Project BLUE BATTERY, Part I:

Analysis of fire risk scenarios of existing and upcoming large maritime battery systems

DBI FIRE AND SECURITY

DANISH TECHNOLOGICAL INSTITUTE

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Content

Preface

This report was produced as a delivery from the project BLUE BATTERY which was completed in collaboration between *Danish Institute of Fire and security Technology* and *Danish Technological Institute*.

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The outcome of the project is two primary reports:

- Project BLUE BATTERY, Part I: Analysis of fire risk scenarios of existing and upcoming large maritime battery systems
- Project BLUE BATTERY, Part II: Assessment of existing fire protection strategies and recommendation for future work

1 Introduction

Vessels are traditionally powered by fuel engines, but in the recent years, the idea of electrically powered vessels or a hybrid where both technologies work together has become increasingly popular in order to reduce sulphur and carbondioxid emissions, and to optimize energy efficiency.

Traction batteries for electrically propelled vessels could be made of different type of battery cells of varying chemistry. However, the current trend is towards lithium-ion cells like in the car industry due to the high energy density, high power density, low self-discharge rate, long service life and decreasing prices of these cells.

Like combustible fuels, large battery pack systems possesses the ability to catch fire and in rare cases, even self-ignite. The causes for a battery fire, the fire development and the measures to prevent a battery fire are not similar to those of combustible fuels, and the methods to extinguish the fire are often different as well.

This report focus on the hazards in lithium-ion cells and battery packs, and in chapter 9 some battery fire incidents from the real life are analysed to extract the lessons which can be learned from these incidents. By recognizing the hazards and taking the measures needed to prevent those, Lithium-ion batteries can be applied safely in vessels as well as elsewhere. Note that millions of lithium-ion batteries are operated safely every day without catching fire throughout their lifetime.

2 Definitions

Balancing:	Equalizing differences in the state of charge between battery cells.
BMS:	Battery Management System
Delithiation:	Extraction or depletion of lithium from an electrode
Intercalation:	Insertion of lithium ions into the electrode lattice
LCO:	Lithium Cobalt Oxide
LFP:	Lithium Iron Phosphate
LMO:	Lithium Manganese Oxide
NMC:	Nickel Manganese Cobalt
NiMH:	Nickel Metal Hydride
SEI:	Surface Electrolyte Interface
SOA:	Safe Operation Area
SOC:	State of Charge
SOH:	State of Health
Short circuit:	An external short circuit is a low ohmic connection between cell or battery terminals. An internal short circuit is a connection through or bypassing the separator inside the cell
TMS:	Thermal Management System

3 The Lithium-ion cell

The lithium-ion battery cell consists of a positive and a negative electrode, a separator that allow lithium-ions to pass through but inhibit the electrons , an electrolyte, which facilitates the lithium ion transport between the electrodes, and current collectors for external electron transport.

When the lithium-ion cell is discharged electrons flow from the negative anode through an external load and into the positive cathode due to an electrical potential difference of approximately 3.7 volts. For every electron moved externally from anode to cathode, a lithium ion must be moved internally from anode to cathode. When the cell is recharged by an external power source, electrons are pumped into the anode as lithium ions are moved from the cathode to the anode. The process is sometimes called the rocking chair principle.

