Fire protection for Li-ion battery energy storage systems

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1 Introduction

Since their market launch in the early 1990s, lithium-ion batteries have found their way into a wide variety of applications including stationary energy storage in smart grids. This is an application that is predicted to grow rapidly, not least because of the increasing expansion of renewable energy generation and the associated decentralization and stabilization requirements of such energy sources.

Li-ion battery storage systems cover a large range of applications from generation to consumption, helping to stabilize frequency and voltage, and balance variations in supply and demand.

Li-ion batteries combine high energy materials with highly flammable electrolytes. Early and reliable fire detection is therefore a must when designing fire protection systems for Li-ion battery systems. Rapid extinguishing is also essential and can be ensured by the use of automated extinguishing systems using an appropriate agent.

This paper discusses the development of a managed-risk fire protection concept for stationary Li-ion battery energy storage systems.

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3 Summary

The fire hazard presented by Li-ion batteries is currently being widely discussed. There are many views, but coordinated or ready-to-use protection concepts are not yet available, a fact which ultimately led to our investigations. As currently available Li-ion battery systems differ widely in price, storage density and other technical specifications, in addition to the degree of intrinsic safety, no single fire protection concept can be suitable for all Li-ion battery applications. To develop an appropriate solution for the specific application of managed stationary storage systems it was necessary to conduct a series of experiments and tests. Our work has shown that Li-ion battery energy storage systems can be a controllable application when it comes to fire protection.

Figure 1: Integrated fire protection system

It could be shown that the key to fulfilling the fire protection requirements lies in the combination of earliest possible detection, e.g. using FDA241 air sampling detectors, together with the Sinorix N_2 extinguishing system.

Very early discharge of the extinguishing agent both prevents the creation of large quantities of explosive electrolyte-oxygen mixtures and deters an initial thermal runaway. Propagation of such runaways is stopped, secondary fires are prevented and long-lasting inertisation prevents any reignition.

With the right products, stationary Li-ion battery energy storage systems can become a manageable risk.

4 Li-ion battery storage systems

This paper deals solely with the issue of fire protection for stationary Li-ion battery energy storage systems.

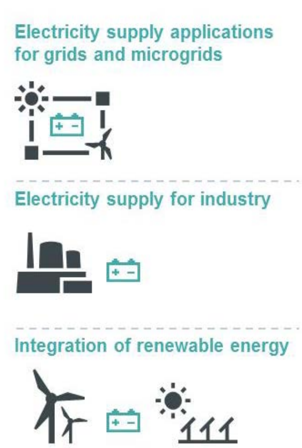


Figure 2: ESS applications

Li-ion battery energy storage systems cover a large range of applications. From generation to consumption, ESS (Energy Storage Systems) help to optimize asset performance by stabilizing frequency and voltage, and balancing variations between supply and demand.

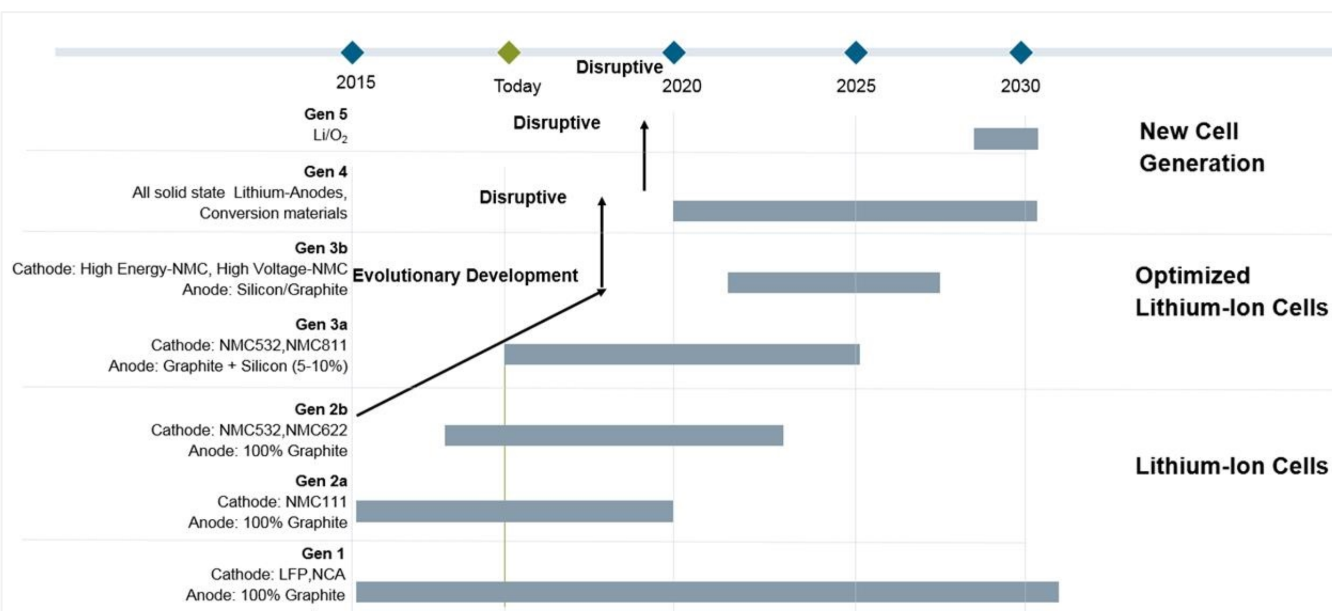
In the majority of cases Li-Ion batteries combine high energy materials with highly flammable electrolytes.

