	0,0	0,3
C7H8 (toluene)	2,0	4,1	0,3	0,5	0,9	0,0	0,0	0,2	0,0	0,1	0,5	0,7
C2H6O (ethanol)	0,3	0,7	2,9	0,1	0,0	3,7	0,4	0,5	0,0	7,0	4,6	4,0
CH4O (methanol)	0,7	0,8	1,1	0,5	0,2	5,6	4,7	0,9	0,4	3,9	4,6	2,5
Volume [L]	527	182	233	245	180	9,4	8,4	27	19,1	5,5	6,1	6,5
Average ambient temperature during Thermal Runaway [C]	131	166	201	221	57	102	99	81	28	91	82	99
Volume normalized to 25C ambient temperature [L]	388	124	146	148	161	7,5	6,7	23,1	18,9	4,5	5,1	5,2
L/Ah normalized to 25C ambient temperature	6,2	2,0	2,3	2,3	2,6	3,0	2,7	9,2	7,6	3,0	3,4	3,5

Notably, hydrogen, H2 is missing from the table above. In all cases the H2 sensor was saturated at a value of 1%. This saturation happens almost immediately upon the onset of thermal runaway, with only a few cases showing trace amount of hydrogen released just beforehand. H2 is an important component to consider in safety and explosion considerations. Thus, a literature review was conducted to determine the best way to incorporate the hydrogen gas content. Most literature sources do not report the full spectrum of gasses shown in Table 3-1; but, when tested under similar conditions, literature is quite consistent in reporting values between 5% to 30%. As a worst-case example, the values of CO2, CO, CH4, & C2H6 are normalized for a 30% H2 concentration, and shown all together in Table 3-2.

Table 3-2 – Calculated off-gas contents incorporating assumed hydrogen content of 30%

Value	**LGC NMC, 63Ah**					**LFP1, 2.5Ah**				**LFP2, 1.5Ah**		
Case	**50**	**75**	**100**	**OC**	**SC**	**50**	**75**	**100**	**OC**	**50**	**75**	**100**
CO2	16	20	30	28	48	40	20	49	18	22	21	31
CO	25	30	9	25	13	7	14	12	23	12	13	10

CH4	11	8	15	9	2	3	5	2	3	6	5	5
C2H6	9	8	9	4	6	14	21	6	13	21	21	18
C2H4	9	4	7	4	1	6	10	1	12	12	8	5
H2 estimated	30	30	30	30	30	30	30	30	30	27	30	30
Average ambient temperature [C]	*131*	*166*	*201*	*221*	*57*	*102*	*99*	*81*	*28*	*91*	*82*	*99*
Volume normalized to 25C ambient temperature [L]	*458*	*193*	*193*	*199*	*223*	*10*	*7*	*30*	*21*	*5*	*5*	*6*
L/Ah	*7*	*3*	*3*	*3*	*4*	*3*	*4*	*12*	*9*	*3*	*4*	*4*

Batteries with layered metal oxide cathodes (i.e. NMC) theoretically release oxygen as the cathode is combusted. During testing, it is not uncommon to observe that lithium-ion battery fires will consume all available oxygen and/or push out oxygen, such that at some point in the event, off-gassing of an NMC cell could be occurring in an oxygen deprived space. More specifically, in these cases O2 levels do not seem to rise or to come back, as would be expected based on this O2 release phenomenon. Thus, it is suggested that the amount of O2 released is not of sufficient volume to affect combustion or combustibility external to the cell. It is considered more likely that O2 is released internal to the cell and may play a very central role in the onset of thermal runaway and the temperature of the fire.

3.2 Gas contents pre-thermal runaway

NMC overheat 50% SOC and the overcharge tests were used to provide an indication of the average content and concentrations of the gasses released before the onset of thermal runaway, shown in Table 3-3.

Table 3-3 - Composition of off-gas released from cell before full thermal runaway

Gas species	Composition in overheating 50% SOC case (%)	Composition in overcharging case (%)
CO	32.1	47.9
Ethane	24.1	13.1
Methane	16.1	7.2
Benzene	11.3	24.0

Gas species	Composition in overheating 50% SOC case (%)	Composition in overcharging case (%)
Ethylene	9.6	4.8
Toluene	5.5	3.0
HCl	0.7	-
Methanol	0.6	-

Notably – hydrogen is not seen. This held true for the vast majority of cases, where hydrogen was not seen until the onset of thermal runaway, though due to anecdotal experience the hydrogen is often consumed rapidly. In only one or two cases was hydrogen seen before the onset of thermal runaway – and then only in small amounts, ramping up in the seconds before thermal runaway occurred.

3.3 Gas release profile

Figure 3-1, Figure 3-2 and Figure 3-3 show the off-gas release from all measured battery gases for overheating NMC at 50%, overcharging NMC and overheating NMC at 100% respectively.

It is seen that for overheating at 50% and overcharging, CO is the most continuously present gas and thus provides a good indication of the full spectrum of gas profiles that may be expected. The CO concentration presented in Figure 3-4 provides a reference for the shape of off-gas release from cells. For the 100% SOC case, a similar profile can be found by monitoring CO2, as shown in Figure 3-3.

In all three cases, it is shown that the full release generally occurs in less than 150 seconds. In addition, initial gas release quantities of 5,000 to 10,000 ppm are relatively small, particularly in comparison to the peak values seen. The rapid increase in gas release directly corresponds to the thermal runaway event as characterized in Chapter 9.

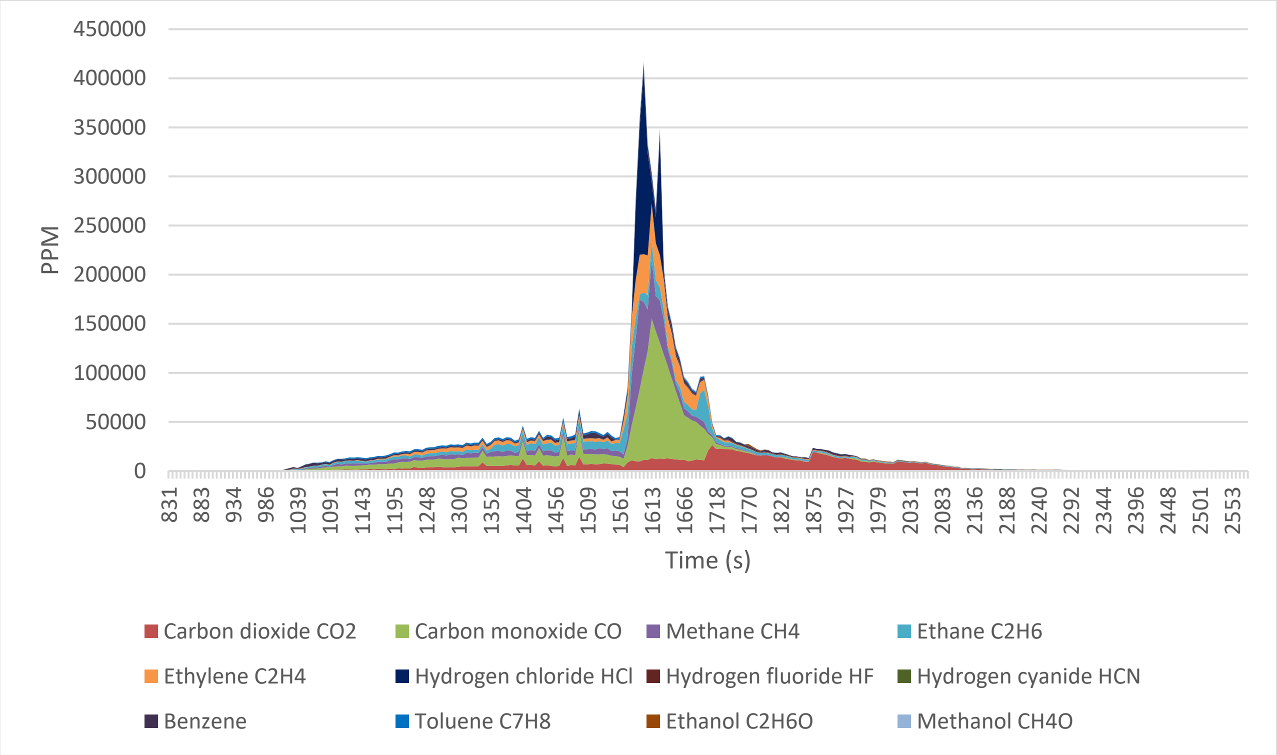


Figure 3-1: Gas release profile for an overheated NMC pouch cell with 50% SOC

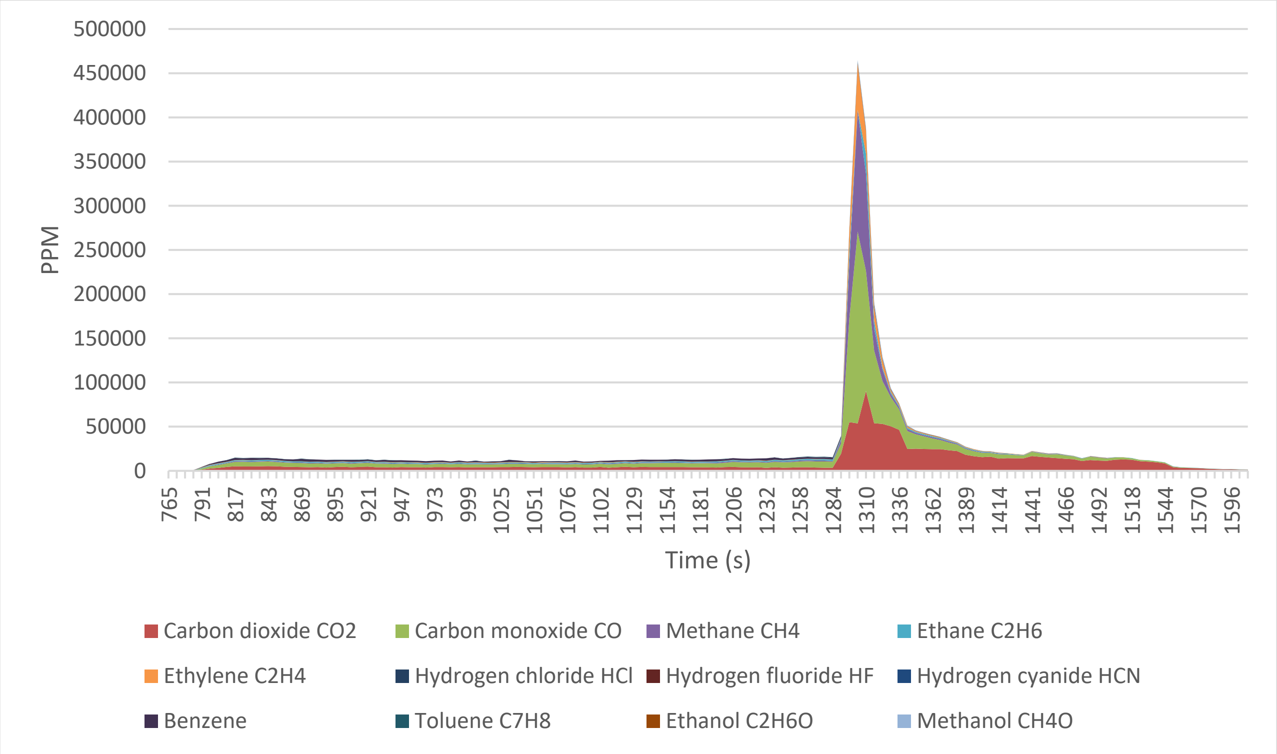


Figure 3-2: Gas release profile of an overcharged NMC pouch cell

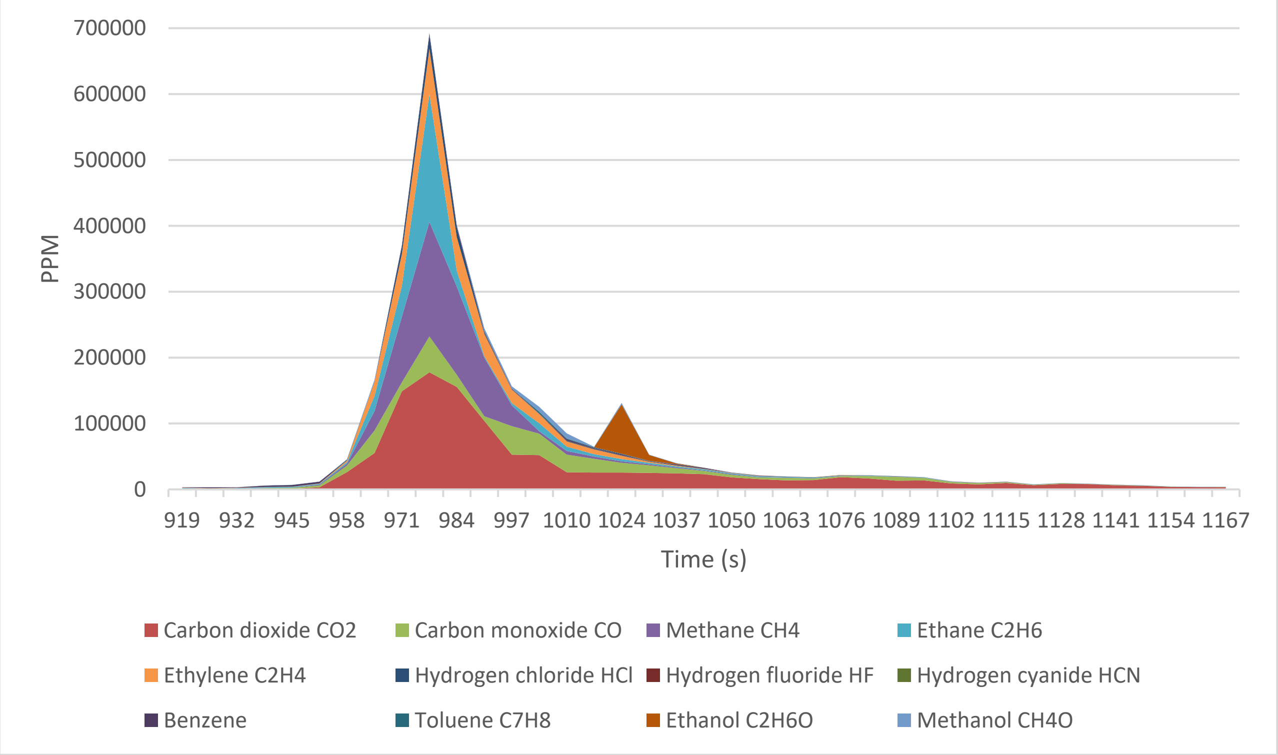


Figure 3-3: Gas release profile of an overheated NMC pouch cell 100% SOC

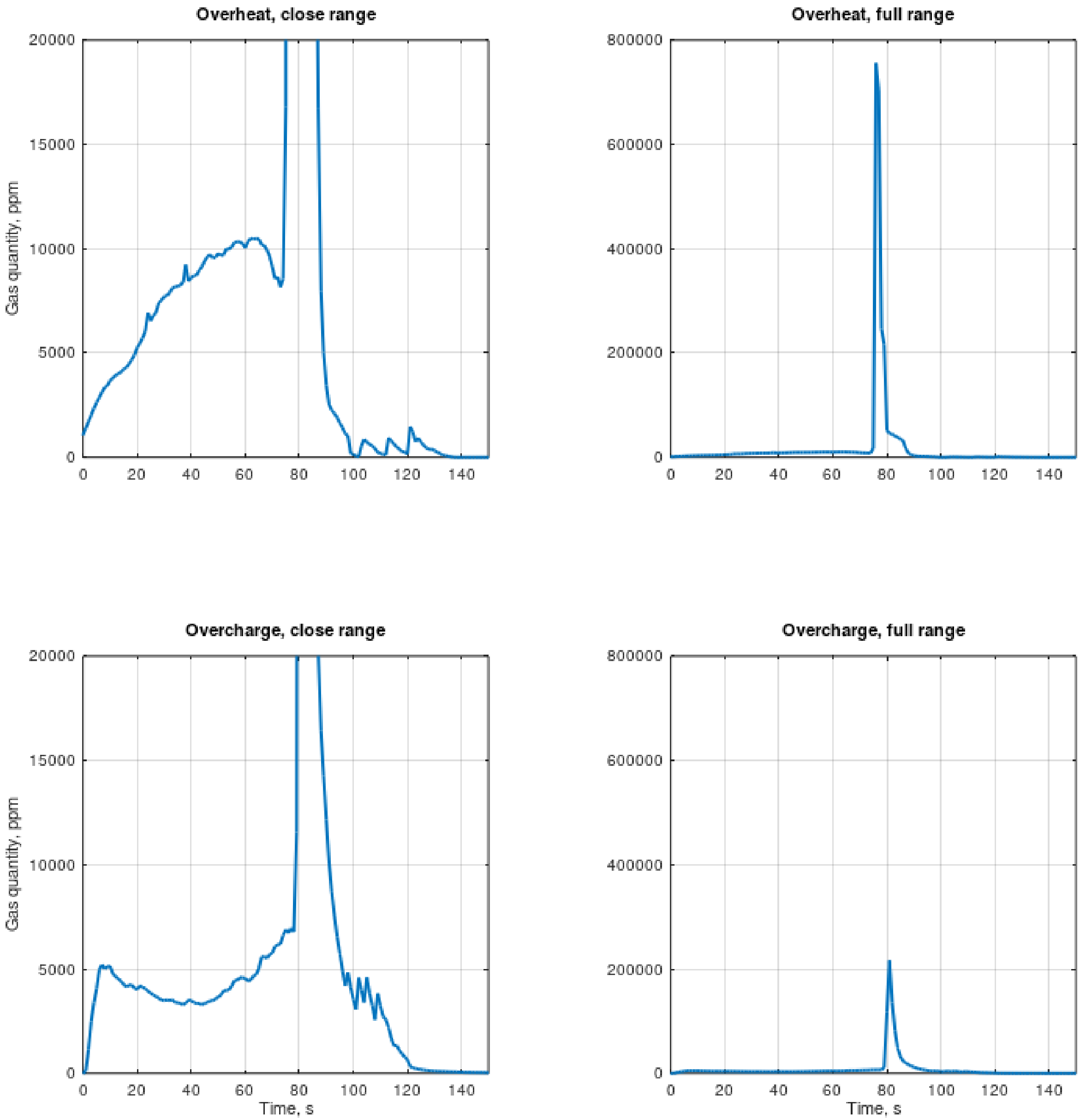


Figure 3-4 – Off-gas release profiles represented by CO for two different failure modes

3.4 Off-gas detection

3.4.1 Single cell gas detection tests

Tests were monitored with thermocouples, a Lower Explosion Limit (LEL) sensor, an off-gas specific sensor called the Li-ion Tamer® developed by Nexceris and cell voltage. From the tests conducted, average values about the rates of detection and indication are provided below. Note, voltage as indicated here is when there is a loss of voltage across the terminals, in cases of overcharging clearly there is earlier indication that voltage is out of spec. LEL indication as reported here is the first time a measurement is indicated – in the vast majority of cases the LEL reading goes from zero to saturated. In addition, in many cases the LEL sensor would display erroneous values and required multiple recalibrations to become functional again if at all. By comparison the Nexceris sensor showed high sensitivity and more stable behavior. However, it should also be mentioned that with regard to standard installations, these devices would not be expected to undergo repeated exposure to high temperature and concentrations as was done in repeated thermal testing.