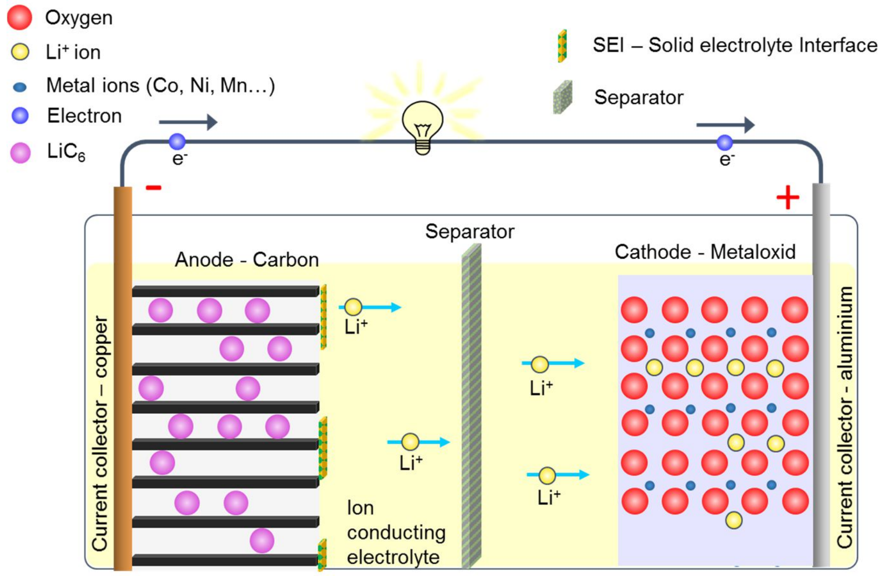

Figure 1: Lithium-ion battery cell during discharge

The anode is normally made of graphite that reacts with the organic electrolyte and forms a thin but complex passivation layer called the SEI (Surface Electrolyte Interface) layer on the anode. The SEI layer forms initially when the battery cell is filled with electrolyte and it grows very slowly throughout the lifetime of the cell. Although the lithium ions can penetrate the SEI layer, this layer is the main cause of capacity decay in normal use. Physically the anode is a fine grinded powder held together and glued to a cobber current collector foil by a polymer binder (PVDF). A more expensive titanium anode is also available in some lithium-ion battery cells.

The cathode is a metal grid where the lithium ions are stored. Different metals supply the battery cell with different properties and the cell is therefore named after these metals. LCO (Lithium Cobalt oxide), LMO (Lithium Manganese oxide), NMC (Nickel Manganese Cobalt), LFP (Lithium Iron Phosphate oxide) among others. Physically the cathode is a fine grinded powder held together and glued to an aluminium current collector foil by a polymer binder (PVDF).

Today most separators are a polymer (PP or PE) separator with the right size of pore holes. For some battery cells, a ceramic coating of the separator that offers a higher safety and retains mechanical stability at higher temperatures are available. The electrolyte is mostly a liquid organic solvent like ethylene carbonate (EC), diethyl carbonate (DEC) or dimethyl carbonate (DMC) with a lithium salt dissolved such as lithium hexafluorophosphate ($LiPF_6$), lithium hexafluoroarsenate monohydrate ($LiAsF_6$), lithium perchlorate ($LiClO_4$), and lithium tetrafluoroborate ($LiBF_4$) [13,19]. These organic solvents are highly flammable and the main combustibles in the battery cell rather than the lithium itself. Normally the electrolyte solvent is 10-20% of the cell ingredient mass.

Lithium-ion cells are available in different packages: button, cylindrical, pouch and prismatic.

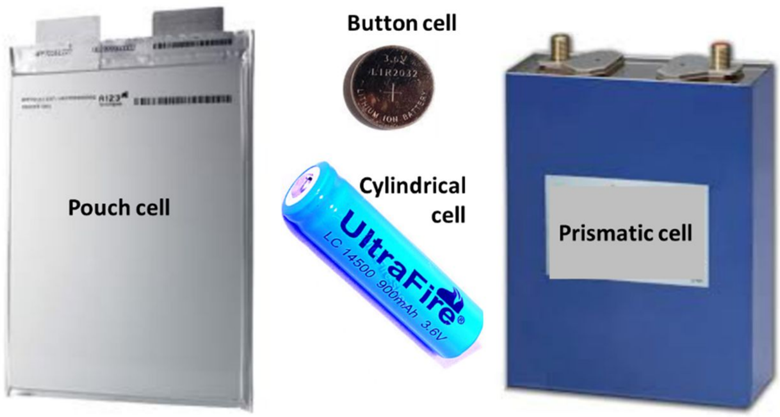

Figure 2: Lithium-ion battery packages.