That is why early and reliable fire detection is a must when designing fire protection systems for Li-ion battery systems. In addition, any embryo fire must be quickly extinguished using automated, targeted extinguishing systems to prevent a large number of cells, batteries or battery modules incurring thermal runaway and catching fire.

Li-ion battery energy storage systems are an application with a clear need for comprehensive fire protection.

5 Li-ion battery technology development

The figure below shows the expected battery chemistry development. It is expected that the 3rd generation batteries used today and considered here (e.g. lithium-nickel-manganese-cobalt-oxide) will still be in wide use until the middle of the next decade.



Source: German Academy of Science and Engineering, Christopher Betzin Siemens EM TI, modified

Figure 3: Battery development

6 Battery management system

The most important electronic component of a storage system is the battery management system (BMS), which, in addition to controlling and monitoring the state of charge at cell and system level, also performs temperature management during charging and discharging.

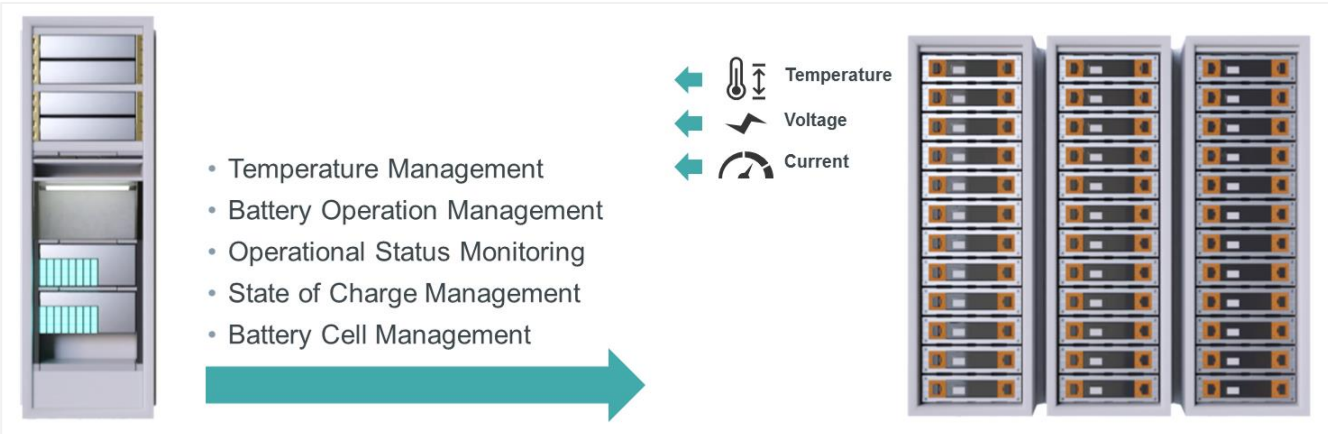


Figure 4: Battery management system

Efficient battery management systems keep the cells in the intended safe operating range, so that over-charging and over-discharging are avoided. Thermal runaways can only be expected under extreme external influences such as high temperatures (due to fire) or mechanical deformation with resulting separator defect, or subsequent to an internal short-circuit (e.g. as a result of dendride formation due to undetected aging).

7 Fire hazards in Li-ion battery storage systems

7.1 Risk analysis and risk assessment

Risk analysis and risk assessment form the basis for the development of viable fire protection concepts, i.e. answering the following questions:

- What are the **fire risks?**
- What is their **probability of occurrence**?
- What is the **expected impact** in each case?

7.2 Electrical fire

Statistics of the GDV (Gesamtverband der Deutschen Versicherungswirtschaft) show that in around ¼ of all cases, electrical fires are the cause of major losses and the main cause of fires in industrial companies. These risks alone require both reliable detection and automatic extinguishing systems for safe operation.

Electrical fires can be detected at an early stage and extinguished safely with automatic gaseous extinguishing systems. Electrical fires are therefore considered to be a manageable standard risk and will not be considered any further in the following discussion.

What remains is the fire risk arising from the Li-ion batteries themselves. Only if this risk is understood can the protection goals be defined and concepts for achieving these goals be developed.