With regard to functionality as indication mechanisms, a summary in Table 3-4 is provided. Times are presented relative to thermal runaway as was indicated by temperature sensors on the cell. It can be seen that LEL sensors and voltage do not provide a mechanism for early warning. In comparison, the Li-ion Tamer® sensor indicates only seconds after off-gassing occurs. In addition, testing was performed where a cell was being overcharged and charging stopped when off-gas was released as indicated by the Li-ion tamer®. The cell temperatures ceased to increase, and off-gassing started to decline until the cell was considered stable. Thus, demonstrating it is feasible to 'pull back' a cell after it has begun off-gassing but before thermal runaway occurs. Meaning early detection, coupled with correct system shutdown measures is an important safety barrier.

Table 3-4 - Average responses from different sensors and indication mechanisms tested in cell level tests

	Off-gas Release	Li-ion Tamer® sensor	Thermal Runaway	Cell Voltage	LEL Sensor
Time of occurrence relative to thermal runaway, average, seconds	-381	-371	0	+7	+28

3.4.2 Module scale gas detection tests

Off-gas detection was also evaluated similarly as a part of the full-scale testing with complete, enclosed modules in the representative battery room. The Li-ion® Tamer sensor was evaluated together with a smoke detector. Sensors were placed on the module above the device under test for this measurement, thus nominally giving a 'best case' capability evaluation.

The key properties of the tests are shown in Table 14-4.

Table 3-5: Key properties of gas detectors for module level tests

Test ID	IP Rating of box	Combustion	Visual external Combustion	Time difference between Li-ion Tamer® and Smoke detector	Max temperature inside the test box before detection
1	44	Yes	No	22 sec	16ºC
3	20	Yes	Yes	9 sec	290ºC
7	44	Yes	No	21 sec	173ºC
9	20	Yes	Yes	44 sec	440ºC

Both the smoke detector and Li-ion Tamer® can detect the gas for cases with and without external combustion. The Li-ion Tamer® detects the gas first in all tests, 10-45 seconds faster than the smoke detector. However, it seems the gas is not always detected before the cells has entered thermal runaway. Compared with the cell level tests, where the sensors were placed in the same enclosure as the battery cells, the gas is detected much later when the sensors are placed outside the modules.

It can be concluded that both the smoke sensor and Li-ion Tamer® gas sensor are capable of detecting the battery gas. The placement of the sensor is a key factor for early detection, and the sensor should be placed as near the battery as possible, ideally within the module enclosure.

3.5 Main Conclusions

Main Conclusions

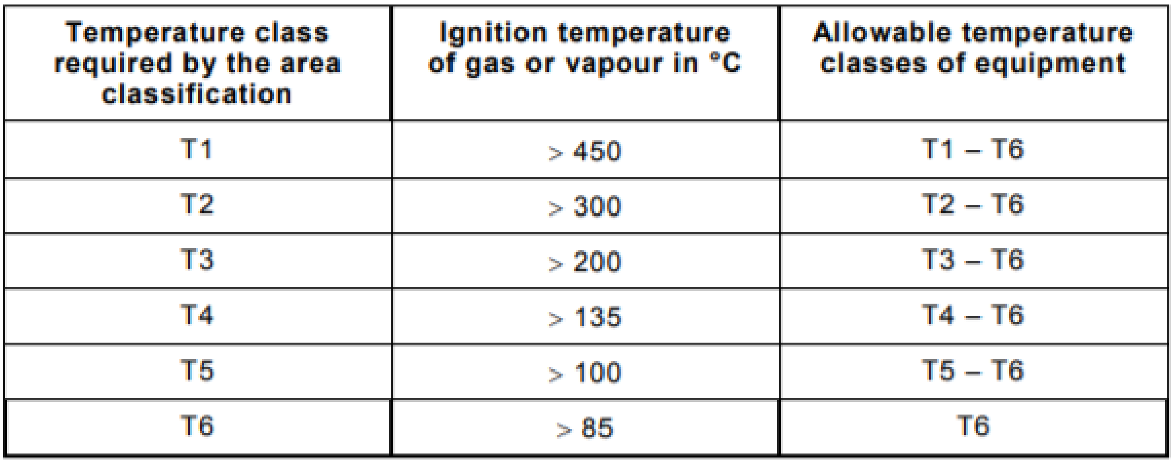
1. The NMC cell which released significantly more volume was the one test that did not induce visible combustion external to the cell. It seems that the gas production is halved when there is visible combustion. However, further tests are needed to quantify the exact number.
2. The amount of oxygen released is not sufficient to affect combustibility external to the cell. It is considered more likely that O2 is released internal to the cell and play a very central role in the onset of thermal runaway. This will also result in more aggressive heat development and increased CO or CO2 production.
3. Carbon Monoxide is the main component present for the longest period and is considered especially important for early stage detection.
4. Off-gas in the early stages of thermal runaway events will be colder than off-gas release in the later stages. The early off-gas can therefore become heavier than the air, collecting at floor level. It should therefore be considered if gas-detection related to room explosion risks should be applied at both levels, close to the floor and close to the ceiling.
5. Solely relying on Lower Explosion Limit sensor(s) and cell voltage levels to detect early stages of a thermal runway event is insufficient.
6. Both the Li-ion Tamer® sensor and smoke detector, when placed close to or inside the affected module, proves the reliable means of pre-thermal runaway warning.

4 TEMPERATURE CLASS AND GAS GROUP

A key motivation for identification of off-gas contents was to provide greater clarity on requirements for EX (explosion proof) equipment to be used in the battery room and ventilation fan(s) installed. The requirements for such identification are temperature class and gas group, which are functions of the gas itself. These characterizations are outlined in IEC 60079. Note that the battery cells themselves can never be EX proof, but equipment installed where high gas concentrations are expected, such as the extraction fan of the battery system or battery room can pose a high threat.

4.1 Temperature class

Figure 4-1 shows the different Temperature Class categories and indicates the dependency on ignition temperature for determination. The requirement states that the surface temperature may not reach the ignition temperature of any of the gasses and thus, it is considered that the lowest autoignition value of any of the gasses expected to exist shall be used. The autoignition temperatures of the gas constituents detected in this project testing are indicated in Table 4-1. As shown, the lowest value is found to be 365°C for ethanol. Thus, the temperature class for battery off-gas EX equipment consideration is recommended to be T2.



Temperature class required by the area classification	Ignition temperature of gas or vapour in °C	Allowable temperature classes of equipment
T1	> 450	T1 – T6
T2	> 300	T2 – T6
T3	> 200	T3 – T6
T4	> 135	T4 – T6
T5	> 100	T5 – T6
T6	> 85	T6

Figure 4-1 - Temperature Class requirements based on gas autoignition temperature as defined in IEC 60079 (Table 4)

Table 4-1 - Autoignition temperatures of key gasses found in lithium-ion battery off-gas

Value	Autoignition Temperature (°C)
Ethylene Carbonate	465
CO2	-
CO	609
NO2	-
H2	536
CH4 (methane)	580
C2H6 (ethane)	515
C2H4 (ethylene)	450
C3H8 (propane)	455
HCL	-
HF	-
HCN	538
C6H6 (benzene)	560
C7H8 (toluene)	530
C2H6O (ethanol)	365
CH4O (methanol)	470

4.2 Gas group

The specific gas group is classified according to their maximum experimental safe gaps (MESG), as defined in IEC 60079-20-1. The groups for equipment for explosive gas atmospheres are:

1. Group I: equipment for mines susceptible to firedamp.
2. Group II: equipment for places with an explosive gas atmosphere other than mines susceptible to firedamp.
    a. Group IIA: MESG ≥ 0,9 mm.
    b. Group IIB: 0,5 mm < MESG < 0,9 mm.
    c. Group IIC: MESG ≤ 0,5 mm.

For mixtures of gasses, the process for identifying the gas group is based on Le Chatelier's mixing rule according to the standard. This equation is shown below.

$$MESG_{mix} = \frac{1}{\Sigma\left(\frac{X_i}{MESG_i}\right)}$$

According to the standard, the calculated MESG value will be higher than the actual value for the mixed gas when CO is greater than 5%.

For calculating combined MESG, the case of NMC at 50% was used as a worst case since it had the lowest proportion of CO2. The values presented Table 3-2 is used in the calculation, since it assumes 30% of hydrogen.

For actual calculation, CO2 was omitted, and the combined amount was calculated as a percentage of remaining gasses. Some gasses are not considered in the assessment, but their omission results only a small deviation towards a more conservative result as the main constituents of CO and H2 contain the lowest MESG values of the gasses present in large quantities.

Using Le Chatelier’s mixing rule the MESG value is found to be 0.5. Since the concentration of CO is 30%, far beyond 5%, the actual MESG value is expected to be lower.

This places lithium-ion battery off-gas within Gas Group IIC according to standard IEC 60079-20-1.

Table 4-2: MESG values of identified battery gases, and the MESG value of the combined battery gas.

Value	MESG	Normalized gas concentration when CO2 is omitted
Ethylene Carbonate	NA	-
CO2	NA	-
CO	0.84	30
NO2	NA	-
H2	0.29	36
CH4 (methane)	1.12	13
C2H6 (ethane)	0.91	11
C2H4 (ethylene)	0.65	11
C3H8 (propane)	0.92	-
HCL	NA	-
HF	NA	-
HCN	0.80	-
C6H6 (benzene)	0.99	-
C7H8 (toluene)	NA	-
C2H6O (ethanol)	0.89	-
CH4O (methanol)	0.92	-
COMBINED	**0.5**	**100**

4.3 Main Conclusions

Main Conclusions

1. The temperature class for battery off-gas explosion proof equipment is recommended to be T2 according to the IEC 60079 standard.
2. The gas group is identified as Group IIC according to the IEC 60079-20-1 standard.

5 TOXICITY

For the most part, lithium-ion batteries are not more significantly toxic than a comparable plastics fire; but there absolutely is the potential for low concentrations of more harmful gasses to be produced, which can depend on the cell being used (particularly the electrolyte formulation; Polyvinylidene Fluoride in particular can directly affect HF levels) /3/. Thus, the primary recommendation is that, following a lithium-ion battery fire, there should be no re-entry without sufficient Personal Protective Equipment. For general guidance on quantities of the more toxic substances that should be expected to be present, see Table 5-1.

Table 5-1 - Volumes of primary gasses of concern with regard to toxicity

Gas	Max % observed from cell level	L of specific gas per Ah (assuming 2.6 total L/Ah)	Immediately dangerous to life or health (IDLH) [ppm]	Relative Vapor density (air = 1)
CO	38.1%	0.9906 L/Ah	1200	0.97
NO2	9.7%	0.2522 L/Ah	20	2.62
HCL	9.7%	0.2522 L/Ah	50	1.3
HF	3.7%	0.0962 L/Ah	30	0.92
HCN	0.7%	0.0182 L/Ah	50	0.94
C6H6 (benzene)	13.6%	0.3536 L/Ah	500	2.7
C7H8 (toluene)	4.1%	0.1066 L/Ah	500	3.1

The relative vapor density is also included in the table to give an indication if the gas will accumulate close to the floor or the ceiling. However, according to /17/, these gases tend to diffuse and mix quickly. Even if the gas starts out stratified, it cannot stay stratified for a long time in a small, confined space. Very small concentrations of gas in the ppm range will make the atmosphere toxic. The placement of a toxic gas detector is then of less importance compared to a LEL sensor, which is in a range of vol%. Explosive gas can be more stratified, and it is important to measure at various levels before entering a confined space. Hence, it can be concluded, that the gas sensor measuring the toxicity level should be placed in the normal operating zone for people, 1-1.8m from the floor /19/,/20/.

Depending on gas compositions released from the various tests performed, the gas types that first reached IDLH limits were CO, HCL and NO2; based on the following formula:

$$IDLH_{Normalized} = \frac{IDLH_i}{x_i}$$

where x_i is the gas concentration of the specific toxic gas.

5.1 Main Conclusions

Main Conclusions

1. Very small gas concentrations will make the atmosphere toxic, and the gas will dilute fast. Hence the sensor detecting the toxic gases can be placed in the normal breathing zone for people, 1-1.8 meters from the floor.
2. Personal Protection Equipment should be used when re-entering the battery space after a battery fire, also after deployment of fire suppression material.
3. If the room is to be entered after an event, all the identified toxic gases needs to be considered. The gasses are carbon monoxide, nitrogen dioxide, hydrogen chloride, hydrogen fluoride, hydrogen cyanide, benzene and toluene.
4. The properties of a battery fire can be compared to burning plastics.
5. When weighting the Immediately Dangerous to Life or Health (IDLH) values with the released gas amounts, CO, NO2 and HCL will first reach its IDLH values.

6 OFF-GAS VENTILATION AND EXPLOSION RISKS

As discussed in the previous subsection, battery off-gas constitute both an explosive and a toxic hazard. In order to avoid high concentrations collecting in the battery space a well-designed ventilation system is required. Different philosophies to diffuse such gases are employed in the market today. The two main principles being either; containing the battery modules and off-gas in gas-tight enclosures leading directly to a safe area on open deck, without passing the battery room first. The other option being; open battery racks where off-gas release first into the room before being diffused by a forced exhaust system of sufficient air changes per hours (ACH). The following tests were conducted in order to further understand the effects of room scale ventilation systems and the impact of such on observed and measured gas clouds during thermal runaway events.

6.1 Module scale tests

Module scale tests were performed (further detail in Section B, 14 and 15) which were used to evaluate the evolution of battery off-gas from a module configuration representative of batteries configured in a rack. This test setup was used to evaluate effects of various enclosures, cell types, ventilation rates, as well as fire suppression materials.

Comparing the effects of different enclosures, it was found that more open systems have a greater possibility of providing oxygen to the fire and this will tend to result in a higher chance of prolonged combustion with higher temperatures. In addition, the primary source for ignition of gasses is the failing battery cell itself, so more open modules also increase the chance of external combustion of gasses.

To measure the amount of gases in the battery room, a LEL sensor is used. This sensor records the LEL% as shown in the formula below.

$$LEL\% = \frac{Gas\ Consentration\ in\ Room\ [vol\%]}{LEL\ for\ Gas\ [vol\%]}$$

When the gasses produced from a lithium-ion battery are combusted, rather than accumulating, the explosion risk goes down substantially. This is represented in the significantly lower maximum LEL% value as seen in the IP2X case of Table 6-1. Limiting the oxygen to the fire will reduce the module heat, while the off-gassing and hence the explosion risk increases. This also indicate that if the ventilation is closed, the heat will eventually go down when the oxygen is consumed, while the off-gassing will increase. This is an important finding when evaluating the explosion risk of the room.

Experimental LEL% measurement results from the case that did not ignite were used to match CFD results and this way the amounts of gas produced from the tests was indicated, see also Chapter 14.

Table 6-1 – Effect of module enclosure on gas and heat produced

Cells	Enclosure	External Combustion	Max measured LEL%	Time to max measured LEL% (s)	Max Internal Temp Module above	Max External Temp Module above
NMC Pouch	IP44	No	69%	120	29	92
NMC Pouch	IP20	Yes	26%	500	152	252

Table 6-2 – More open modules have a higher incidence of combustion

Module Enclosure	IP4X	IP2X	Open Lid
Percentage of Tests with External Combustion	0	60%	80%

NOTE: the IP2X test indicated also consisted of a NOVEC release approximately 30 seconds after the identification of the fire.

Figure 6-1 – 30 seconds after thermal runaway for a IP4X module (top) compared to a IP2X module (bottom) shows how much combustion consumes and removes gas.

6.2 Guidance to needed ventilation

Two CFD models and different gas release scenarios are used to analyze further ventilation rates and different rooms to provide guidance on how ventilation can be expected to reduce explosive atmospheres. Simulations were also run for different gas release volumes which represent failure of different sized modules. The main results are shown in Figure 6-3 and Table 6-3.

6.2.1 Determine the gas volume released

Assessment of the needed ventilation rates requires knowledge of how many liters of gas that are expected to be released from a cell and how many cells and modules will be involved in the event. In this way the total volume of gas to be released is found and used for an assessment. The total volume of gas released is hence used as the decisive design parameter for the ventilation system.

For instance, the event under consideration may be several cells, or a full module or potentially a full string. Tests of the battery cell or module are needed to determine the amount of gas produced. This can then be used to give an indication of the total amount of gas that is produced for the worst case scenario considered. The total gas production volume tends to be proportional to the Ah size of the battery that is involved in the off-gas scenario. If one module is 1000 Ah, and the amount of gas produced from one cell is 2 l/Ah, then the total amount of gas from the module becomes 2000 L. The amount of gas produced as a function of battery size and type is considered further in Chapter 3.

6.2.2 Propagation rate

Propagation rate is the next crucial factor as shown by preliminary CFD analyses performed in Chapter 15.1. This scenario can in general be quantified by a release profile that first rises to a certain value, then continues with a more constant value as long as the propagation goes on from cell to cell, before it either escalates to another module, or dies out. Fast propagation between cells significantly increases the rate of gas accumulation in the room. Based on experience from all members of the JDP team it was considered reasonable to assume that cells will propagate, starting from a single cell with a significant amount of thermal mass and cooling capability, at a rate of 2 additional cells every 60 seconds. For a typical event as observed in the module experiment, the amount of gas rises quickly to a stable value (within 10-20 seconds is applied) and continues until it starts decaying after 100 to 250 seconds (or more, depending on the number of cells in the module), see also Section B 15.2. The event will further decay until it dies out unless it also propagates to another module.