4 Lithium-ion cell hazards

Operated within their safety boundaries, lithium-ion cells of high quality are basically safe to use. The safe operation area (SOA) comprises limits for overcharge, overdischarge maximum charge current, maximum discharge current and a temperature range for charge, one for discharge and one for storage. However, in rare cases flaws introduced in the manufacturing process may develop an internal short circuit, which may lead to thermal runaway (see section 4.5)and the cell may self-ignite.

Operation or storage outside the SOA is considered to be abuse and battery cells may intentionally or unintentionally be exposed to abuses such as:

- Mechanical abuse
- Electrical abuse
- Thermal abuse

4.1 Mechanical abuse

Deformation of the battery cell, such as crushing, bending, impact blows or compression, may cause the separator to be torn followed by an internal short circuit and a subsequently thermal runaway. Penetration into or through the cell creates an instant and more severe short circuit. Simulations of a nail penetration test indicate that 75 % of the current passes through the electrodes or an external circuit created by the electrode foil rather than taking the path through the metal nail [03]. Hence, an object made of a non-conductive material penetrating the cell may still inflict a severe short circuit. In addition, the cell package may be ripped or punctured thus releasing electrolyte aerosols or droplets and flammable gases. A spark may ignite these gasses and if the conditions are right the cell catches fire.

{The qualitative study in this project, section 3.1.3, describe that ships' crews receive training on the handling of the batteries and how to move around with them in order to avoid situations with mechanical abuse}

4.2 Electrical abuse

Electrical abuse occurs when the cell is operated outside the SOA. Excessive discharge current caused by an excessive load or by an external short circuit where the only current limitation is the mass transfer speed of the cell, will heat up the cell by the inherent ohmic heat generation [09]. In some lithium-ion chemistries like NMC, the internal resistance, Ri, increases dramatically with aging and consequently the self-heating increases as well at high currents. Excessive self-heating may lead to thermal runaway and real life examples of this phenomenon can be found [03, 09]. Excessive charging current may cause a high self-heating like high discharge currents, but there is also a risk of lithium plating at the anode especially when charging at low cell temperatures. Lithium plating is a formation of metallic lithium, which deposit on the anode in a partly reversible process. Metallic lithium tends to form dendrites, which are capable of penetrating the separator, and thereby establishing an internal short circuit (see section 4.4) contributing to the internal self-heating and eventually leading to thermal runaway.

Lithium plating and dendrite formation results from overcharging as well. At overcharge, the upper voltage limit is exceeded and when there is no more room for the intercalated lithium in the anode, a metallic lithium layer will build up on the anode surface. If the overcharge persists, the excessive de-intercalation at the cathode will make the cathode collapse with further heat generation and oxygen release as a result. Side reactions with the electrolyte will produce flammable gasses, which eventually will be released by the safety valve or by a violent cell package rupture. The outcome of overcharge depends on numerous factors such as cell chemistry, voltage level, and current rate among others. In some cases, the cell may just swell, whereas the cell burst into fire in other cases.
Another reason to protect a lithium-ion cell from overcharge is that the capacity of the cell degrades exponentially with the overcharge level.

In the other end of the voltage scale, overdischarge impose a safety risk. Experiments have shown that delithiation of the anode causes the SEI layer to decompose. The decomposition releases CO and CO_2 gasses which results in cell swelling. Other experiments have shown that the copper current collector (anode) dissolves in the electrolyte during overdischarge and deposit on the anode surface due to migration. Once at the anode surface, the copper ions may form dendrites, which can penetrated the separator, or simply migrate through the separator and create an internal short circuit if the cell is cycled after the overdischarge. In worst case, the internal short circuit will lead to thermal runaway.