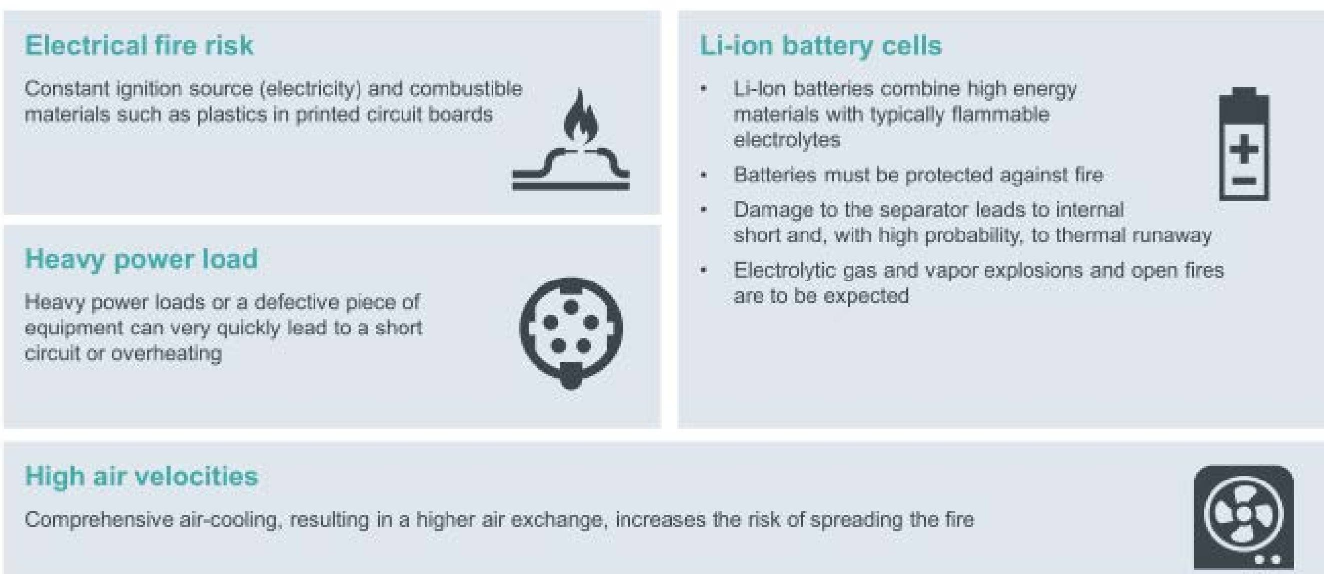


Figure 5: Fire risks in Li-ion battery energy storage systems

7.3 The risks inherent in Li-ion batteries

To understand the inherent fire risk of Lithium batteries and the associated storage systems we have to understand the battery technology.

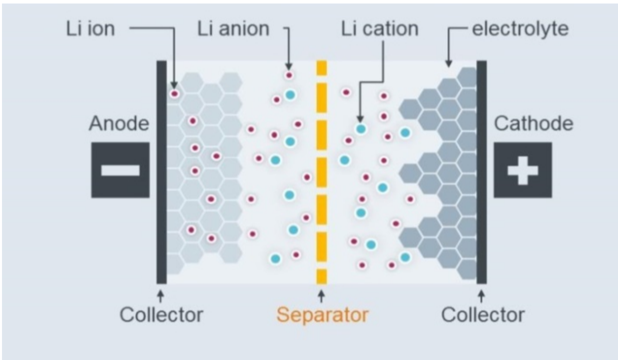


Figure 6: Li-ion battery structure

At the heart of the battery system are the electrochemical battery cells. Each Li-ion cell consists of two electrodes, the negative electrode (anode) and the positive electrode (cathode).

The electrodes consist of a collector and an active material applied to it. In between the electrodes is the ion-conducting, typically flammable electrolyte, which acts as a mediator of the processes in the cell and the separator that ensures the electrical separation of the electrodes.

As Li-ion batteries combine high energy materials with flammable electrolytes, any damage to the separator (caused either mechanically or by high temperatures) will lead to an internal short-circuit with the high probability of thermal runaway. Safety-critical situations are almost inevitable.

7.4 Fire hazard thermal runaway

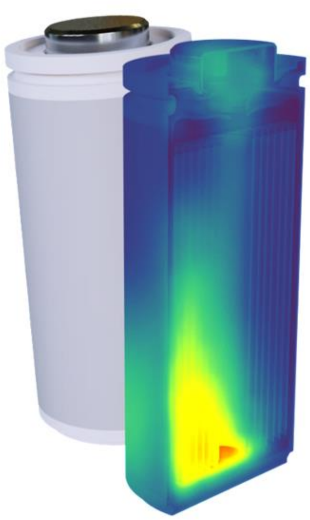


Figure 7: Thermal runaway

The filigree design, the ever increasing energy density and aging of the battery are the causes of the danger.

If external mechanical forces are excluded, then a fire caused by battery cells themselves is always due to age-related damage to the separator and a subsequent internal short-circuit. The resulting temperature increase causes the (usually highly flammable) electrolyte to start evaporating. As a consequence, the internal pressure within the cell will continue to build up until electrolyte vapor is released either via a relief valve or by the bursting of the shell.

Without countermeasures, an explosive gas-air mixture will be generated: only an ignition source is needed and the result will be an explosion. If the heating is not stopped, thermal runaway will occur.

8 Development of the fire protection concept

Having identified the fire risks, we can now turn our attention to defining a protection concept. The detection and control of ordinary electrical fires can be regarded as adequately solved, so the questions remaining are:

- How can we detect and extinguish a battery cell fire?
- How does the development of a thermal runaway become noticeable?
- How and when can we detect a thermal runaway?
- Can we stop the propagation of the runaway from cell to cell?

To be able to answer these questions we prepared two test set-ups.