If more than one module is involved in the dimensioning scenario, then the release rate is assumed to increase further instead of decaying when it is escalating to the next module. Then the release rate will get a new step up and continue with a higher total rate as long as both modules are releasing gas. The time to escalation to another module will vary, and 3 minutes is applied in the CFD analysis. This is assumed to be a possible, but quick escalation time. Hence, it is assessed to be on the conservative side. A plot and further discussion of how the release scenarios are quantified is given in Section B 15.3.

The CFD analysis that is performed finds the maximum size of a gas cloud inside the room during the off-gassing event. It is assumed that ignition occurs at the point of maximum flammable atmosphere – thus are considered worst case. It is further assumed that the walls can withstand 0.5 barg overpressure without breaking for a typical battery space forming a part of the vessel structure. This explosion pressure occurs during combustion of a stoichiometric gas cloud that is 1/16th of the room volume. The pressure is generated due to expansion of the gas during combustion where it is applied that the expansion causes maximum 8 barg when the room is filled up to 100%, see Section B 15.1.1 and Figure 15-3. This is a finding that is quite constant for different compositions of flammable gases from natural gas to pure hydrogen /4/. Structural strength of maritime walls, bulkheads, decks, ceilings, etc. can vary a lot, and the pressure of 0.5 barg is assumed a typical strength of a bulkhead wall. When new or retrofit battery rooms are designed, it is important to know the strength of the bulkheads and relate it to the design explosion pressure. Results provided can be used to find needed ventilation rates for different design pressures. For example, if a stronger bulkhead than 0.5 barg is designed, then the needed ventilation rates can be reduced compared to the rates in Table 6-3.

The CFD assessments are based on two rooms with a free volume of 15 and 25 m^3, respectively. Results are considered applicable to other room volumes through the use of ACH for ventilation rates but for cases significantly departing from this setup (i.e. crowded, oddly shaped, very large, or very small rooms) it is recommended to perform an analysis for the specific case. Note, increased room volume will also reduce the overpressure caused by expansion and thus reduce the magnitude of the structural impact.

Results from the simulations are summarized in Figure 6-3 and Table 6-3. The results show that a relatively high ventilation rate is needed when 500Ah battery is failing; 22 and 70 ACH is needed for the large and the small room, respectively.

A higher ventilation rate is needed for the small room partly because in this room the air extraction duct is located 80 cm down from the ceiling (to the centerline of the duct). In the large room, this extraction duct is located 40 cm down from the ceiling. If the air extraction ducts are located higher up, the needed ventilation rate is reduced. If the room has extraction in the ceiling, then the calculated cloud size is reduced further. From the initial simulation results presented in Figure 15-9 and Figure 15-10 in Section B 15.1, the cloud size at 10 ACH and 30 ACH can be reduced by approximately 20% and 60% respectively. If it is assumed that this trend is general, the results from the large room can be reduced further as shown in Figure 6-2 and Figure 6-3. This is an indication of the benefit from designing ventilation suction from the ceiling.

For the largest release rate, no ventilation rate is found that would reduce the cloud to an acceptable size. It is simulated a ventilation rate up to 100 ACH, and this was found not to be sufficient.

For releases that are smaller than 1000 l, the needed ventilation rate will decrease further, however, the ventilation rate should not be zero. At zero ventilation, gas can accumulate even with a small release rate. By interpolating the test results between 120 liters and 500 liters, the typical ventilation requirement of 6 ACH is assessed to be sufficient for 350 liters of gas. This corresponds to a battery of 115-175 Ah, depending if 2 l/Ah or 3 l/Ah is assumed.

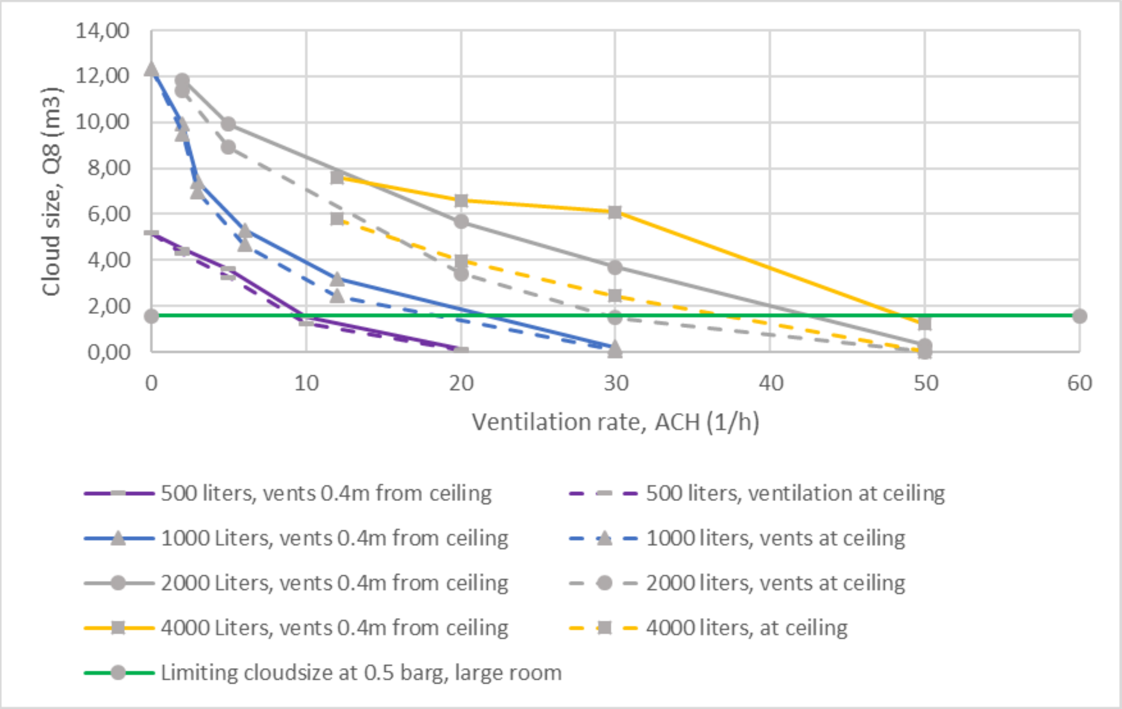


Figure 6-2 – Effect of ventilation located at ceiling for large room at 25m3.

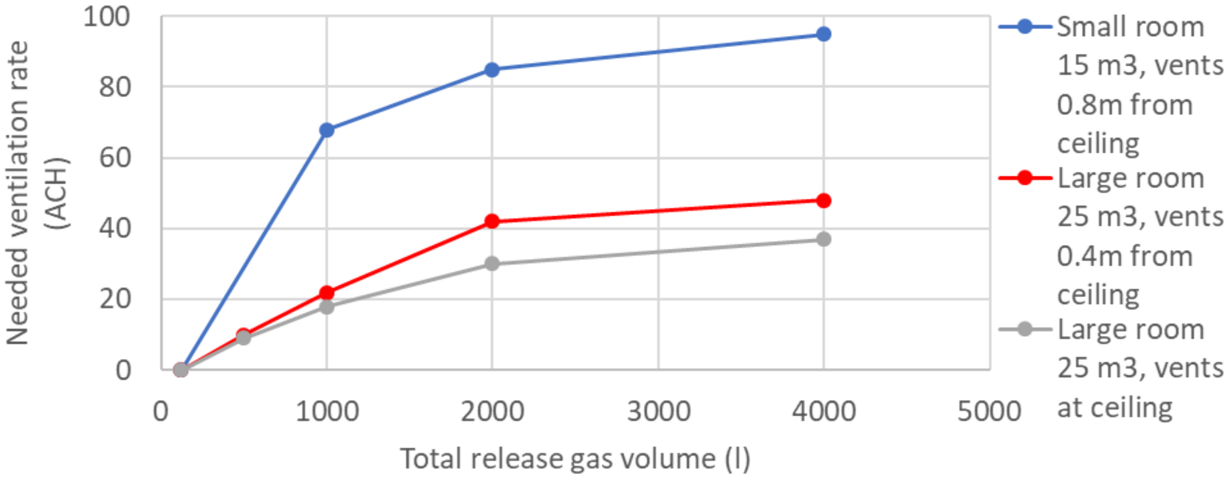


Figure 6-3 Needed ventilation rates as a function of the total volume of gas released from the battery. Note that the biggest contribution is the vent distance from the ceiling, and not the size of the room.

Table 6-3 – Needed ventilation rates (ACH) from CFD analysis based on gas volumes produced and types of room. The battery size in Ah is shown assuming a gas production rate of 2 L/Ah. This gas production rate may change between different cells.

Battery size releasing* (Ah)	60	250	500	1 000	2 000	4 000
Total gas released (l)	120	500	1 000	2 000	4 000	8 000
Small room 15 m3 ventilation, vents 0.8m from ceiling (ACH)			68	85	95	NA (>100)
Large room 25 m3 ventilation, vents 0.4m from ceiling (ACH)	0	10	22	42	48	NA (>100)
Large room 25 m3 ventilation, vents at ceiling (ACH)	0	9	18	30	37	NA (>100)

* Assuming gas production is 2 l/Ah.

It is critical to take into account fire suppression with regard to ventilation requirements. Some fire suppression systems operate based on principles that require shutting down ventilation in order for them to be effective – particularly gas-based systems, such as CO_2 or Novec 1230.

6.3 Derivation of ventilation formula based at CFD results

Based at the CFD results, a formula for the ventilation for a typical battery room is here presented. This formula should only be for the assumptions listed in Section B 15.3.1. More specifically,

- Free volume from 10-30m^3.
- Leaking gas volume less than 4 000 liters.
- The extraction duct should be located less than 0.8 meter from the ceiling.
- If the extraction duct is at the bottom only, the formula is not valid.

If the room volume, release profile, ventilation arrangement and the shape of the room is severely different, a separate CFD analysis should be carried out.

The derivation is solely based at inspecting the curves from the CFD results, and a suitable function taken into account max $Q8_T$ size, the amount of battery gas released, the vent distance from ceiling and the room volume. The required air changes per hour (ACH) can be expressed as shown in the equation below,

$$ACH = A\frac{(1+Bh)}{v}e^{C\frac{(Q8_T+D)}{g}}$$

where $Q8_T$ (m3) is the critical stoichiometric gas cloud size, h (m) is the vent distance from the ceiling, g (liter) is the total liters of gas from the batteries and v is the room volume.

The variables $Q8_T$ and g can be replaced such that the function considers the design pressure p and the size of the failed batteries Q instead. The relationship between design pressure p, room volume v and threshold cloud size $Q8_T$ are $Q8_T = p\ v/8$, as discussed in Section 15.3.3. The total battery gas released can be expressed as $g = r\ Q$, where r is the gas released per ampere hour and Q is the size of the failed batteries in ampere hours. To account for CFD model uncertainties and simplifications made in the curve fitting process, a safety factor S should also be included.

Hence, the ventilation rate can be expressed as:

$$ACH = SA\frac{(1 + Bh)}{v}e^{\frac{C}{8}\frac{(vp+8D)}{rQ}}$$

where p (barg) is the design pressure of the bulkhead, h (m) is the vent distance from the ceiling, Q (Ah) is the size of the failed batteries and v (m3) is the room volume. The parameter *r* is in this chapter assumed to be 2 l/Ah, which is an established rule of thumb. However, the single cell CFD results in this project indicates that this number can be increased up to 3 l/Ah for cases where no external combustion is observed. Cases with no combustion may happen although it is more likely that the gas ignites early without explosion. Since cases with combustion are observed and possible, it is advised that this scenario is accounted for. A proposed value of S = 1.1 gives a margin of 10%.

The values for the parameters are listed in Table 6-4. The values for A, B, C and D are found by using curve fitting. Adjusting the parameters to find an optimal fit for the CFD results at 0.5-1.0 barg design pressure has been prioritized. Also, the room with free volume of 25m3 has been given priority over the small room of 15 m3. Finally, the release of 500 liters, 1 000 liters and 2 000 liters have been prioritized over the 4 000 liters case.

Table 6-4: Ventilation formula parameters

Parameter	Value
A *)	1282.7
B *)	0.498
C *)	-311.8
D *)	1.579
r **)	2-3 l/Ah
S **)	1.1

*) Parameter found by *curve_fit* in Python

**) Parameter chosen by rule of thumb, and can be changed by the user

The CFD simulation plots for the large room with vents 0.4m from the ceiling are plotted together with the proposed function in Figure 6-4. The ventilation rates with a design pressure of 0.5 barg is shown in Figure 6-5.

Table 6-5 provides example values with *r* = 2 l/Ah and *S* = 1.1.

Table 6-5: Example values for the formula presented.

Battery size releasing with 2 l/Ah	60	250	500	1 000	2 000
Small room 15 m3 ventilation, vents 0.8m from ceiling (ACH)	0	27	60	89	108
Large room 25 m3 ventilation, vents 0.4m from ceiling (ACH)	0	10	25	41	53
Large room 25 m3 ventilation, vents at ceiling (ACH)	0	8	21	35	44

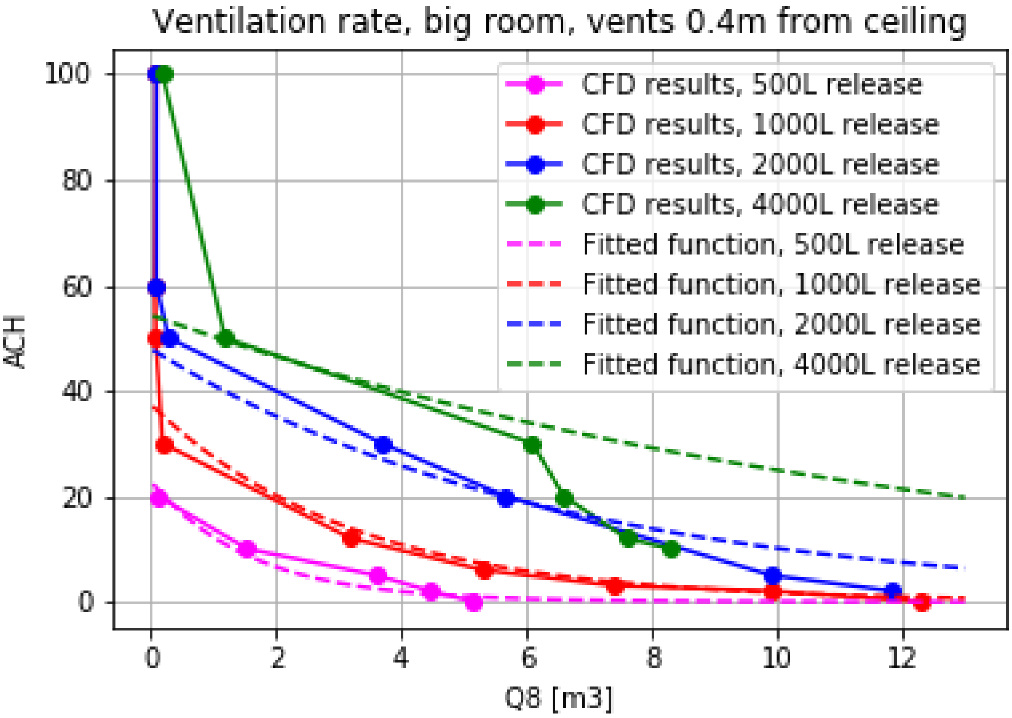


Figure 6-4: Ventilation rates for the big room with vents 0.4 m from the ceiling. Both the CFD simulations and the corresponding fitted function is plotted. *S* = 1.0.

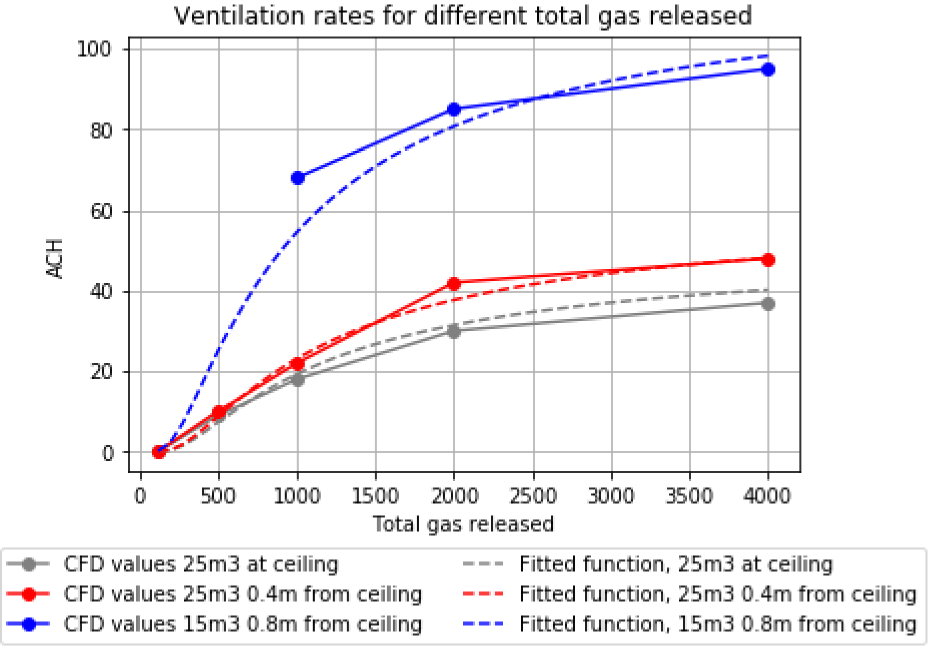


Figure 6-5: Ventilation rates for different gas releases with a design pressure of 0.5 barg. CFD results and the corresponding fitting function is shown. *S* = 1.0.

6.4 Main Conclusions

Main Conclusions
1. More open modules have greater possibility of providing oxygen to the fire and this will tend to result in a higher chance of prolonged combustion with higher temperatures and increase the chance of external combustion of gasses. 2. When the gasses produced from a lithium-ion battery are combusted, rather than accumulating, the explosion risk goes down substantially. 3. Limiting the oxygen to the fire will reduce the chance of prolonged combustion with lower temperatures. However, the off-gassing and hence the explosion risk increases. 4. The CFD results for two battery rooms with free volume of 15 and 25 m^3, show that a relatively high ventilation rate is needed even for the smallest gas release rate. 22 and 70 ACH is needed for the large and the small room, respectively. The ventilation can be turned on demand based at early off-gas detection with sensors close to or inside the modules. 5. The further the extraction duct is located down from the ceiling; the higher ventilation rate is needed. 6. The typical ventilation requirement of 6 ACH is assessed sufficient for "small" gas releases of 350 liters, which corresponds to a battery of 115-175 Ah. 7. If batteries of 4 000 Ah is failing, it will not be sufficient with 100 ACH to avoid an explosion magnitude of 0.5 barg. 8. A ventilation formula for a battery room is proposed. The formula calculates the air changes per hour (ACH) with the size of the failed batteries, the design bulkhead pressure, the room volume and the vent distance from the ceiling as input variables.