4.3 Thermal abuse

Examples of thermal abuse could be extreme ambient temperatures due to external fire, direct sunlight or the presence of other heat sources. Normal battery operation may also produce excessive heat if the cooling is insufficient. In addition a battery cell may be heated up through the cell terminals if high current passes a bad terminal connection with high contact resistance. Inside the cell, the binder material gluing the electrode to the current collector may form a bad connection that produces heat in some areas. Regardless the cause, temperatures beyond the thermal runaway on-set point will lead to thermal runaway, and the cell temperature must always be kept within the specified limits during operation and when the cell is inactive.

{See also section 3.2.2 and 3.2.3 in the qualitative study, where it is described how the battery rooms and modules onboard are cooled with air to avoid incidents of thermal abuse}

4.4 Internal short circuit

An internal short circuit is a direct internal electrical connection between the anode and the cathode due to tearing, penetration, collapse or misplacement of the separator. Internal short circuits are mostly caused by an abuse condition and they may produce enough heat to trigger thermal runaway [12] in high power battery cells and other cells.
However, a spontaneous short circuit may develop inside battery cells, even though they have passed all safety tests required. Spontaneous internal short circuits are most likely created by contamination or defects introduced during the manufacturing process and they may take weeks or months to develop [10, 11]. Normally it starts with a low current connection which produces almost no measurable heat. Then the short circuit current and the heat production increases over time, and in the end it may lead to thermal runaway.

4.5 Thermal runaway

The temperature of a battery cell is determined by the heat generated by the cell itself and the heat dissipated to the surroundings. At normal use the cell generates heat when charging and discharging and if the ambient temperature is sufficient, the heat will be dissipated during operation so the self-heating of the cell is less or much less than 10^oC (Depending on the thermal management system). If, however, the cell generates excessive heat due to an abuse condition or an internal short circuit, the thermal management system may be inadequate to dissipate the excessive heat and the cell temperature will rise. When the cell temperature exceeds approximately 80 ^oC some exothermic chemical reactions inside the cell start contributing to the heat generation, driving the cell temperature further up. At a certain temperature, these chemical reactions will generate so much heat that other even more heat generating reactions are initiated whether the battery cell is shut down or not, and a cell fire is inevitable. This is called thermal runaway.

Thermal runaway is a chain of reactions triggered by the temperature and influencing each other. The vast majority are exothermic reactions contributing to the heat and pressure build up in the cell. Figure 3 shows the main reactions taking place during thermal runaway. The rate at which the temperature rises is indicated by the blue arrow and the small arrows on the right side. As the thermal runaway progresses, the temperature and the temperature rise increases.