8.1 Fire detection and extinguishing testing

8.1.1 Characteristics of thermal runaway development

Figure 8: Principle structure of the thermal runaway detection test setup

8.1.1.1 Test setup

- Heating plate mounted in battery cabinet
- Placement of the test battery directly on the heating plate
- Aspiration pipe and sampling point in the battery cabinet
- Aspiration pipe with filter
- ASD FDA241

8.1.1.2 Test sequence

- Continuous heating of the heating plate from room temperature (20°C) to 400°C in 450 s.
- Continuous air sampling and signal analysis with FDA241 in parameter setting 1

In a number of experiments with different battery chemistries we have gained the following insights.

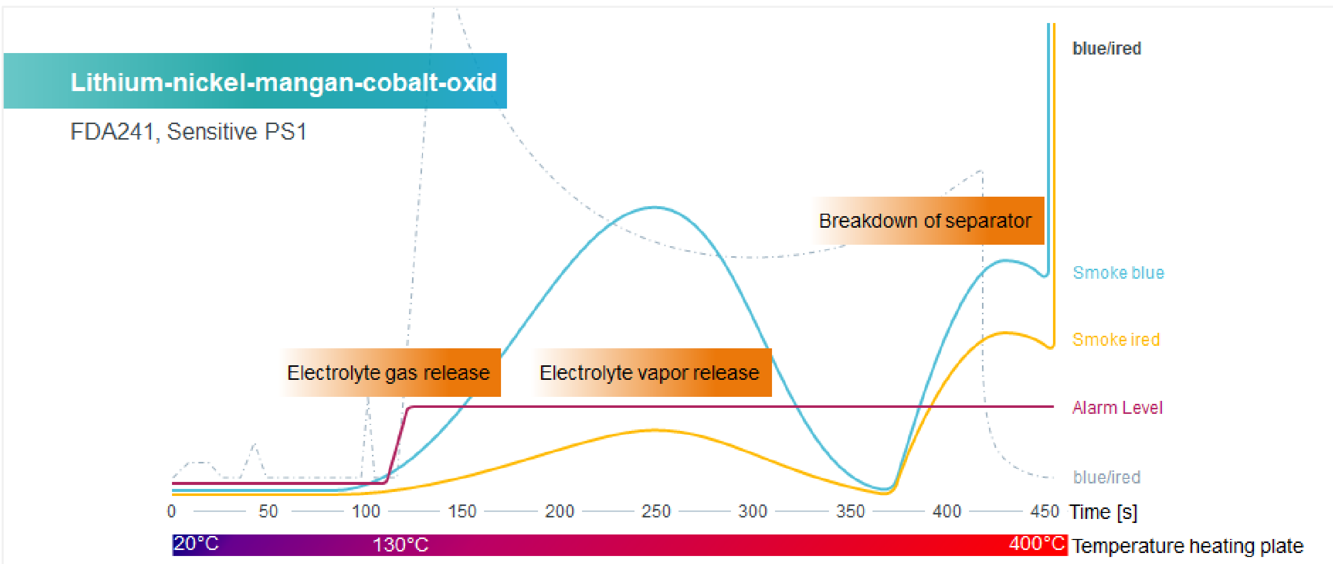


Figure 9: FDA241 sensor signals during thermal runaway development

Observing the process with our ASD system we saw the IR sensor signal remaining quiet for almost 100 s [T≈ 130°C], then slightly increasing after 125 s, followed by a decrease of the signal [electrolytes having largely evaporated], only to increase rapidly again after about 360 s and to thermal break after 450 s [breakdown of separator].

The signal of the blue LED - sensitive for small particles from 50 micrometers - is basically the same, but more pronounced.

We can recognize three phases:

i. invisible electrolyte gas release
ii. visible electrolyte vapor release
iii. separator breakdown

In most test cases the electrical breakthrough of the separator was strong enough to ignite the flammable electrolyte gas-vapor-air mixture, which in normal atmosphere caused an explosion-like combustion.

This process is typical for all batteries that we tested. Tested cell chemistries were lithium-cobalt-oxide, lithium-nickel-manganese-cobalt-oxide and lithium-manganese oxide.

Observing the ratio of the blue and IR sensor signals and the alarm levels derived from them, we see that the ASD FDA241 is already detecting the developing runaway in its early phase of electrolyte gas release.

8.1.2 Propagation of thermal runaway

Based on a large number of documented cases, it is known that if no countermeasures are taken then thermal runaway can propagate from cell to cell throughout a complete battery system causing large-scale fires.

In order to investigate runaway propagation in real cell arrangements, a test setup was built that enabled a thermal runaway to be initiated by creating an internal short-circuit in Cell 1 (Figure 10)