7 FIRE SUPPRESSION SYSTEMS

7.1 Li-ion fire hazards

The core of a lithium-ion battery fire – the cell itself – is typically not accessible and extremely difficult to extinguish, having elements of multiple types of fire (metallic, chemical, etc.) as well as being exothermic and potentially producing its own oxygen. However, a single cell fire is typically not of significant concern with regard to safety or survival of the ship. The prime concern is that a battery is made up of tens of thousands of cells, and this fire will tend to propagate to additional cells – thus increasing the heat load and increasing the likelihood that it will propagate further, to a worst case of having involved the entire battery system. Thus, extinguishing the fire at the single cell level is not the focus of fire suppression systems. The key role of fire suppression systems is to absorb heat and reduce the degree of propagation, or the number of batteries which will be involved in the fire.

Based on this arrangement, several principles become evident. First, detection and early release of suppression medium greatly increase its effectiveness. The more a fire has propagated, the more heat is being produced and the more difficult it is to put out. It is recommended that fire suppression, detection and release systems still are fully functional after a single failure in any other subsystem, such as the BMS. With regard to all of these issues and integration complexity, it is imperative that the battery manufacturer is involved and provide recommendations to necessary safety barriers. Each battery system is different, and each installation is potentially unique. However, a standardized comparative test method has been proposed in Section 7.5, to evaluate the performance of the fire suppression systems.

A fire external to the battery itself presents a significant danger. The battery system normally has no way of protecting itself in such an event, and an external fire is likely to heat up multiple cells and modules simultaneously. A designated battery room thus provides significant protection from such an event – particularly with the requirements for no fire-risk objects to be installed in the room and with fire rated boundaries. Should the passive barrier fail, a fixed total-flooding fire suppression system constitute an important secondary barrier.

7.2 Means for suppression

It is considered a credible failure mode that more than one module can catch fire – nominally occurring at a full string level, due to BMS failure, a contactor failure or welding, power converter failure, or ground isolation fault.

The fire suppression system shall be able to swiftly extinguish a fire in the space of origin, and in order to fulfill the functional requirements as stipulated in SOLAS Chapter II-2 Regulation 2.2, the following objectives should be met in particular:

- Preventing module-to-module propagation
- Multiple battery module fire suppression

The functional requirements above must be evaluated considering the particular battery system being considered – for instance: whether active fire suppression is used to prevent module-to-module propagation or whether different suppression media will be able to access and remove heat from the neighboring battery modules. A key metric used to evaluate effectiveness was the external and internal temperature of neighboring modules as the device under test went through failure – the fire suppression system role is considered primarily to manage the heat transferred to these neighboring modules. The different functional requirements, combined with the testing conducted, point to several key attributes of different fire suppression media necessitating consideration. In general, the different fire suppression systems all excel in different areas and there is no identified ‘silver bullet’ solution. The fire suppression media or systems evaluated were:

- Sprinklers: Offer a common method for fire extinguishment that is in line with lithium-ion expected requirements – large amounts of volume can be supplied to provide for maximal heat absorption.
- Hi-Fog: Is a high-pressure water mist system that produce a fine mist which increases surface area for heat absorption. A typical water mist system would have capacity for a minimum of 30 min freshwater release, followed by back-up access to seawater from the vessel fire main providing cooling properties over time. However, the time duration of the discharge can be increased based upon required protection time limits defended in the design phase of the system.
- NOVEC 1230: Is an equivalent gas-based fire suppression system. The primary function of NOVEC is to put out flames by physically cooling below the ignition temperature of what is burning and chemically inhibiting the fuel source. The agent does not deplete oxygen levels in the room, where fire itself is the only actually consuming oxygen. Sealing of the space is key for ensuring adequate concentrations of NOVEC 1230.
- Direct injection of water: For the purpose of combating heat generation, direct injection of water is considered as the most efficient alternative. In the stationary industry today, this method is generally included as a last resort back-up since the affected module(s) will be considered lost after deployment. This method is not recommended to be used in practice for high voltage applications, due to the risk of short circuit and hydrogen production. The test setup included a fire hose connection with direct access to the interior of the battery module under testing.
- FIFI4Marine CAFS: Is a foam-based system, that can be installed to deploy directly in to the battery modules, their surroundings in the racks or in the room. The concept evaluated in this report is only direct injection into the modules. The FIFI4Marine CAFS system is designed to re-deploy several times during an incident as the foam will degrade over time as it participates in combating the battery fire.

7.3 Test results

All the tested systems where able to extinguish visible flames, except for the sprinklers. Not enough water was able to get in between the modules, such that flames was observed even during deployment of the water drops. Water mist, NOVEC 1230 and the direct injected foam from FIFI4Marine was able to extinguish the flames.

The cooling capabilities of the sprinkler and the water mist system were found to be very similar. Both resulted in maximum temperatures external on neighboring modules of just above 600°C, though these persisted longer in the case of sprinklers; but both reduced all external temperatures to lower than 200°C within 100 seconds (systems deployed 30 seconds after thermal runaway initiates) and temperatures continued to decline after the initial 100 seconds. In addition, video as well as anecdotal evidence from several project participants indicates that sprinkler system had a difficult time suppressing flames and, in some instances, appeared to increase the intensity of the fire. By comparison, NOVEC 1230 reduced temperatures quickly – within 30 seconds – to under 250°C, but these temperatures remained stable for 1000+ seconds. Considering such a long-time scale, neighboring module external temperatures when using sprinklers or water mist can be expected to reduce to less than 30°C or 60°C, respectively.

Suppression systems' capability to affect off-gas concentrations in the battery space was also measured. Indication of gas concentrations was taken primarily from LEL% measurements. The values presented in Table 7-1 represent the percentage of a given LEL% limit. These measurements were taken in the center of the room. Hence, the values do not correspond to a stoichiometric mixture that would be assumed to exist in the whole space. The measurements are nonetheless representative of the relative capability of the different systems to affect the amount of explosive hazard existing in the space. The LEL% was not recorded for the sprinkler test. Based upon experience and other tests performed by the project participants, it is concluded that the sprinklers are not capable of reducing the gas concentration. It can actually be argued that it increases the explosion risk, since the water displaces the gas into pockets with higher concentrations.

Table 7-1 – Effect of fire suppression system medium on LEL

Fire Suppression System Used	Maximum LEL% recorded (%)
None	69 %
Hi-Fog	10 %
NOVEC 1230	26%

The effect of injecting fire suppression media directly into a battery module was also evaluated for comparison. Direct injection of water is not expected or recommended to be used in practice in high voltage systems due to the risk of short circuit and hydrogen production. However, the method is presented as a reference point for the best flame extinction and heat absorption capabilities, that can be expected by a fire suppression system. The direct water injection test also provides a valuable reference point for evaluating the capabilities of the FIFI4MARINE CAFS (foam) system which is designed and engineered to be injected directly into the module. Another key differentiating factor is that the foam-based system is likely to require a significantly reduced volume of water compared to pure water-based injection. Additionally, the foam-based system is deployed using de-ionized water to limit conductivity and corrosive effects.

Due to limited amount of suppression media available onboard the vessel it should be considered how much suppression media that should be used, how many modules that should be sprayed and how many releases the system should be able to produce. This applies for all the tested suppression systems.

Both the foam-based and the water-based systems reduced the main battery fire temperatures to under 80°C within 600 seconds. This represents a significant improvement over what can be achieved with fire suppression media applied outside of the module – where the main battery fire temperature was unaffected and quite stable at around 900°C. External temperatures on neighboring modules are also significantly reduced from the use of direct water injection – reducing to below 20°C within 150 seconds after release. The direct injection foam-based system had recorded temperatures below 50°C within 700 seconds, while the total-flooding water mist system achieved temperatures that were just above 60°C after 700 seconds. Although some of the results may be similar, ultimately it is difficult to compare the capabilities between direct injection and external suppression systems since the reason behind the results were so different in each case. In general, it can be considered that direct injection of fire suppression media is much more effective compared to external application. In cases where the approach to safety may be different – such as a battery installed without a dedicated battery room – this may be a particularly attractive approach to evaluate.

7.4 Performance comparison

Fire extinguishing systems can be designed to combat fires based on different principles, by limiting oxygen supply, reacting chemically with the fire or by removing heat. It is therefore not self-evident that a given fire-suppression media will act as efficiently with a lithium-ion battery fire involving many types of fires as described in Section 7.1.

A summary of the test results is shown in Table 7-2 and aim to summarize the results achieved during a full module thermal runaway event. Parameters are split into those considered primary in combating a lithium-ion fire and those considered as secondary safety barriers during such an event.

To deliver on the primary function – mitigating heat transfer to neighboring modules – our results show that some suppression systems with low or non-existent long-term heat absorption properties will require a passive barrier to propagation or additional coolants to achieve the necessary safety level.

Due to the prevalent risk of a lithium-ion battery reigniting – which can happen several hours or days after an event – it is recommended that the fire suppression system is engineered for multiple releases if no other mitigating measures can be made. Actual volumes and release rates need to depend on the battery system as well as the suppression media being used.

Table 7-2: Fire suppression systems' capability matrix

	Primary objective			Secondary objective		Suppression method properties	
	Flame extinction	Long Term Heat Absorption	Short Term Heat Absorption	Reduce Gas Temp in room	Gas Absorption in room	Can be Used with Ventilation	Suppression method
Sprinkler	🟦	🟦	🟨	▨	⬜	YES	Total-flooding
Hi-Fog	▨	🟦	🟨	▨	▨	YES	Total-flooding
NOVEC 1230	▨	⬜	🟦	🟦	⬜	NO	Total-flooding
FIFI4Marine	▨	▨	▨	Not evaluated	Not evaluated	YES	Direct injection
Direct Water injection *)	▨	▨	▨	Not evaluated	Not evaluated	YES	Direct injection

*) Not expected or recommended to be used in practice for high voltage applications, due to the risks of short circuit and hydrogen production. The method is presented as a flame extinction and heat absorption capability reference.

▨ High capability

🟨 Low capability

🟦 Medium capability

⬜ No or very low capability

7.5 Defining a test program for fire suppression

In waiting of internationally recognized maritime test programs for lithium-ion fire suppression systems this project aimed to develop a methodology for comparative tests between different fire suppression systems available in the maritime market. When dealing with lithium-ion battery fires the identified primary threat that a suppression system should be tested for is that of a full module going into a thermal runaway event with combustion. Thereby the single module fire scenario is designed to capture the main threat based on risk and consequence to a battery system.

This subsection aims to highlight key considerations made and to summarize learnings from tests conducted in order to establish a base for future tests and standardization work.

7.5.1 The test setup

To establish a common baseline, it is important to consider what the key parameters are for normalizing the tests. The following parameters are considered the most important for comparative results in further studies.

- Test room volume – 19.25 m^3 (20ft container): Chosen to be representative of a smaller scale battery space in addition to limiting the amount of installed equipment and/or batteries needed in the space. A limited space is crucial in order to asses risks related to off-gas concentrations and ambient temperatures, as a bigger test hall would not be representative of maritime installations typically characterized by volume and weight constraints.
- Battery chemistry – NMC pouch cells: These cells should be used as they represent the highest fire risk, being more susceptible to thermal runaway and obtaining the highest temperatures when combusted. The NMC cells are also the most commonly used cell in the maritime industry.
- Module size – 1.3 kWh: The energy contained in such a module is on the lower scale compared to more sophisticated modules found in the market. The relative effectiveness of suppression systems is nonetheless achieved by keeping the module to a constant energy capacity.
- Module casing – IP2X mild steel enclosure of 0.5 mm thickness: The low IP rating is chosen to more easily establish a full module fire as the free access to oxygen is necessary for combustion.
- Battery rack configuration: Modules were fitted in 3 columns distributed in 6 rows. The live module placed in the bottom 3rd row, second column. This configuration was chosen to represent a typical rack setup and providing enough neighboring thermal mass to effectively simulate a module-to-module heat transfer during the single module fire scenario.
- Temperature measurements: Thermocouples should be placed on the live module, along the faces of the neighboring modules, in addition to internal module thermocouples. Additionally, each neighboring dummy module should be fitted with internal thermal mass to represent missing battery cells. Figure 7-1 show an example of a thermocouple placement in the test setup.
- Concentration of flammable gas measurements: Even if explosion risk is not considered as a primary function for a fire suppression system it is still identified as a secondary function or additional benefit. It is recommended that tests include gas measurements at different heights due to possible stratification effects of temperature gradients in the test hall.
- Fire suppression installation: Nozzle configurations and fire-extinguishing system installation should always follow the maker’s specifications and installation requirements. For a NOVEC 1230 system it should be noted that different battery electrolytes could require higher than normal

design concentrations of the extinguishing media and the maker should always be consulted prior to installation for a given battery system.

- Ventilation: During the tests the ventilation system was closed for comparison. When conducting system specific tests, it is recommended that the test hall ventilation is designed to run as intended during a thermal runaway event based on the characteristics of that system.
- Initiating thermal runaway: This should be achieved by installing resistive heat elements in-between the installed battery cells, providing thermal stress until the point of thermal runaway is initiated. Alternatively, comparable behavior can be achieved by overcharging the cells.
- State of Charge (SOC): 100% SOC should be chosen to provide the most consistent combustion results.
- Fire suppression release: The fire suppression systems should be all employed after a 30 seconds time delay. This time delay is considered as the worst case between sensor activation and the automatic system release.
- Re-ignition: While not the focus in the comparative tests presented in this report, temperature and gas measurements should continue after an initial extinguishing operation has been carried out. As the DUT internal temperatures remain largely unaffected during an initial release of a fixed fire-extinguishing system it is important to monitor the systems for re-ignition or further temperature spikes.

These parameters where chosen to provide a comparative result for a bare-bones battery system, completely lacking safety measures other than the fire suppression systems. A commercial battery system, approved for marine use, would necessitate additional barriers such as passive propagation protection. Conclusions of absolute nature with regards to effectiveness of a given fire suppression system should only be done after system specific tests at this point.

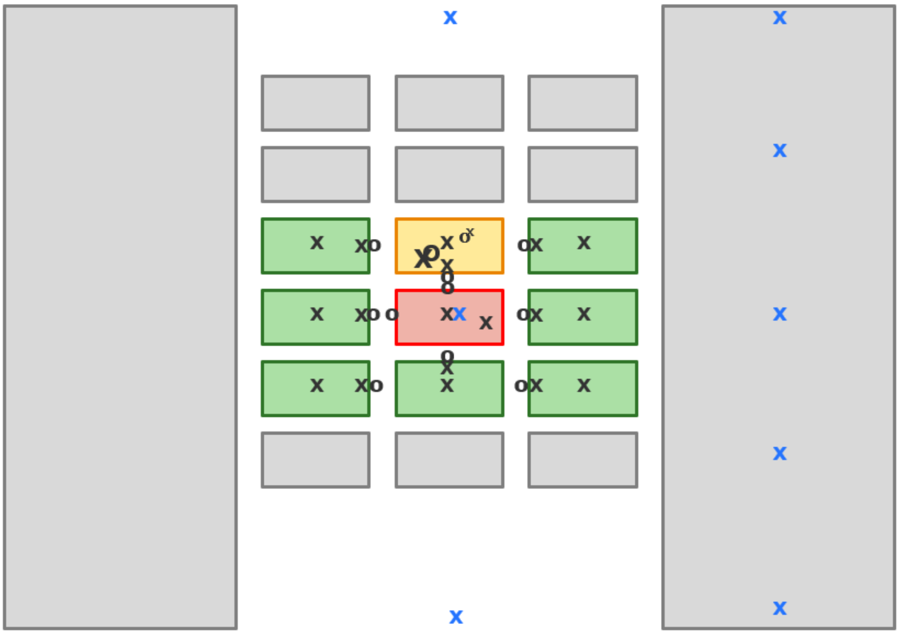


Figure 7-1 – Placement of thermocouples for all module testing – black 'x' internal to modules, black 'o' external to modules, blue 'x' indicating ambient room thermal gradient temperatures.

7.5.2 Total flooding versus direct injection tests

For fire-extinguishing systems that are to be installed to combat any fire in the battery space, applicable IMO test standards for such systems are considered a pre-requisite for lithium-ion battery fire application. For a water mist system (Hi-Fog) this would refer to IMO MSC.1/Circ.1165 as amended, or for the equivalent gas-based systems (NOVEC 1230) this would refer to IMO MSC.1/Circ.848 as amended. The IMO standards referred to are established to primarily combat petroleum fires, while the tests performed in this report are made to assess effectiveness for a lithium-ion battery fire in particular.

For direct injection systems, designed to primarily protect against battery fires, a test as carried out in this report is crucial in order to assess effectiveness in accordance with identified functional requirements unique for lithium-ion battery fires. For external hazards, these systems would typically require the installation of a complementary room protection. From the tests presented in this report the FIFI4Marine CAFS had the highest potential for module-to-module fire mitigation, especially when designed for sufficient capacity to flood the modules/racks over longer time periods.

7.6 Main Conclusions

Main Conclusions

1. Tested fire suppression systems provide different benefits, with unique strengths and drawbacks, providing no ‘silver bullet’ solution. The different properties are presented in Table 7-2.
2. Direct injection of foam shows the best heat mitigating performance compared with all tested methods. This method had the highest potential for module-to-module fire mitigation, especially when designed with capacity to flood the modules/racks over longer time periods. In cases where alternative ship integration concepts are to be evaluated – such as a battery installed without a dedicated battery room – this may be a particularly attractive approach to evaluate the equal level of safety. The gas temperature and gas absorption are not evaluated.
3. High pressure water mist protection provides good heat mitigation at module level in addition to providing full battery space protection from external fires. It also shows good gas absorption and gas temperature reduction capabilities.
4. NOVEC 1230 extinguish the battery fire flames, but performs poorer with regards to heat mitigation, gas temperature reduction and gas absorption compared to water mist. Room ventilation needs to be closed for this suppression method to be functional. This can increase the toxic and explosive battery gas concentration in the room until ventilation can start again.
5. Sprinklers do not extinguish the visible flames but records similar heat mitigation capabilities at module level as high-pressure water mist. Since water can displace the gas into pockets with high concentrations, the explosion risk is considered to become more severe with sprinklers.
6. Each battery installation will have to assess necessary barriers in consultation with the battery manufacturer to identify the application most suited for that project. Due to limited amount of available suppression media onboard a vessel, the actual volumes and release rates needs to be calculated and are dependent on the battery system.
7. A methodology for comparative tests between different battery fire suppression systems available in the maritime market is proposed. Both heat and gas mitigation performance are evaluated.