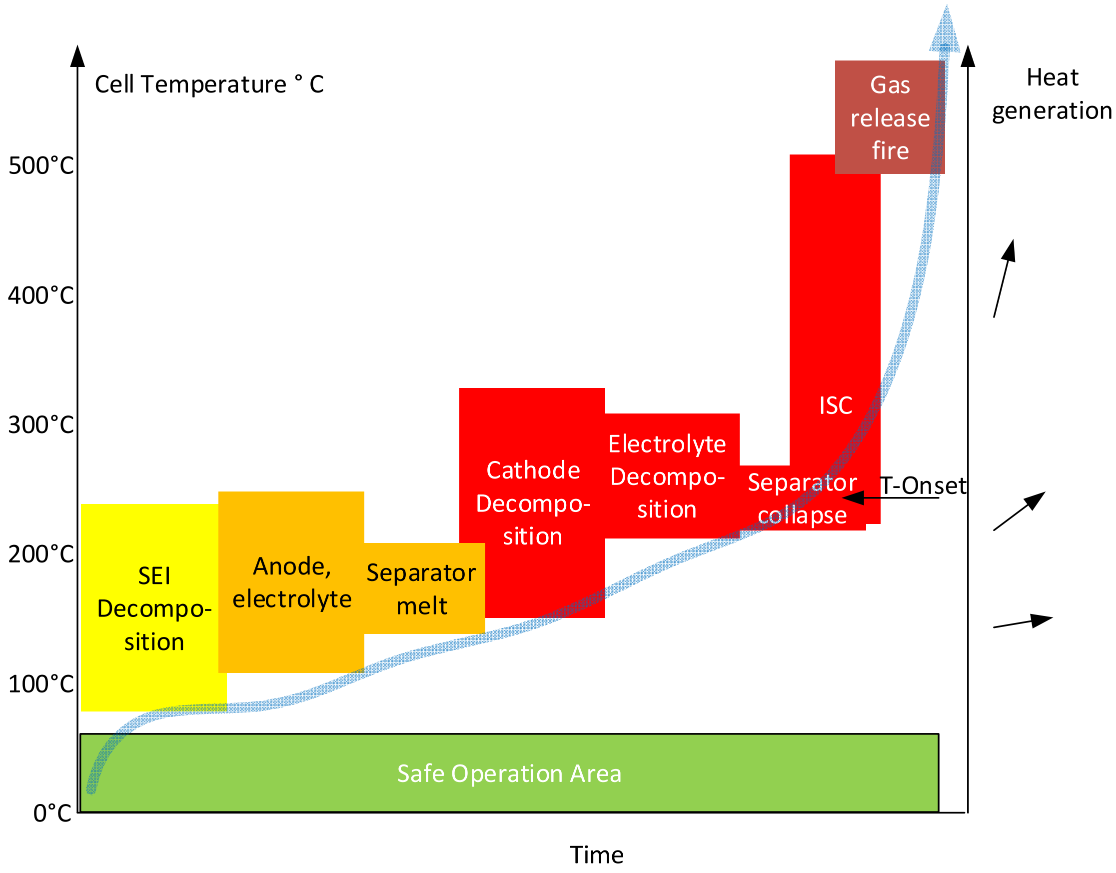

Figure 3: Thermal runaway events at different temperatures.

At relatively low temperatures between 69 °C - 80 °C the SEI layer (Solid Electrolyte Interface), which forms a protecting passivation layer on the anode, starts decomposing, exposing the carbon anode to the electrolyte. Thereby a new SEI layer is formed in an exothermic chemical reaction between the anode and the electrolyte producing an uncontrolled amount of internal heat. The residues from the former SEI layer may decompose exothermically at temperatures between 90 °C and 130 °C contributing to the internal heating. Once the SEI layer is broken down, new SEI is generated, and there is balance between SEI decomposition and SEI regeneration between about 80 °C and 250 °C.

If the SEI layer decomposition processes manage to raise the temperature to around 100 °C (for some electrolytes down to 68 °C), the intercalated lithium starts to react with the organic solvents in the electrolyte resulting in lithium loss and decomposition of the electrolyte. This process releases highly flammable gasses like ethane, methane and other hydrocarbon gasses, but since no free oxygen is available in the battery cell and no oxygen is yet being produced, the cell will not catch fire. The gas development increases the pressure in the cell and makes it swell, especially for pouch cells.

At a temperature of 130 °C a decomposition of the cathode material starts in some highly exothermal processes during which free oxygen will be released along with still more pressure and heat. The oxygen released at this stage is insufficient to sustain an internal fire, but the reactions with the oxygen produces still more heat. The temperature at which the cathode starts decomposing and thereby releases oxygen depends on the cathode chemistry. LCO starts at 130 °C, NMC at 240 °C, LMO at 270 °C and LFP at 310 °C. Therefore, and because LFP release less energy during decomposition than the other chemistries, LFP is often considered a more safe cathode chemistry [15].