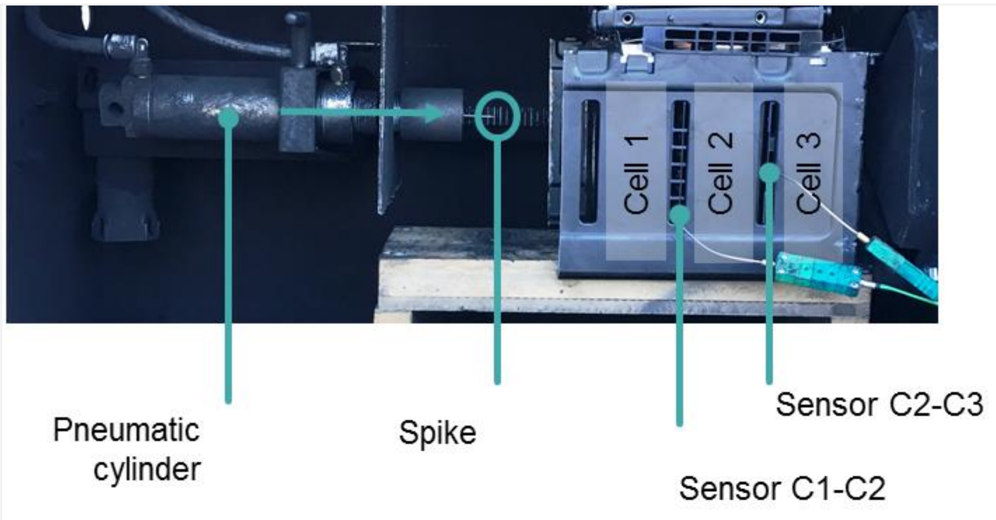


Figure 10: test setup runaway propagation

8.1.2.1 Test setup:

- 3 battery cells in the original battery module housing, directly adjacent to a penetration mechanism consisting of pneumatic cylinder and a spike.
- 2 temperature sensors positioned as follows:
  - one sensor in the space between cells 1 and 2
  - one sensor in the space between cells 2 and 3.

8.1.2.2 Test sequence

Initiation of a thermal runaway by the penetration of cell 1 with a metal spike (thus creating a cell-internal short circuit)

a) at 21.0% oxygen concentration and

b) at 11.3% oxygen concentration

Continuous measurement and recording of the temperature development between the battery cells.

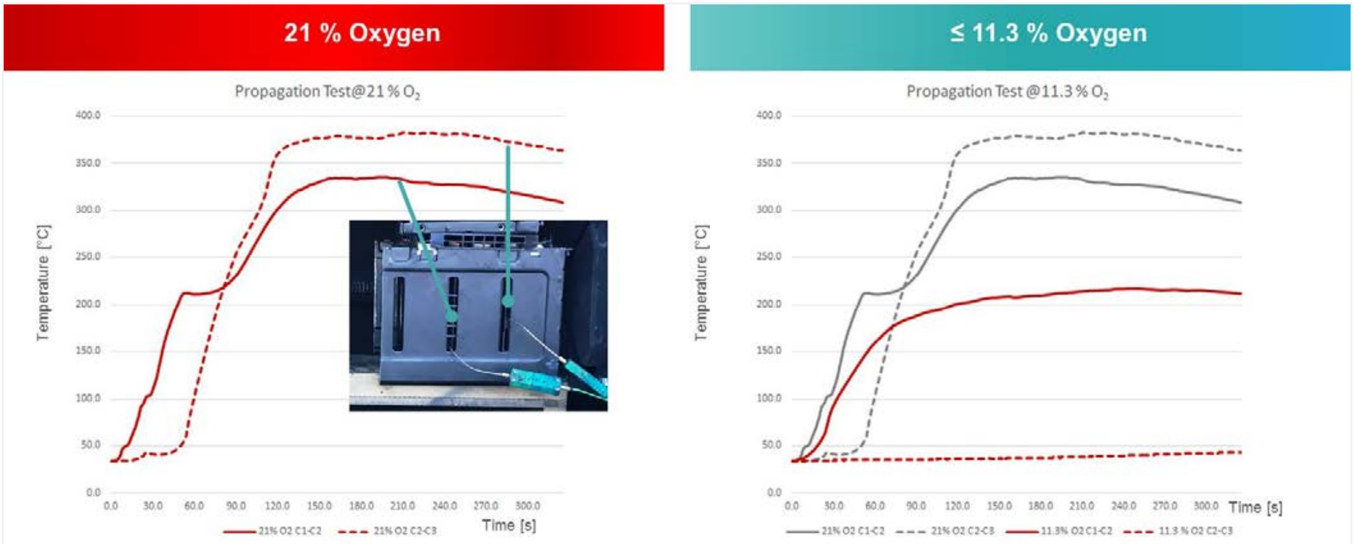


Figure 11: Temperature curves during propagation test

Starting the thermal runaway under normal atmospheric conditions at 21% oxygen concentration we see a rapid temperature rise recorded by the sensor between cell 1 and 2, followed 45 s later by an even more pronounced temperature increase between cell 2 and 3 - a clear indication that cell 2 has also gone into thermal runaway.

Repeating the test under an oxygen-reduced atmosphere[1] of 11.3 % shows a limited temperature rise recorded by the sensor between cells 1 and 2 and no significant temperature increase between cells 2 and 3. This is an indication that cell 2 has not gone into thermal runaway.