8 RISK COMPARISON & ACCEPTANCE CRITERIA

8.1 Risk evaluation

Since no statistics of maritime battery fires are available, an approach to Quantitative Risk Assessment (QRA) of a battery thermal failure has been developed. Quantifying the risk through an analysis like this can be used to determine how the system compares to acceptance criteria. The risk model is shown in Figure 8-1. Various threats and safety barriers have been identified for a battery system. The frequency of occurrence of these threats and failures in the barriers are to statistics found in Center for Chemical Process Safety (CCPS) /1/ and Institute of Electrical and Electronics Engineers, Inc. (IEEE) /2/. Details of the threats and barriers considered in the QRA is outlined in the detailed report in Section B 17.

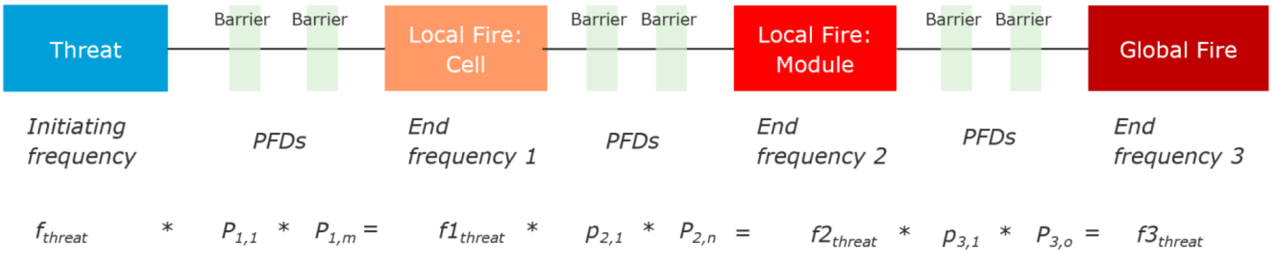


Figure 8-1 – Scheme for calculating frequencies for the different consequence categories caused by a threat

The frequency for each failure event is summarized and presented in Table 8-1.

Table 8-1 Fire frequencies for generic battery system

Consequence Category	Total frequency (per year)
Local Fire: Cell	3.8E-04
Local Fire: Module	1.4E-04
Global Fire	1.3E-07

Although the results may be uncertain in terms of absolute values, the analysis can be used to highlight the importance of different barriers, and the relative effect of not having them in place. To illustrate this, the risk resulting from the following system variations is studied:

- No barrier against cell propagation
- Less effective BMS
- Without independent shutdown
- Without CID
- As a (unrealistic) extreme case, removing all of the above.

It is seen that the fire propagation protection and the Current Interruptive Device is two of the most important safeguards to be installed in the battery system.

A comparison with an engine room fire probability has also been made. For the engine room fire, a ballpark frequency is calculated by using the engine room fires registered in the global HIS Fairplay database for the period 1998-2017.

Table 8-2: Calculated frequency of a fire in a battery room vs reported frequency of a fire in the engine room in the HIS Fairplay database

System	Total frequency of a fire (per year)
Battery System	5.2E-4
Engine Room	6.8E-4

Based at the numbers presented, it seems that the likelihood of a battery fire is lower compared to a diesel fire. However, engine room fires as registered in the HIS Fairplay database include fires of many different magnitudes not necessarily correlating to the Global fire scenario established in battery system QRA. This means that better data would be necessary to fully evaluate if a battery system is safer than a conventional combustion engine.

8.2 Main Conclusions

Main Conclusions
1. A model for Quantitative Risk Assessment for a battery system has been proposed. 2. Fire propagation protection and the Current Interruptive Device is two of the most important safeguards to be installed in the battery system. 3. More and better data would be necessary to fully evaluate if a battery system is safer than a conventional combustion engine.

Table 8-3: Fire frequencies for systems without barriers compared to base case with all barriers present

Consequence Category		Local Fire: Cell	Local Fire: Module	Global Fire
Base case: system with all barriers		3.8E-04	1.4E-04	1.2E-07
Without cell propagation design	Frequency	3.8E-04	4.8E-04	3.5E-07
	Relative to base case	**0 %**	**248 %**	**177 %**
Less effective BMS	Frequency	5.2E-04	1.5E-04	1.4E-07
	Relative to base case	**37 %**	**10 %**	**11 %**
Without independent shutdown	Frequency	9.3E-04	1.9E-04	1.4E-07
	Relative to base case	**143 %**	**40 %**	**11 %**
Without Current Interruptive Devise	Frequency	2.9E-03	3.9E-04	2.6E-07
	Relative to base case	**664 %**	**183 %**	**105 %**
Extreme case: Without any of the above	Frequency	2.2E-02	2.3E-02	1.7E-05
	Relative to base case	**5785 %**	**16197 %**	**13562 %**

9 THERMAL RUNAWAY TEMPERATURE PROFILES

Accurate characterization of ‘thermal runaway’ is important from the standpoint of understanding when it has occurred. Typically, thermal runaway infers the point at which the battery is ‘self-heating’ in an exothermic reaction. However, this still does not give distinct guidance for an observer to be able to identify if a cell has been successfully put into thermal runaway to for example initiate a given propagation test.

The literature /9/ define the thermal runaway into three main steps, as the temperature increases:

1. The solid-electrolyte interface (SEI) decomposes in an exothermic reaction. Can occur at 90 °C with a temperature increase of 0.00167 °C/sec.
2. An exothermic reaction between the intercalated Li-ions and the electrolyte starts. Can occur at 130 °C with a temperature increase of 0.4°C/sec
3. An exothermic reaction between the positive material and the electrolyte takes place. Can occur at temperatures above 200°C with a temperature increase of 1.7-17.0 °C/sec

The aim is to identify the worst case scenario, when the cell has reached stage 3, which is when the cell releases the largest amount of heat.

Thus, data is presented from tests conducted in this project to show different cases and what may be expected. Results are based on surface temperature measurements of the cell. In the cases of external heat application, this heat would be affecting the temperature indicated by the thermocouple. The intention here is to provide reference such that it can be better understood if a given phenomenon shown should be considered as thermal runaway.

9.1 Heat release profile results

9.1.1 NMC pouch cells

Figure 9-1, Figure 9-3, Figure 9-5, Figure 9-7 and Figure 9-9 provide visual indication of what the temperature profile looks like as a cell goes into thermal runaway. Figure 9-2, Figure 9-4, Figure 9-6, Figure 9-8 and Figure 9-10 show the temperature raise profiles for all NMC tests. In almost all cases, there is a point at which heating of the cell accelerates, characterized by a point that does visually appear as an inflexion point relative to the rate of temperature increase. However, detailed inspection shows that these points still only increase at a rate of less than 1 degree Celsius per second. Following this, it is common to see a point where the temperature will dip down – this coincides with a preliminary gas release. However, we see that this is still clearly not ‘thermal runaway’. The primary points of focus are the sharp spikes in temperature, where we see close to 25°C per second temperature rise, or several hundred in the overcharge case shown here. This will define the onset of the thermal runaway. Table 9-1 provides a summary of key data points to use for comparison.

In addition, as shown in Figure 9-9 and included in Table 9-1; the thermal result of an external short circuit is found to be very mild compared to an actual thermal runaway event. This can be misleading as external short circuit does produce a sharp increase in temperature, but the actual rate as well as particularly the highest temperature reached are significantly lower than in other cases.

Table 9-1 – Characteristics for identification of thermal runaway NMC pouch cells

	Max Temp (°C)	Max Temp increase rate (°C/second)	Temperature at onset (approximate)
Overheat at 50% SOC	417	29.27	250
Overheat at 75% SOC	481	24.36	200
Overheat at 100% SOC	475	66.07	173
Overcharge	602	229	80
Ext Short Circuit	177	13.6	30

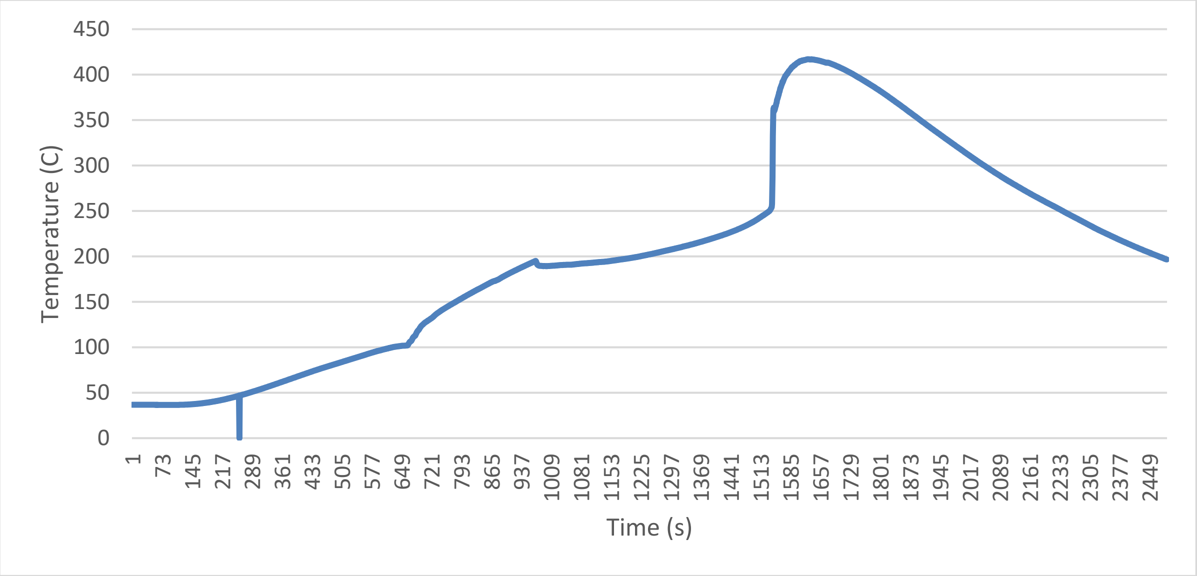


Figure 9-1 – Battery surface temperature for overheating a cell at 50% SOC distinguishes thermal runaway from other points of rising temperature

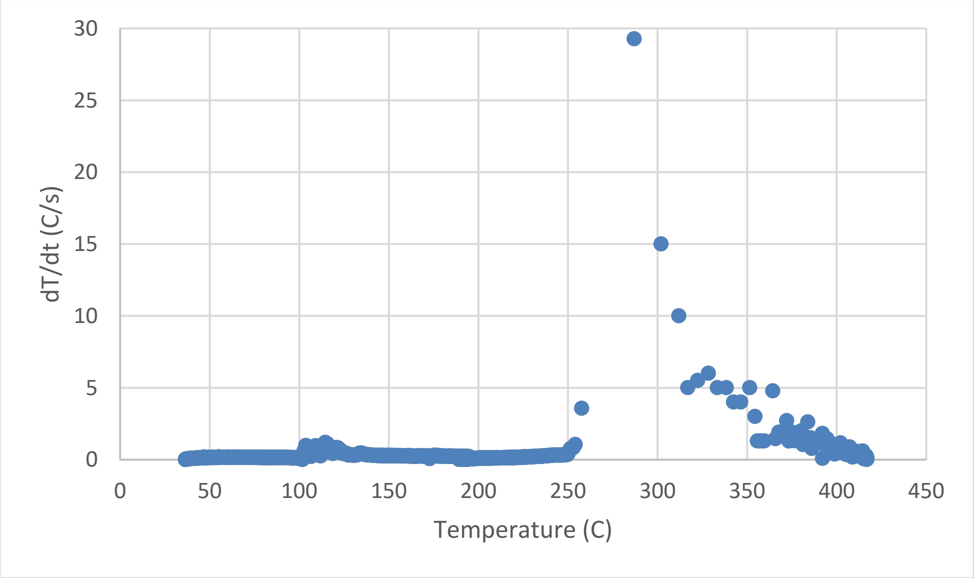


Figure 9-2: Temperature rate curve for test JDP2, NMC 50% SOC overheat

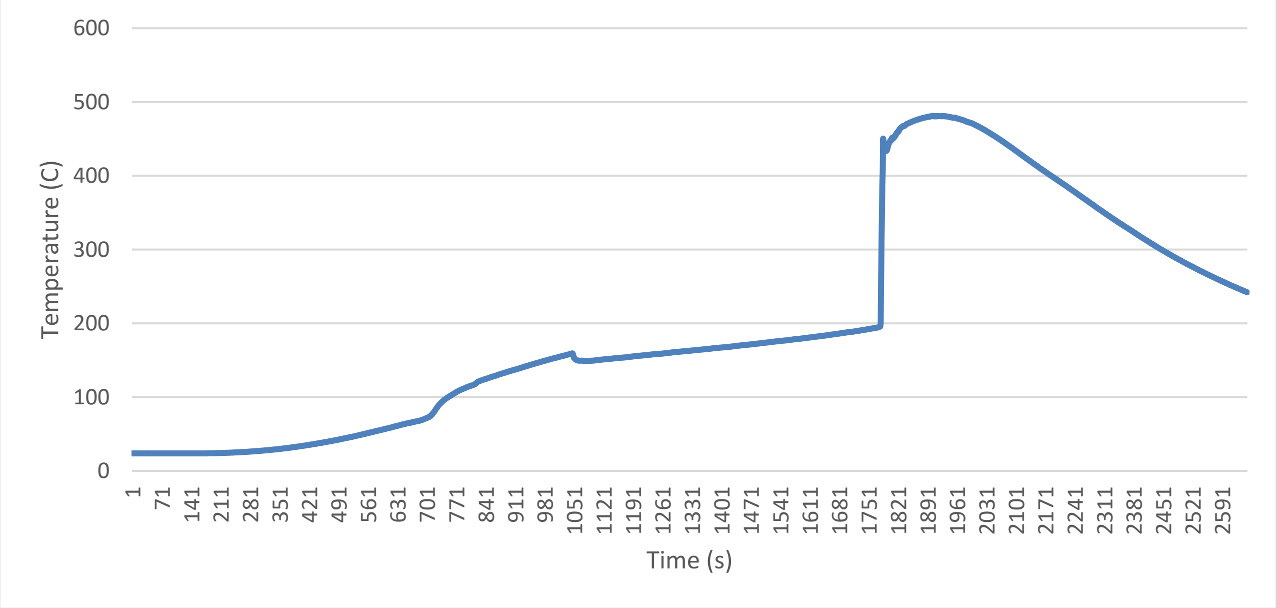


Figure 9-3 – Battery surface temperature for overheating a cell at 75% SOC distinguishes thermal runaway from other points of rising temperature

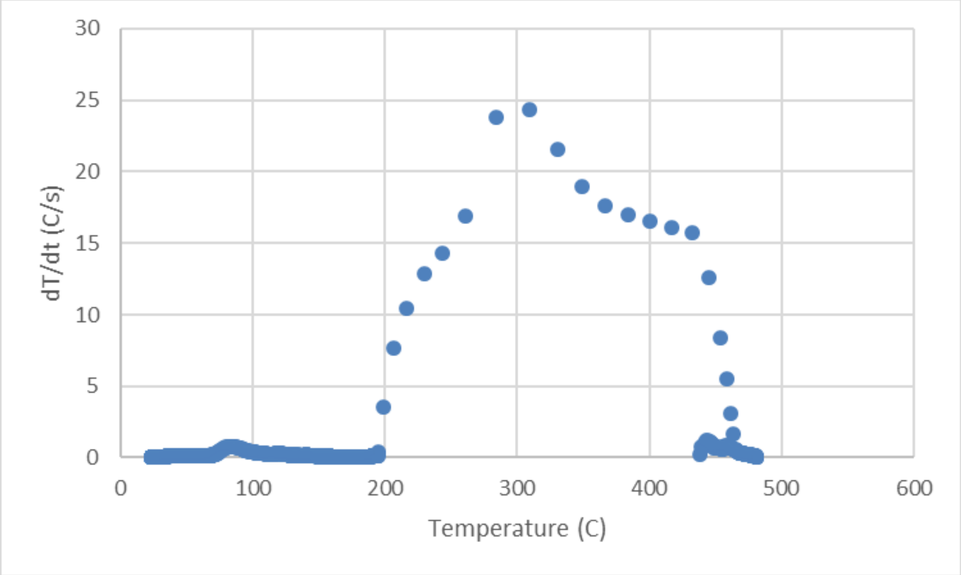


Figure 9-4: Temperature rate curve for test JDP5, NMC 75% SOC overheat

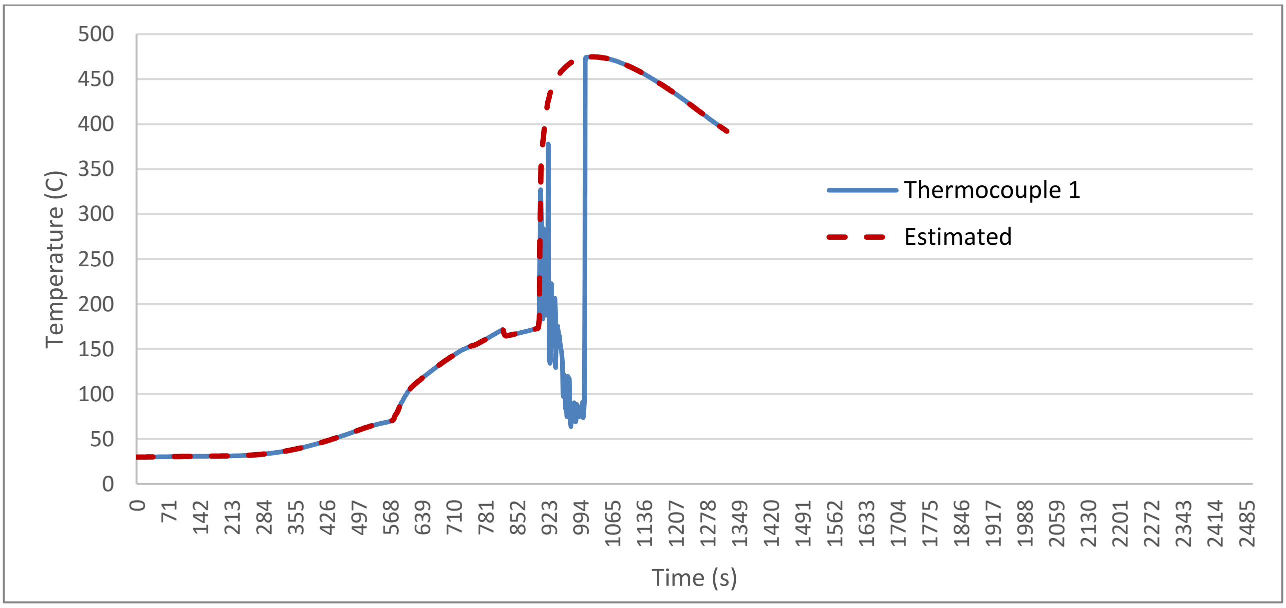


Figure 9-5 – Battery surface temperature for overheating a cell at 100% SOC distinguishes thermal runaway from other points of rising temperature