The PE polymer separator starts melting at about 130 °C. A PP separator melts at 170 °C and a ceramic-coated separator may sustain the structure of the separator above 200 °C. At first the consequence is that the pore holes closes and the battery operation shuts down. The endothermic phase change of the separator and shut down of the cell operation means that the temperature rise of the cell decreases. During further temperature increment, however, micro internal short circuits are formed and at about 230 °C the separator breaks down resulting in a severe internal short circuit. Then the temperature rises exponentially and if not yet started then reactions such as cathode decomposition, electrolyte decomposition and binder decomposition will take place leading to extreme temperatures above 750 °C and an extreme pressure inside the cell.
Cylindrical and prismatic cell packages are normally supplied with a safety valve in order to release the gasses when the internal pressure in the cell exceeds a predefined level. This valve will open or in case of a pouch cell the cell packaging will rupture one or several places and release hot flammable gasses, which most likely burst into a violent fire with fresh supplies of oxygen from the ambient air.

5 Li-ion battery pack

Large battery packs would normally consist of a number of modules, each containing a number of battery cells, some safety devices and electronics for control, safety and monitoring purposes. In order to achieve the power and energy needed from the battery pack, the cells can be connected in series to increase the voltage or in parallel to increase the capacity as shown in Figure 4. The parallel arrangement is cheaper whereas the series connection is safer, because the voltage of each cell can be measured in a series arrangement only.

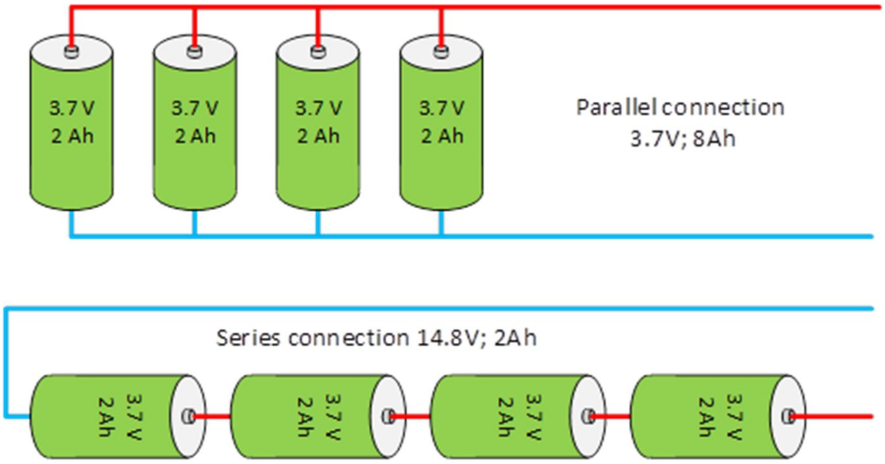

Figure 4: Series and parallel connections of cells.

When each module is made of cells in a series connection providing the voltage wanted, the modules can be connected in parallel to obtain the specified capacity, but many configurations are possible, and sometimes the battery pack is divided into some sub-packs or some battery packs are connected to form a battery system as shown in Figure 5.