Disassembly and examination shows the following picture

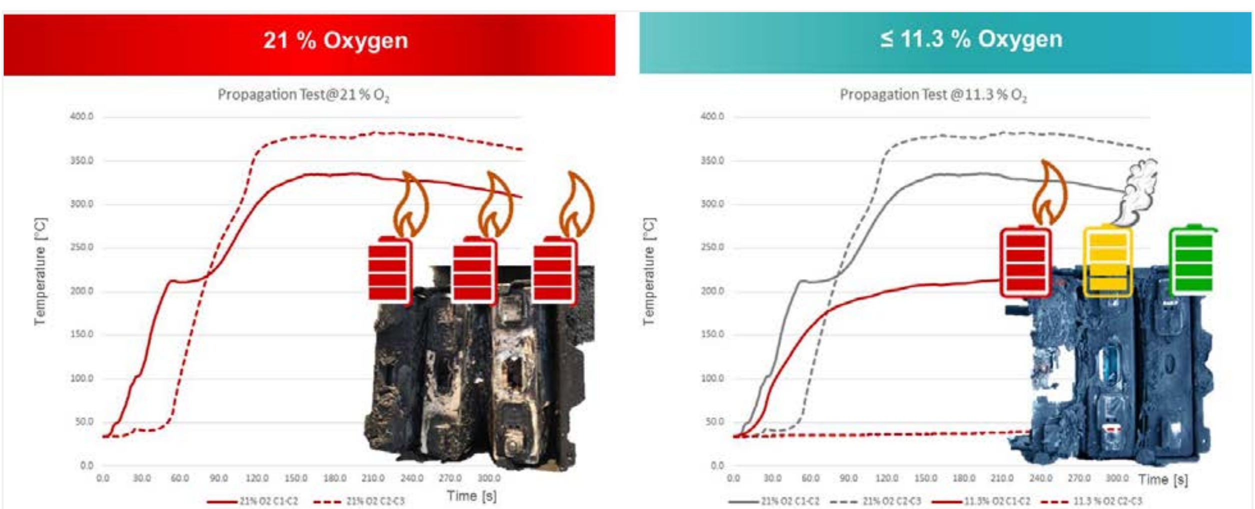


Figure 12: Prevention of thermal runaway propagation

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[1] The remaining oxygen concentration of 11.3 % corresponds to 45.2 % extinguishing agent concentration, the EN15004 agent concentration for nitrogen for class high hazard risks. Depending on the electrolyte used, higher design concentrations may be necessary.

Penetration at 21% oxygen concentration leads to a complete propagation of thermal runaway over all battery cells. Penetration at reduced oxygen atmosphere below 11.3% shows no propagation of thermal runaway. The limited temperature increase at cell 2 leads only to outgassing of the electrolyte, and thermal runaway development stops at phase 2 - electrolyte vapor release. Cell 3 shows no functional limitations apart from heavy exposure to dirt. Cell 3 is completely intact.

These experiments have also been repeated with other battery types, confirming that an initial thermal runaway can be contained by the extinguishing agent atmosphere and that propagation to neighboring cells was prevented in all cases tested.

9 Fire protection targets and fire protection concept

The tests described in the previous section enable us to specify realistic protection objectives for stationary Li-ion battery storage systems.

9.1 Protection targets

i. Battery systems, modules and cells must be protected against external (electrical) fires.
ii. Depending on the battery configuration, cell fires must be limited to individual cells or affected modules. The propagation of thermal runaways beyond the affected module must be prevented.
iii. Secondary fires must be prevented!

A developing thermal runaway must be recognized as early as possible by the detection of electrolyte release and an adequate concentration of the extinguishing agent must be generated before the separator of the first battery cell breaks down.

9.2 Protection concept

9.2.1 Boundary conditions for automatic detection and extinguishing

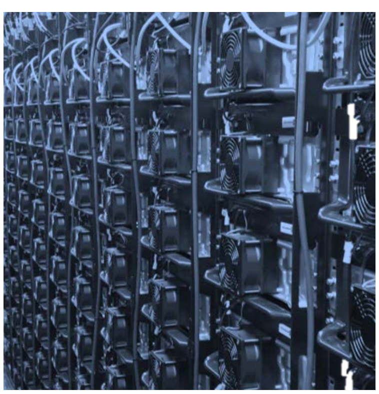

Figure 13: Typical battery module arrangement

The number, arrangement and packing density of the battery modules can have a significant influence on the requirements for fire detection and extinguishing:

i) High power load with high air velocity cooling systems
ii) Covered seat of fire
iii) Long-lasting heat sources
iv) Sensitive technical equipment

9.2.2 Selection of the most suitable detection and extinguishing systems

Detection

A detector is required which can reliably detect both electrical fires and electrolyte gas. This simplifies the selection, because the detection of electrolyte gas requires a detector with the combination of blue and IR sensors. High air velocities also make aspirating smoke detectors necessary. This leads us directly to the FDA241as the most suitable detector for this application.

Extinguishing

Due to the danger of hidden or covered fire sources, only gaseous extinguishing agents would be appropriate. If the production of dangerous extinguishing agent decomposition products is to be avoided and if extended floodings are to be realized, only natural extinguishing gases can be used.If the extinguishing agent itself is not to be dangerous to persons, the use of CO_2 can also be excluded. Nitrogen, argon or mixtures would be suitable, however, since we are dealing with secondary batteries in this application, we can also ignore argon. Consequently the choice almost automatically falls to nitrogen.

9.3 Earliest possible detection with aspirating smoke detection FDA241

Figure 14: FDA241

The FDA241 detects electrolyte vapor early and reliably, due to the patented dual-wavelength optical detection technology.

In accordance with normative requirements, two independent FDA241s are required to trigger the activation of the automated extinguishing system.

The positioning of the aspiration points must take the airflow generated by the air conditioning system into account.