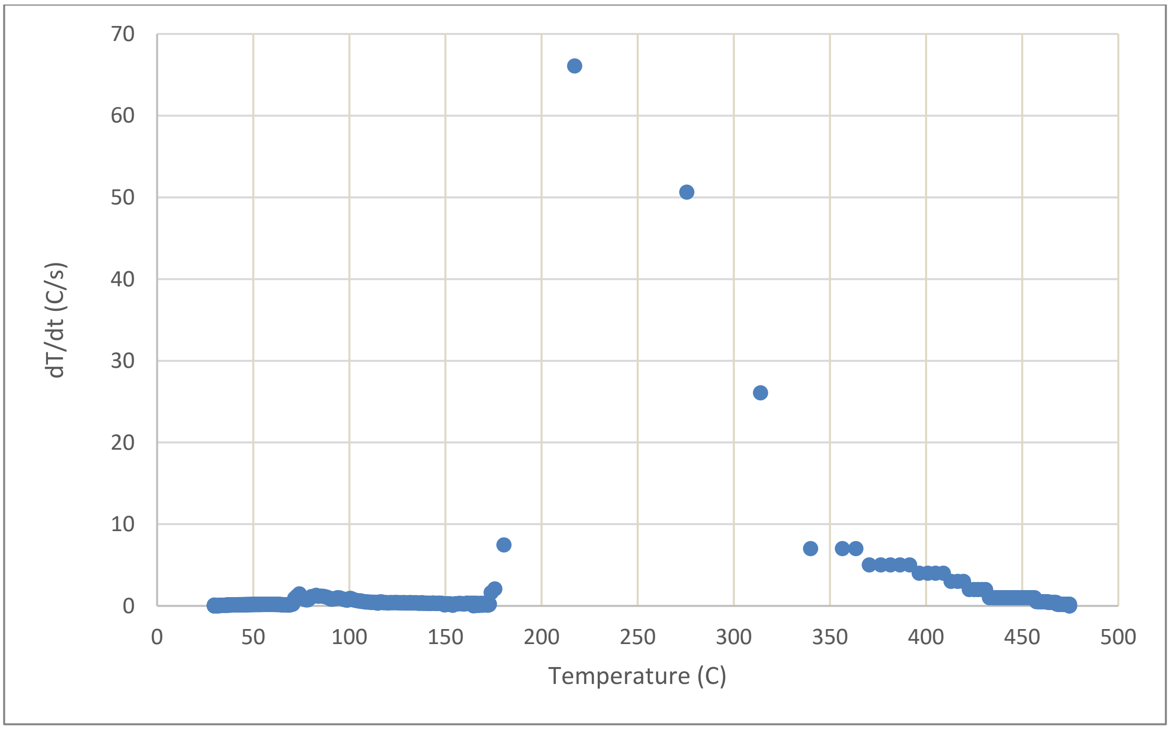


Figure 9-6: Temperature rate curve for test JDP1, NMC 100% SOC overheat

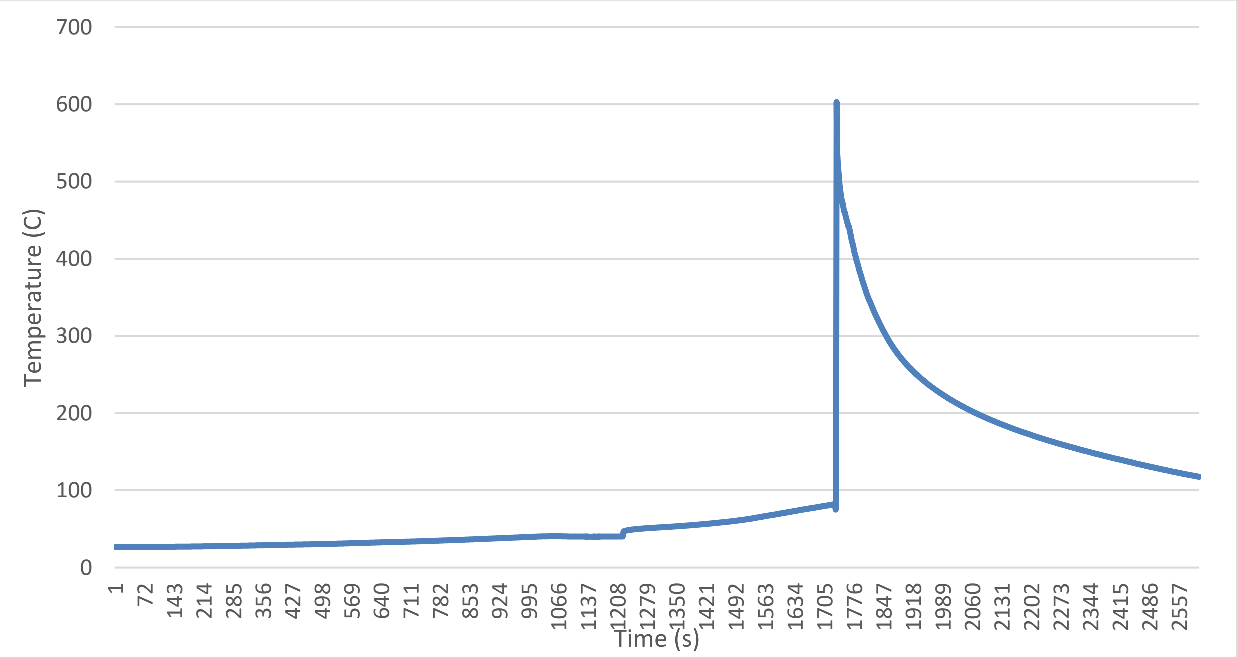


Figure 9-7 – Battery surface temperature for overcharging distinguishes thermal runaway from other points of rising temperature

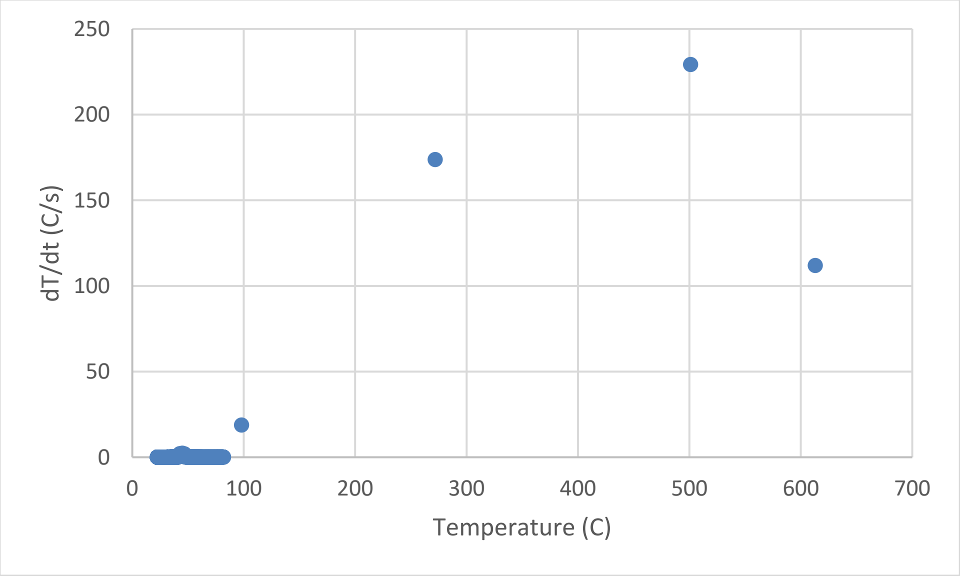


Figure 9-8: Temperature rate curve for test JDP3, NMC Overcharge

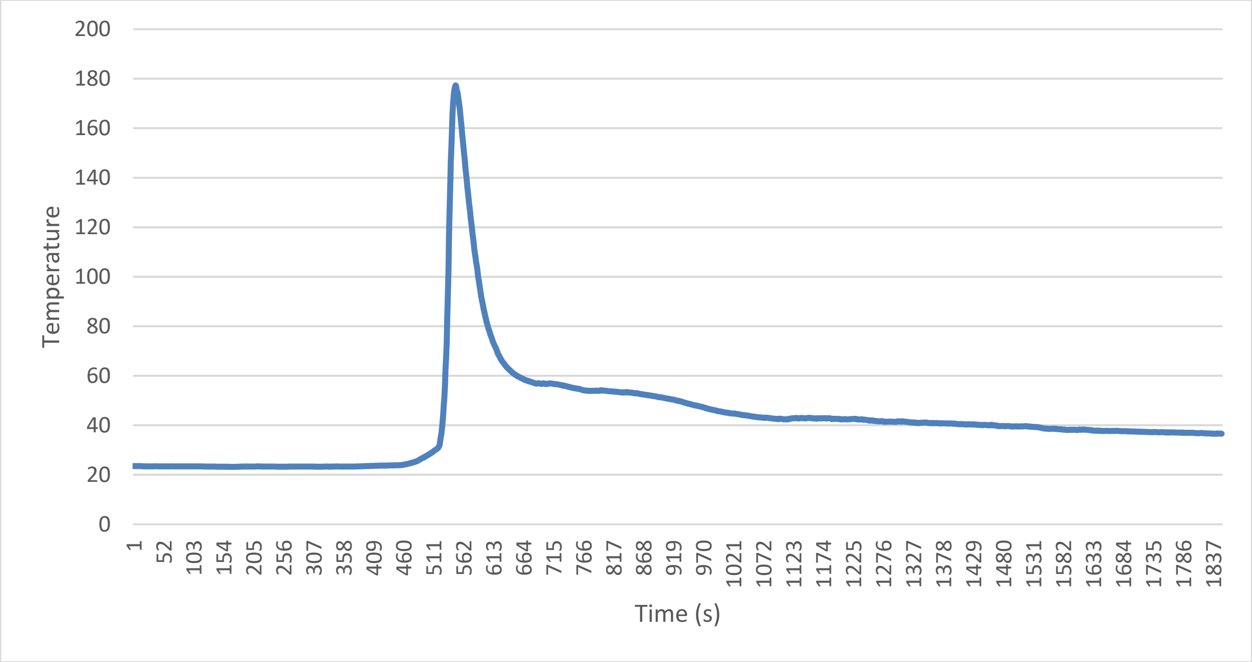


Figure 9-9 – The thermal result of an external short circuit can provide a fast temperature rise, but the rate and maximum value are not similar to other cases or considered to have entered thermal runaway

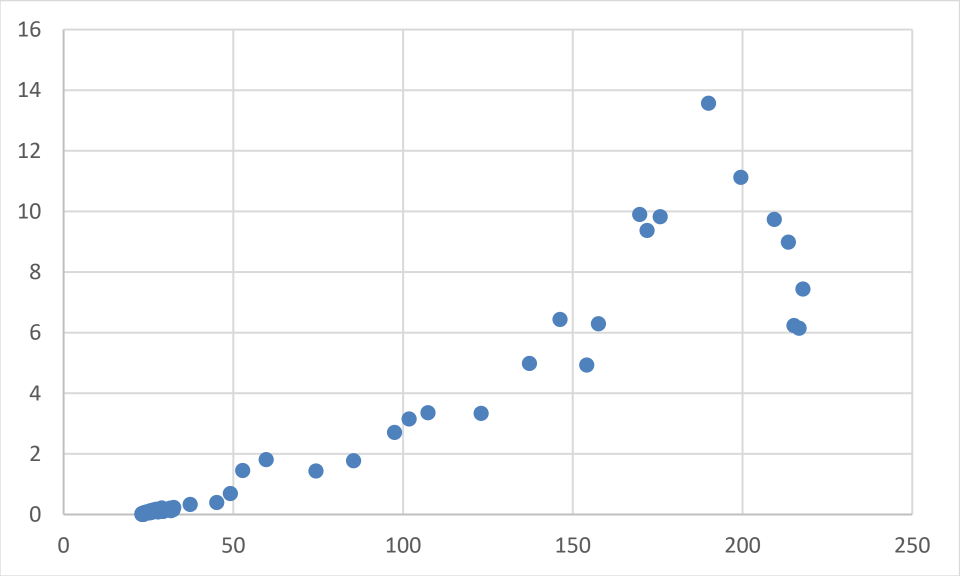


Figure 9-10: Temperature rate curve for test JDP7, NMC external short circuit

9.1.2 LFP cylindrical cells

Two sizes of LFP cylindrical cells where tested, one 26650 type of 2.5 Ah and one 18650 type of 1.5 Ah. The battery surface temperatures for all the tests are shown in Figure 9-11, Figure 9-12, Figure 9-13, Figure 9-15, Figure 9-17, Figure 9-19 and Figure 9-21. The heat raise curves are shown in Figure 9-14, Figure 9-16, Figure 9-18, Figure 9-20 and Figure 9-22. As seen from the figures and from the key data provided in Table 9-2, the temperature characteristics for these cells differs a lot from the NMC pouch cells in terms of max temperature and temperature rise.

For the 2.5 Ah type, the point of thermal runaway cannot be identified based at the surface temperature, since it has a steady growth when exposed for external heat. No visual combustion was observed, and the temperature increase rate is also very low compared to the NMC pouch cell. From the temperature plots it seems that no of the cells reached stage 3 in the thermal runaway process.

The onset of the thermal runaway was easier to identify for the 1.5 Ah cells. In Figure 9-17 and Figure 9-19 a dip in the temperature rise can be seen when the cell starts to vent, followed by an increase in the temperature rise when the thermal runaway is started. Note however that the temperature increase at that point is very low in all cases compared to the NMC pouch cells. Since the data was corrupted at the time the cell went into thermal runaway in the 100% SOC test case, a temperature estimation has been done based on two measurements at the cell surface, as shown in Figure 9-21. This is consistent with the results presented by Golubkov /8/. It is also debatable whether the 18650 cells with 75% SOC reached step 3. It seems that the 18650 cell with 50% and 100% SOC reached the step 3 with a max temperature increase of 3.37°C/sec and 5.06°C/sec respectively.

Table 9-2 – Characteristics for identification of thermal runaway LFP cylindrical cells

Cell type / size	Failure mode	Max Temp (°C)	Max Temp increase rate (°C/second)	Temperature at onset (approximate)
26650 / 2.5 Ah	Overheat at 50% SOC	243	0.57	Not able to identify based at temperature
	Overheat at 75% SOC	201	0.60	Not able to identify based at temperature
	Overheat at 100% SOC	170	0.14	Not able to identify based at temperature
	Overcharge	162	0.93	75
18650 / 1.5 Ah	Overheat at 50% SOC	330	3.37	233
	Overheat at 75% SOC	298	0.60	210
	Overheat at 100% SOC	383 (estimated)	5.06	225