The FDA241 is the ideal solution for early detection of electrical fires.

In addition to controlling the automated extinguishing system, the fire protection system triggers all other necessary control functions.

9.4 Safe and sustainable fire suppression and extinguishing with Sinorix N_2

Figure 15: Sinorix N_2

Sinorix N_2 extinguishing systems extinguish electrical fires, contain initial thermal runaway, stop propagation of thermal runaway and reliably prevent the spread of secondary fires.

Fire extinguishing and suppression systems for this risk are to be

designed as total flooding systems with remaining oxygen concentration below 11.3 % [remaining oxygen concentration of 11.3 % corresponds to 45.2 % extinguishing agent concentration, the EN15004 agent concentration for nitrogen for class high hazard risks] [depending on the electrolyte used, higher extinguishing concentrations may be necessary*].

A holding time of 30 minutes not only allows the fire brigade time to react, but also deters possible delayed runaways.

*Our tests have shown that the lower the remaining oxygen concentration, the better the protection against explosive combustion of electrolyte vapor.

Stationary lithium-ion battery energy storage systems – a manageable fire risk.

10 Appendix

10.1 Detection test results

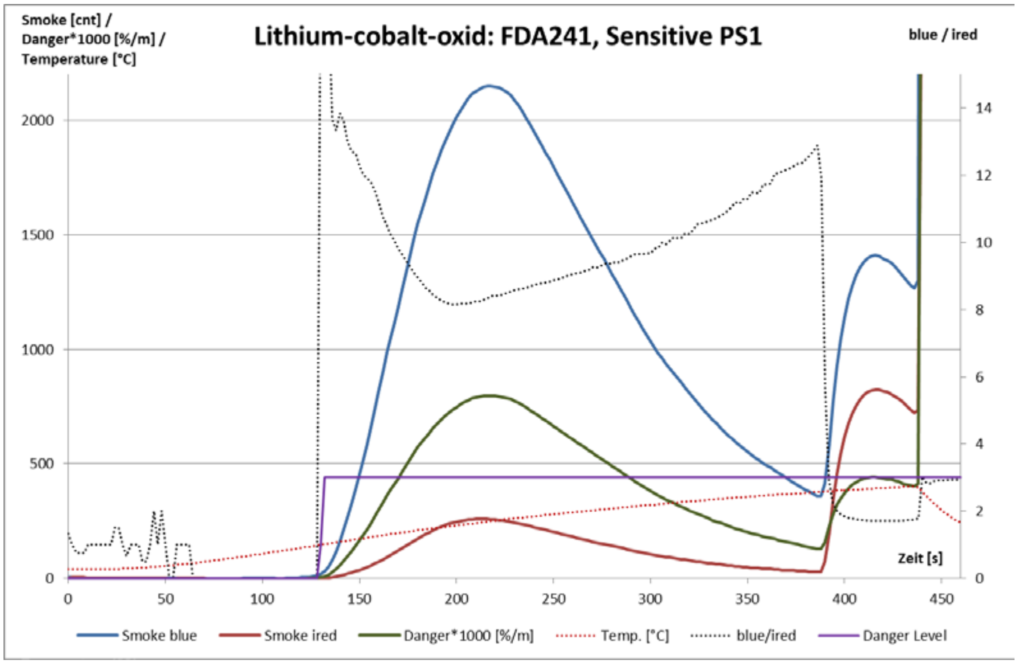

Figure 16: Thermal runaway development LCO cell

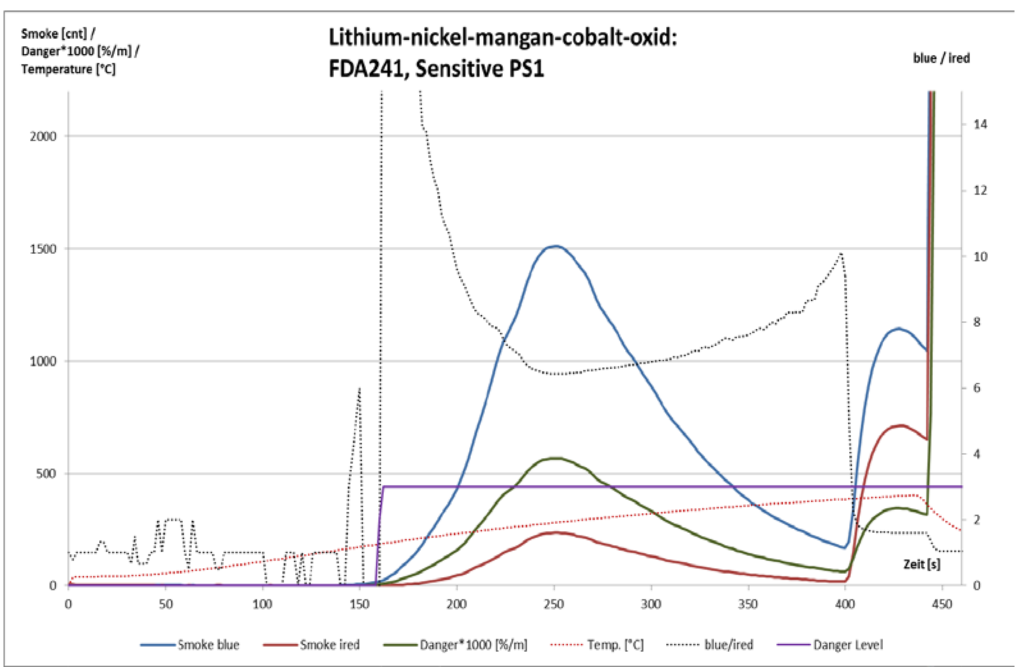

Figure 17: Thermal runaway development NMC cell

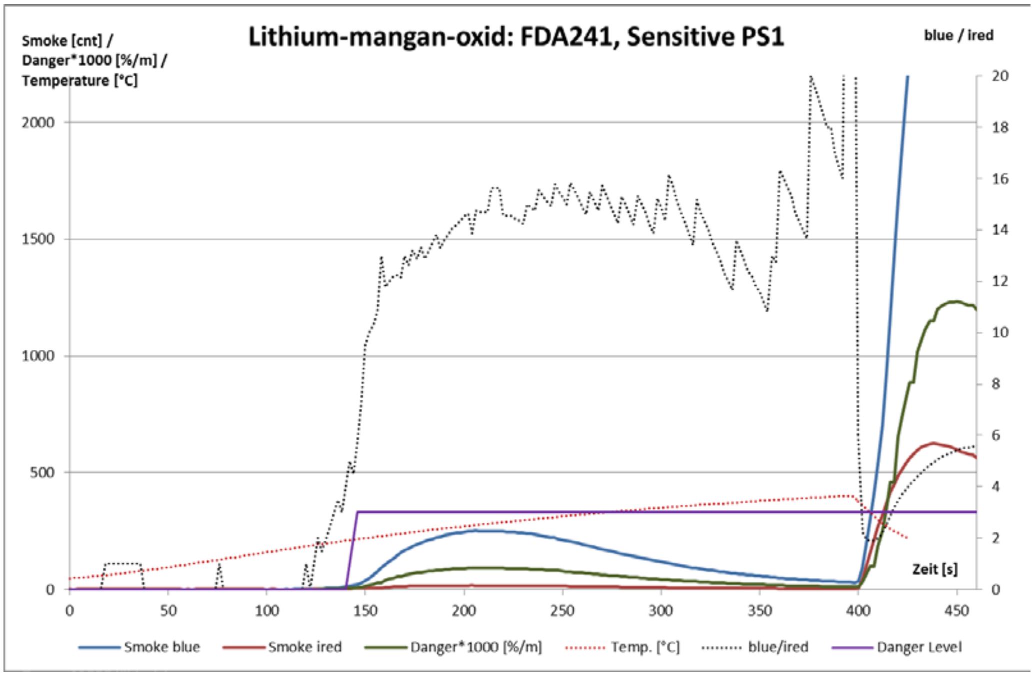

Figure 18: Thermal runaway development LMO cell

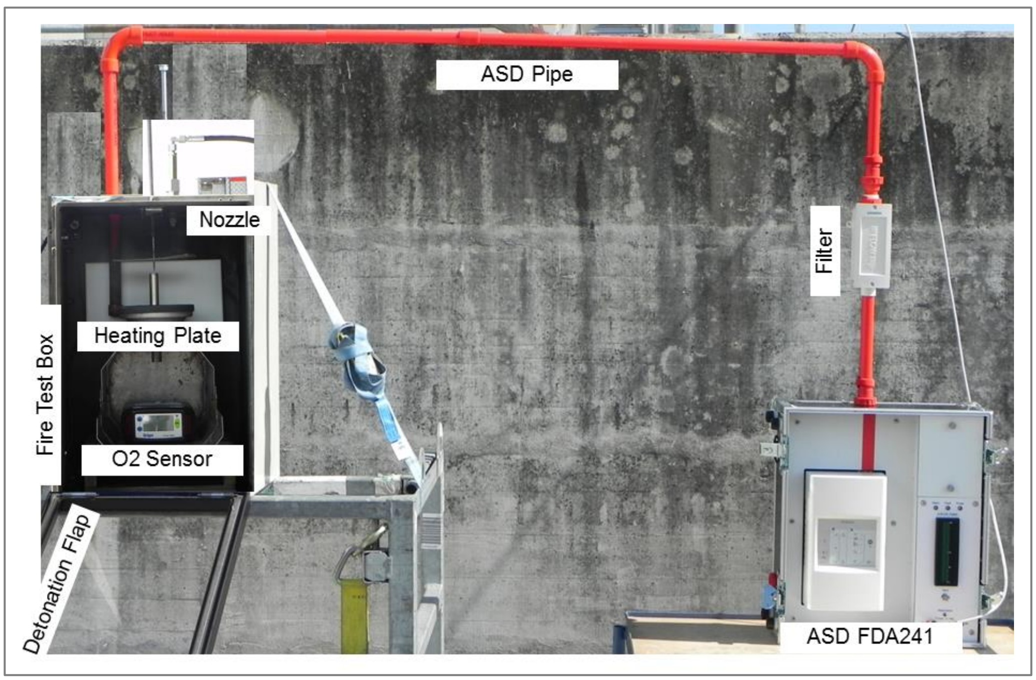

Figure 19: Thermal runaway detection set-up

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