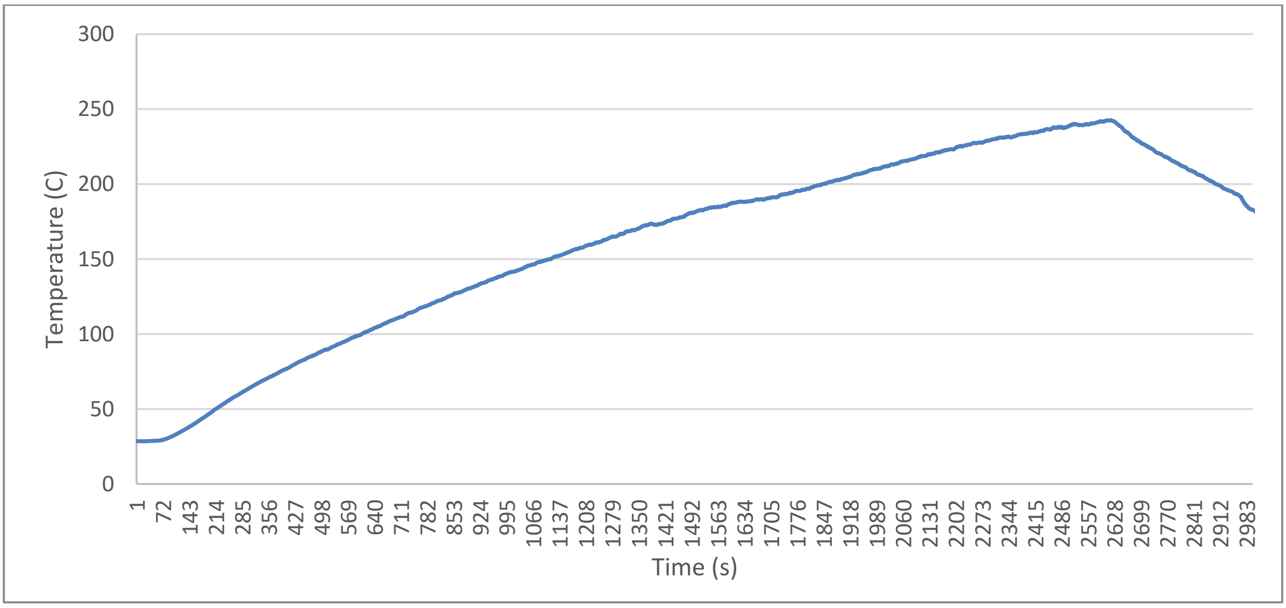


Figure 9-11: Battery surface temperature for 2.5 LFP 50% SOC with overheat

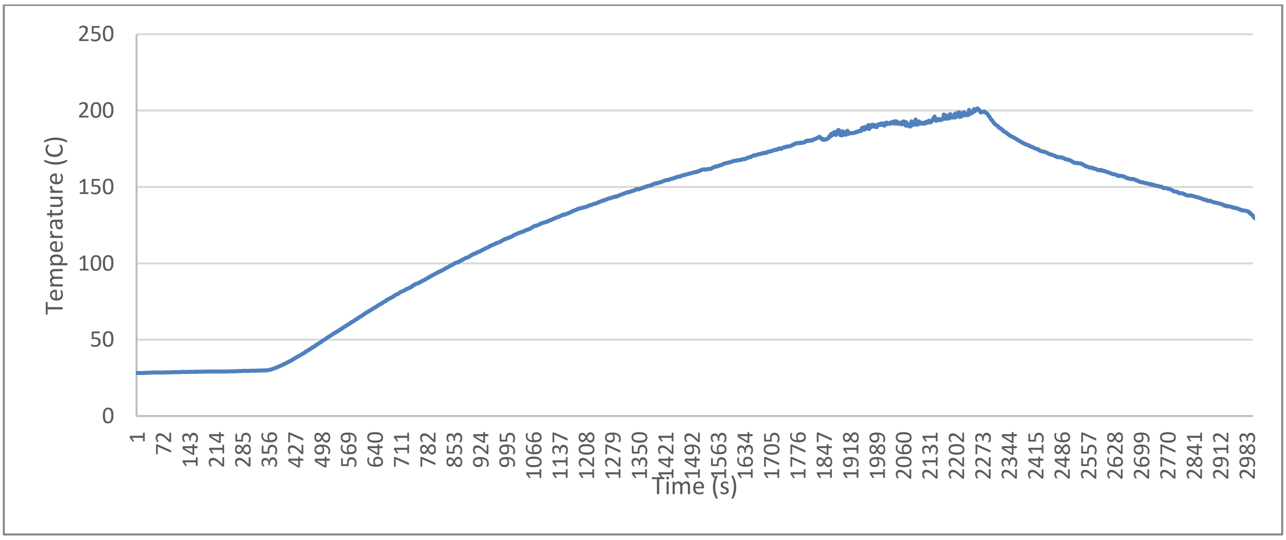


Figure 9-12: Battery surface temperature for 2.5 LFP 75% SOC with overheat

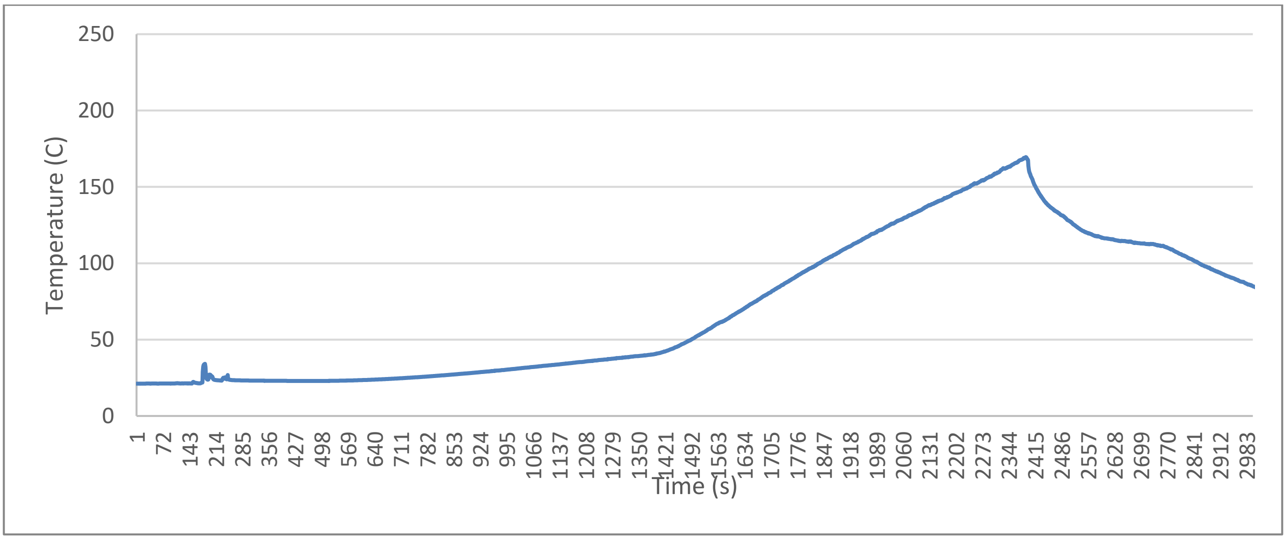


Figure 9-13: Battery surface temperature for 2.5 LFP 100% SOC with overheat

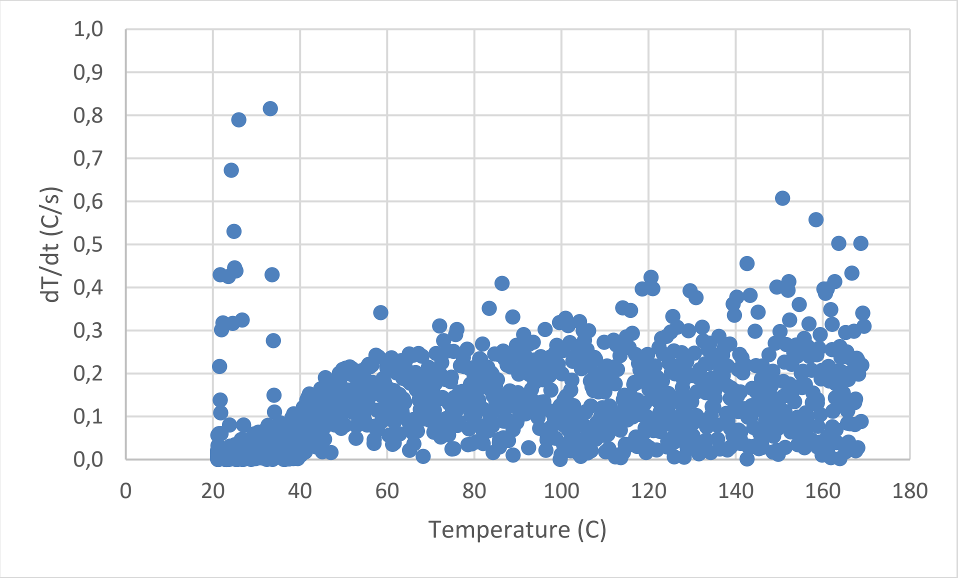


Figure 9-14: Temperature rate curve for test A3, LFP 2.5 26650 100% SOC overheat

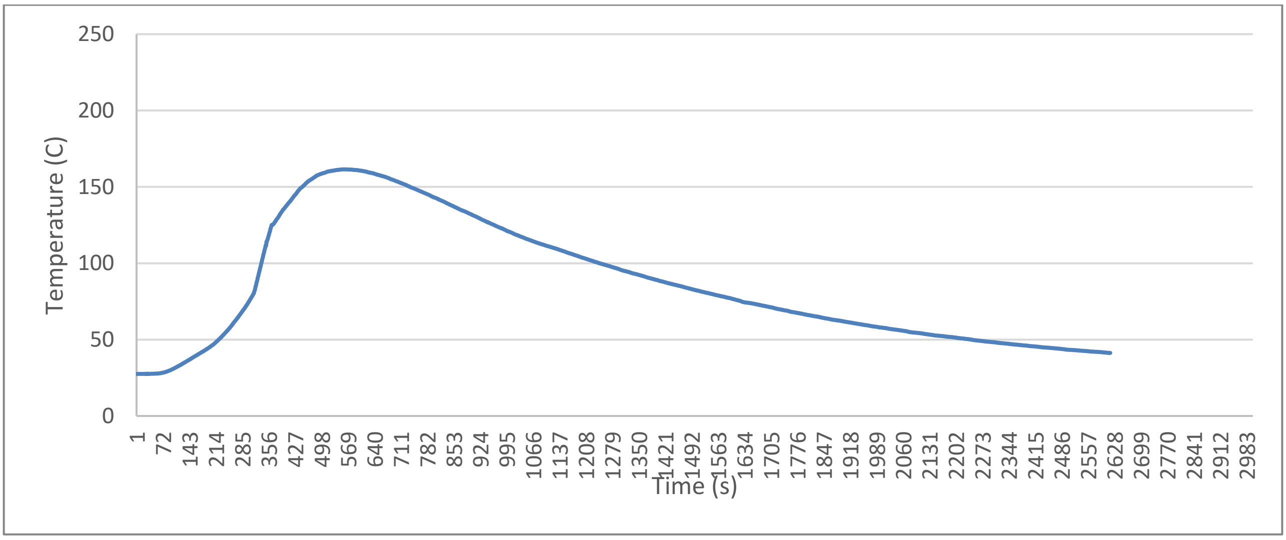


Figure 9-15: Battery surface temperature for 2.5 LFP 100% SOC with overcharge

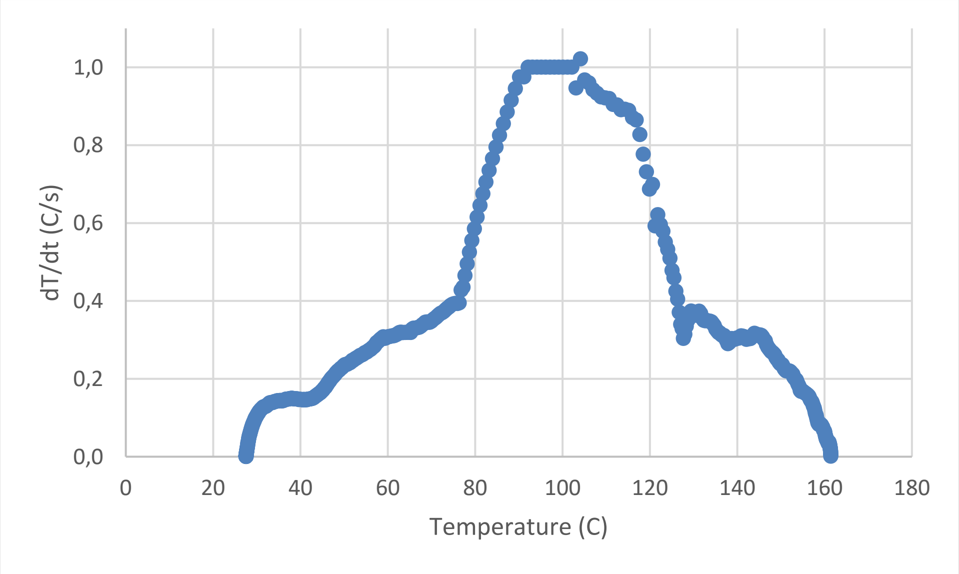


Figure 9-16: Temperature rate curve for test A4, LFP 2.5Ah 26650 overcharge

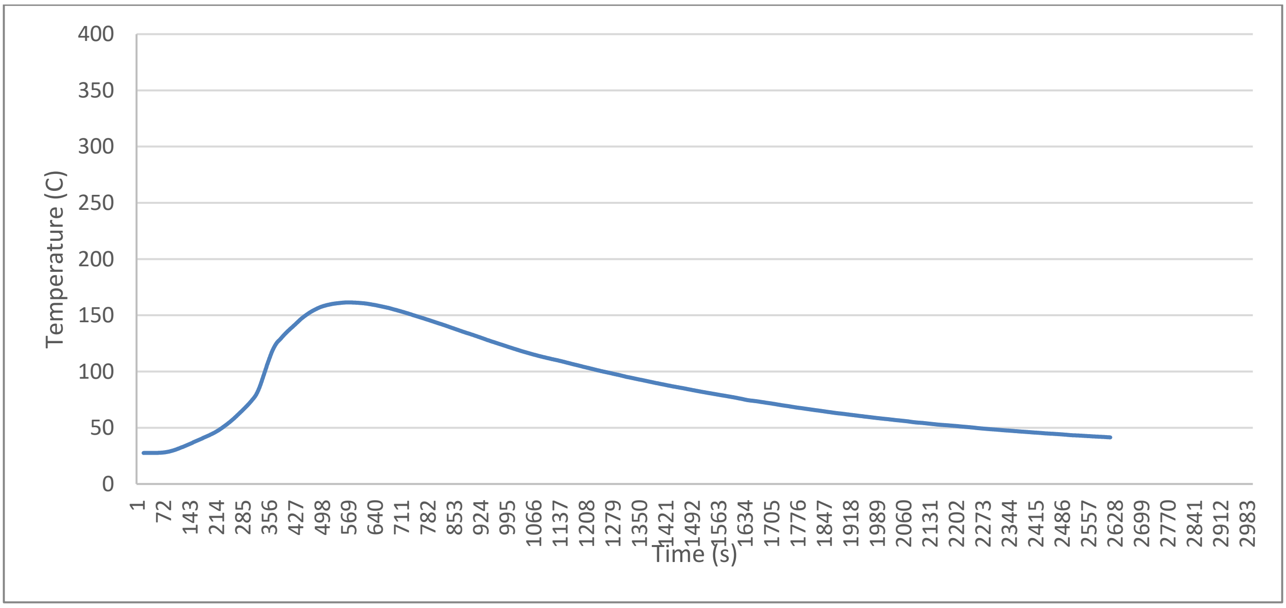


Figure 9-17: Battery surface temperature for 1.5 LFP 50% SOC with overheat

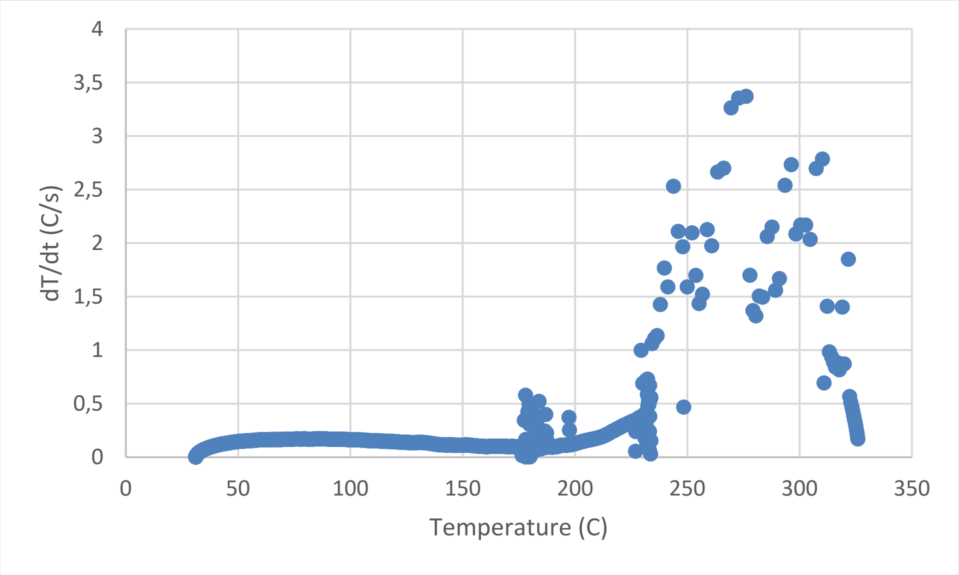


Figure 9-18: Temperature rate curve for test B1, LFP 1.5Ah 18650 50% SOC overheat

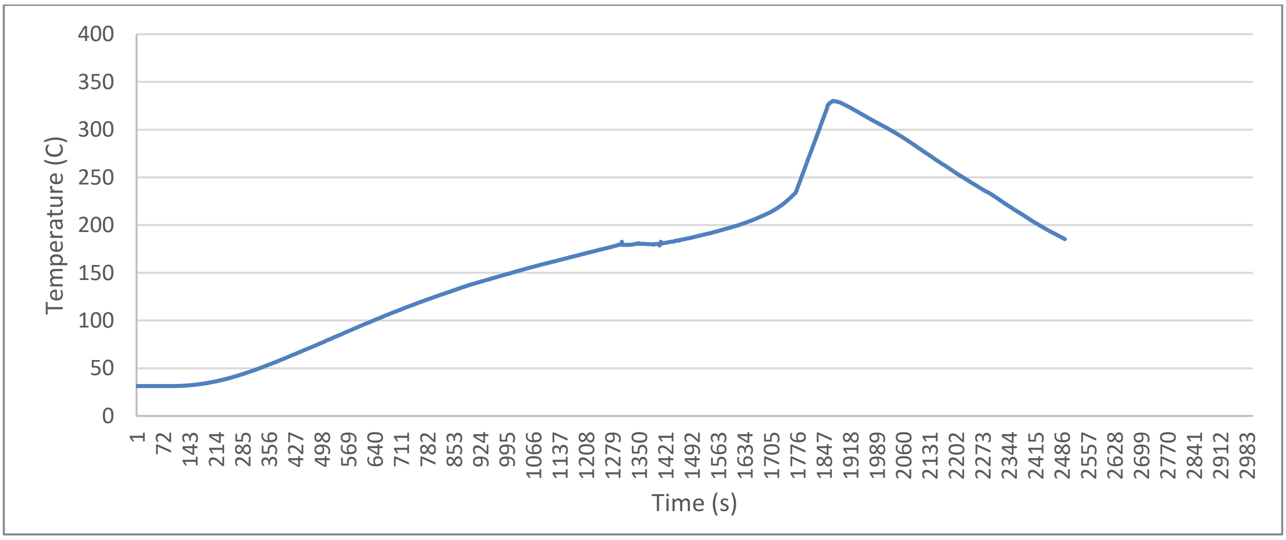


Figure 9-19: Battery surface temperature for 1.5 LFP 75% SOC with overheat

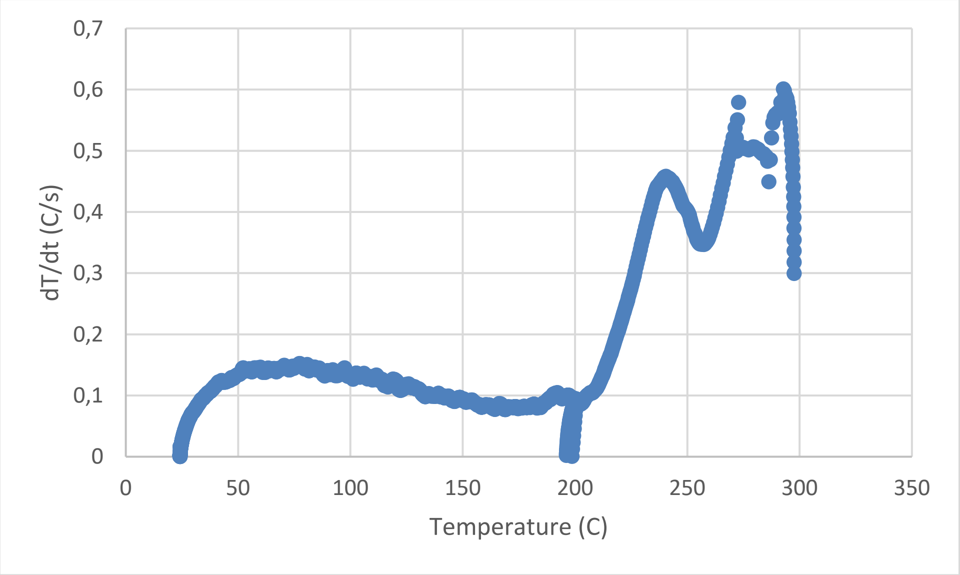


Figure 9-20: Temperature rate curve for test B2, LFP 1.5Ah 18650 75% SOC overheat

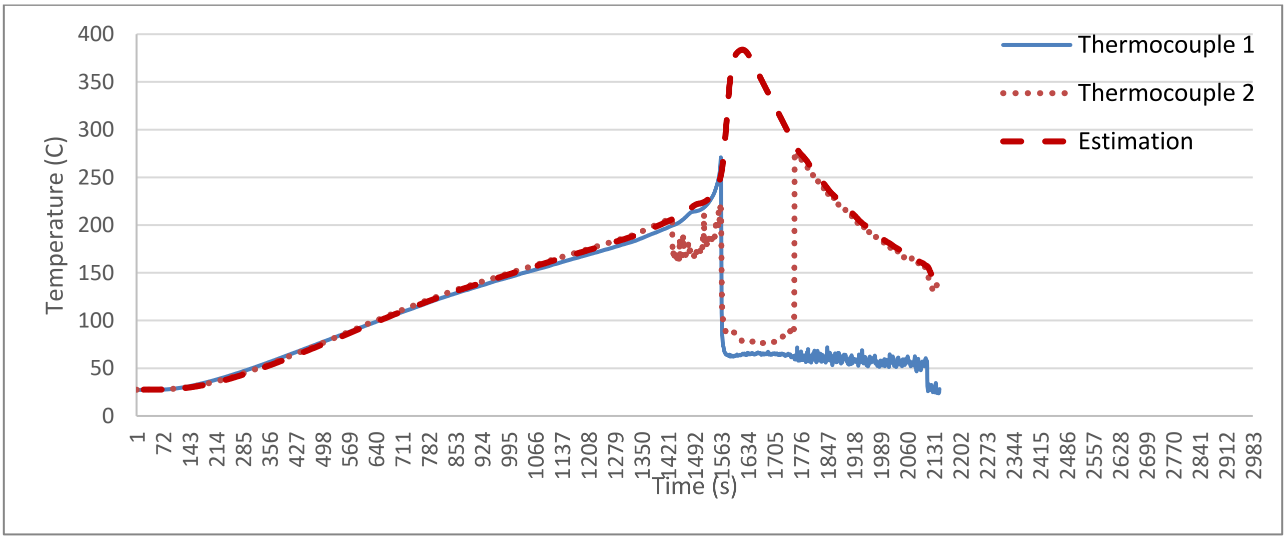


Figure 9-21: Battery surface temperature for 1.5 LFP 100% SOC with overheat

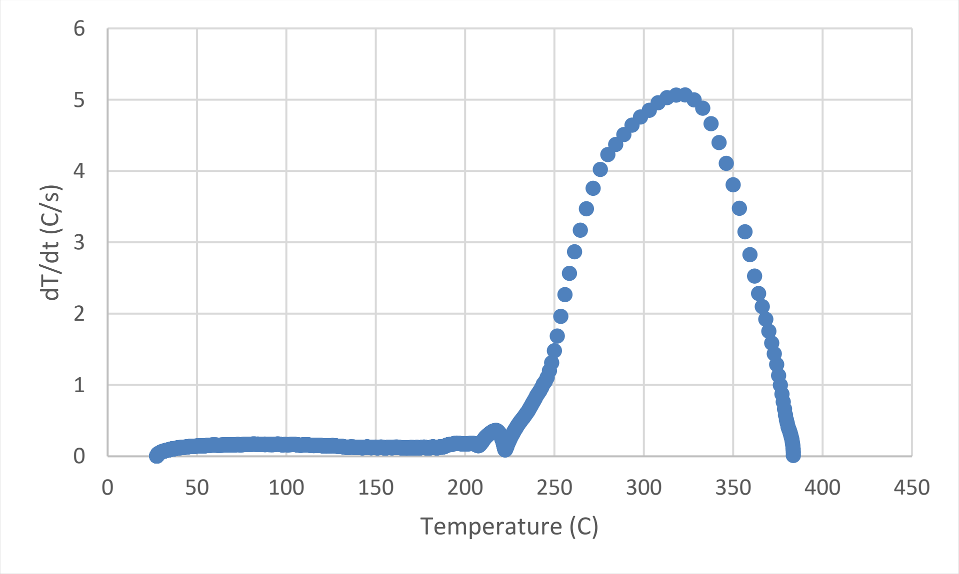


Figure 9-22: Estimated temperature rate curve for test B1, LFP 1.5Ah 18650 100% SOC overheat

9.2 Literature review of thermal runaway heat release profiles

The temperature rates for NMC and LFP cells reported in the literature is discussed below. The results in presented by Golubkov /8/, shown in Figure 9-23, are quite consistent with the test results in this report. The results by Lei /9/, shown in Figure 9-24, indicates that stage 3 in the thermal runaway process was not reached for the LFP 18650 cells with only a max temperature increase of 0.05 °C/sec. Ouyang /7/, shown in Figure 9-25, reports a similar temperature increase rate between the tested 18650 NCM and LFP cells. Note that the LFP cells are charged to 4.2-5.0V when overheated. Normally the nominal voltage is 3.6V at 100% SOC. This can explain the more aggressive behavior of these LFP cells compared to the tests performed in this study and the reported results in the two other reports.

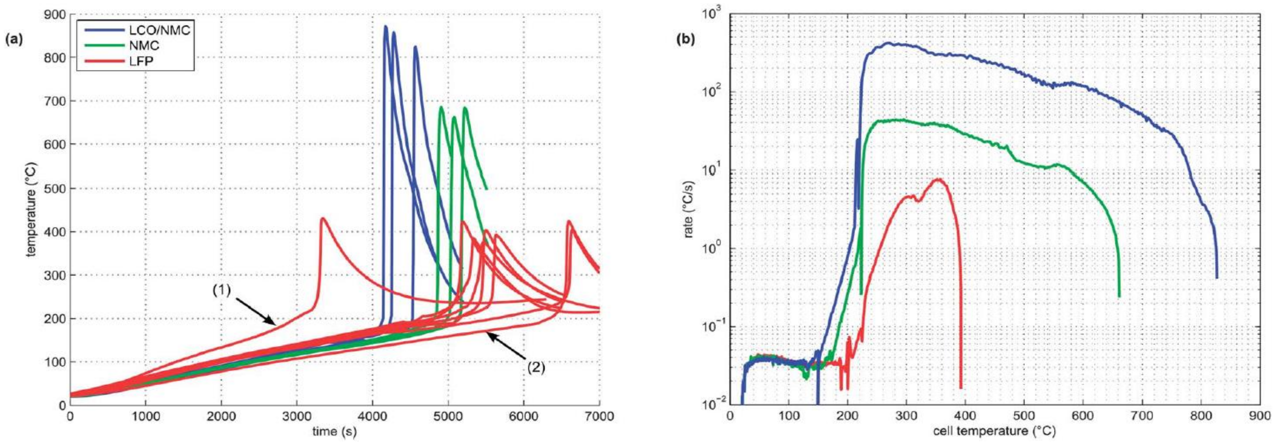


Figure 9-23: (a) Overview of the time–temperature profiles for the cells tested in /8/. (b) Temperature rates from three representative experiments in /8/

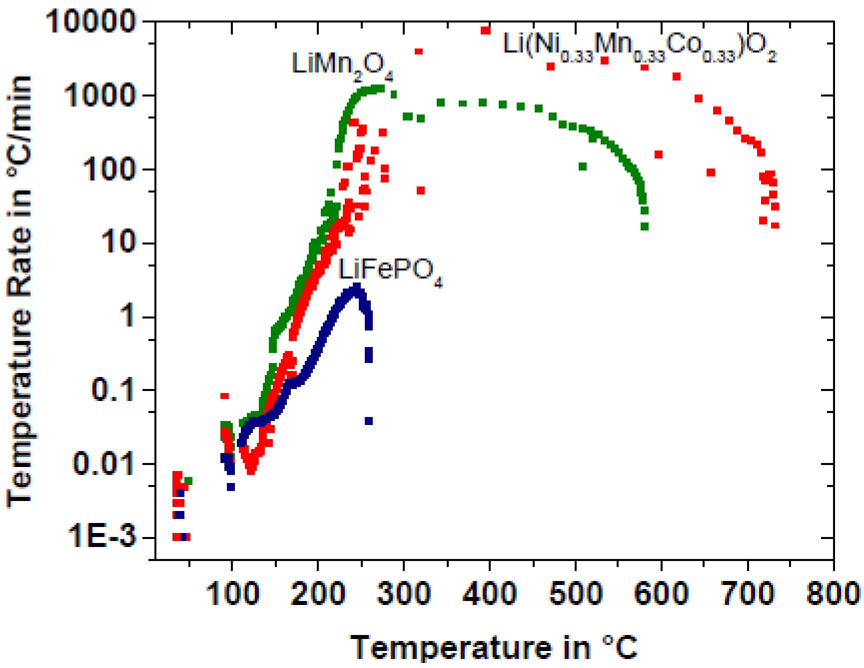


Figure 9-24: Temperature rates for the cells tested in /9/

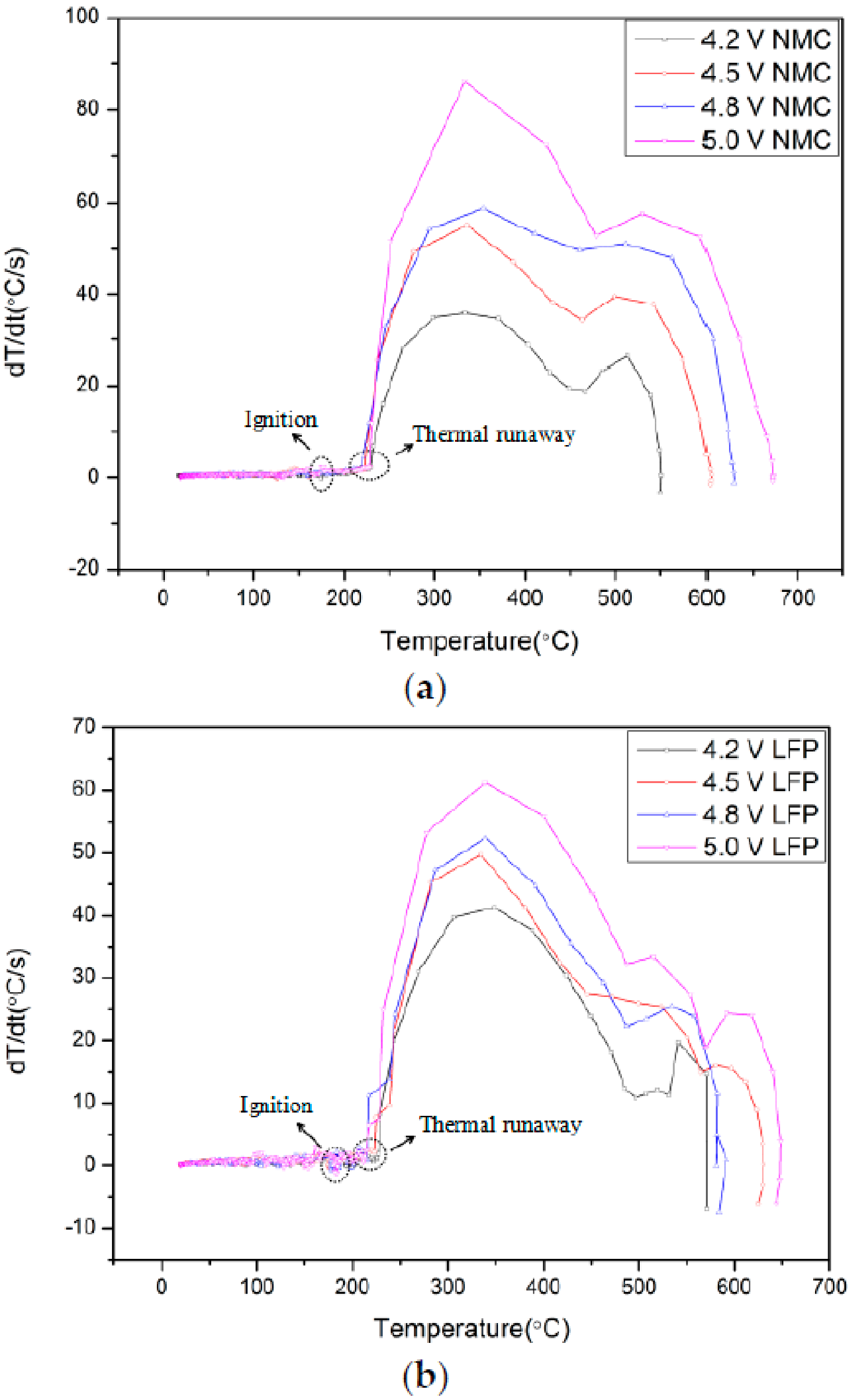


Figure 9-25: Temperature rate curves for the cells tested in /7/.

9.3 Thermal runaway identification discussion

Based at the observed temperature increase rate, the NMC cells all reached step 3 in the thermal runaway process. All tests that had external combustion had a max temperature at 475°C or above, together with a temperature rise of approximately 25°C/ sec. Visual combustion was not observed for 50% overheat and short circuit. In these tests the max temperature observed was 417°C.

Based at the observed test results and the literature review, it seems that none of the 2.5 Ah 26650 went into thermal runaway. The temperature increase rate more or less flat during the test period.

The LFP cells are generally harder to force into thermal runaway compared to the NMC cells. The temperature increase rate is also lower for these cells. Only the 18650 cell with 50% SOC and the 18650 cell with 100% SOC exceeded 1.7°C/sec, which indicates that step 3 in the thermal runaway process has been reached /9/.

From the test results, it seems that the ability to monitor thermal runaway, will vary based on cell packaging. For cylindrical cells, packaging is often more robust, and failures will thus be more delayed and then also more drastically as more temperature and pressure nominally has been built up (for instance a very quick pressure release or pop) after building up, rather than a clear thermal runaway. Further, in cases of fire and distinct thermal runaway, high temperatures are concentrated at the ends where gasses are released, often visually representing specific jet flames.

Based at the temperature increase rate reported in the literature and the tests performed in this study, a temperature increase rate above 10 °C/sec together with a max temperature above 450°C seems to be sufficient to identify the onset point for a thermal runaway with visual combustion for NMC pouch cells. No combustion can be observed at the same temperature increase rates, but with lower maximum temperatures.

For the LFP cells, the increase rate is lower. It should be possible to force these cells into a stage 3 thermal runaway, but this is harder for these cells. Based at the reported literature and the tests performed in this study, a temperature increases of 4 °C/sec seems to be sufficient to identify the onset point for stage 3 of the thermal runaway process for the LFP cells. The chance of achieving this increase with the SOC, and it might be necessary to charge the LFP battery beyond 100% SOC to provoke visual combustion.

9.4 Main Conclusions

Main Conclusions

1. The LFP cells are generally harder to force into thermal runaway compared to the NMC cells. The temperature increase rate is also lower for these cells.
2. For cylindrical cells, packaging is often more robust, and failures will thus be more delayed. Temperature and pressure nominally build up and is followed by a quick pressure release or pop, rather than a clear thermal runaway. High temperatures are concentrated at the ends where gasses are released, often visually representing specific jet flames for cylindrical cells.
3. For NMC pouch cells, a temperature increase rate above 10 °C/sec together with a max temperature above 450°C seems to be sufficient to identify the onset point for a thermal runaway with visual combustion.
4. For the LFP cells, a temperature increases of 4 °C/sec seems to be sufficient to identify the onset point the thermal runaway stage 3.
5. It might be necessary to charge the LFP cells beyond 100% SOC to provoke a thermal runaway with visual combustion.

10 RISKS ACOSIATED WITH WATER BASED FIRE SUPPERSION

10.1 Discussion

When water-based fire suppression system is used – will the water conductivity result in heat generation in neighboring modules and hydrogen gas formation through electrolysis?

Testing of lithium-ion battery modules being submerged in water has not been performed in this project, but was conducted as a part of Consolidated Edison project /3/ and the discussion below stems from those results as well as other test results that have been conducted or observed by the JDP members.

Experiments have included submersion of batteries on fire as well as new battery modules. In cases for batteries on fire, the act of submerging helped significantly to reduce temperatures – and thus reduced the risk of propagation to new/additional cells. In addition, the release of CO that was occurring before submersion continued for over 30 minutes but did not appear to increase in rate. New batteries were visibly damaged and corroded, and temperatures raised from 22 to over 70 °C but there were no signs of any cells venting or exploding.

Thus, it is generally suggested that water will not escalate the failure mode of a battery system. These are results for fully submerged battery modules with voltages in the range of 24-48V.

Cases where water build up in the room, submerging high voltage contactors, breakers or other electrical components at string level, the risks for short circuits and H2 production by electrolysis needs to be evaluated.

To avoid water inside the battery modules when water based total flooding systems are used, battery modules with IP44 is recommended. Most notably, when submerged or extinguished batteries can produce a severely alkaline solution in the water used, climbing to pH 10-11. Other solutions gradually became slightly acidic (pH 6), where the most severely burned batteries produce the most basic solution. This is considered to be the primary risk or consideration with regard to the use of water-based suppression measures.

10.2 Main Conclusions

Main Conclusions
1. Water will not escalate the failure mode of fully submerged battery modules with voltages in the range of 24-48V. 2. Cases where local water build up in the room, submerging high voltage switchgears or components at string level, the risks for short circuits and hydrogen gas production by electrolysis needs to be evaluated. 3. To avoid water inside the battery modules when water based total flooding systems are used, battery modules with IP44 is recommended. 4. The water can become severely alkaline, climbing to pH 10-11. Some solutions gradually became slightly acidic (pH 6), where the most severely burned batteries produce the most basic solution.

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