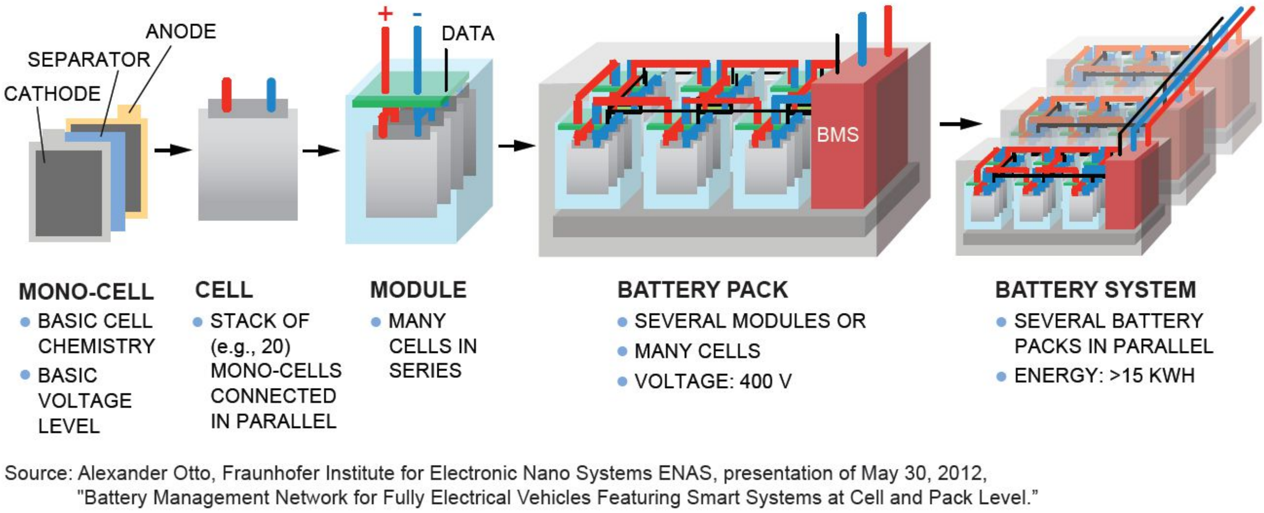

Figure 5: Example on a battery system.

The heart of the safety system is the BMS (Battery Management System). The main purpose of the BMS is to keep all battery cells safe by controlling the voltage, the current and the temperature. Additional devices like fuses and contactors are normally part of the safety system and the charger may be integrated with the safety system as well. Furthermore, the BMS offers information about the SOC (State Of Charge), and it can hold information about the battery pack and cell use, status and historical data. Balancing of cells in a series string is normally performed by the BMS, and different parts of the BMS may be located in different parts of the battery system.

The battery modules and the battery pack normally provide an enclosure for the battery cells to protect them against mechanical abuse and moisture or even water intrusion. Normally, a thermal management system is installed in these enclosures as well.

Figure 6: The 1.04MWh battery system on board MF Ampere, Norway. (Source: Corvus Energy)

6 Lithium-ion battery package hazards

The battery system may be subjected to unintended abuse. In stormy weather at sea, loose objects may penetrate or deform the battery enclosure, or displace the battery cells or modules, thus abusing the battery mechanically. Most certainly, a collision or grounding may be even more abusive.

Overheating or mechanical wear of cables and wires anywhere in the battery system may create a short circuit leading to thermal runaway, especially because there's a risk of creating a short circuit in an area not protected by safety devices. Human errors during installation, service and maintenance impose a similar risk of electrical abuse as well. Many large battery packs are designed for high voltages (300V-500V). Therefore, a short circuit is likely to create a light arc heating up one or more battery cells, which also may lead to thermal runaway. Although unlikely to happen both incidents are possible.

{See also qualitative study, section 3.2.2, which indicates that this is exactly why the crews put great trust in digital systems: they are perceived to reduce risk of human errors}

An important feature of a large battery system is a thermal management system, which can remove excess heat from the battery cells and keep the temperature within the temperature range specified as the SOA. The lack of thermal management or lack of correct response to malfunctions in the system may lead to thermal runaway in one or more cells. Uncontrolled external heat sources like an open fire near the battery pack or extreme weather conditions may exceed the capabilities of any thermal management system. Finally, the battery interconnections may degrade over time either by different types of corrosion or simply by lose screws. A bad power connection will often increase the resistance in the connection, thus forming a local heat source on or near the battery cell terminal and eventually overheat the cell.

The objective of the battery safety system is to protect the battery cells against abuse and keep all of them within the safe operation area (SOA). The battery safety system normally consists of a large number of components and interconnections and any of these may fail with thermal runaway as a result. For instance a main contactor can weld itself in the closed position, and so the load or the charger cannot be cut out. The BMS can be designed in many ways, but it is often a complex computer based system comprising electronics and software, both which may also fail. Hence, the risk of a BMS failure leading to a cell fire must be considered.

As mentioned earlier a lithium-ion battery cell may form a spontaneous internal short circuit and start a battery fire without being abused.

A fire in one cell may well spread to the neighbouring cells with a short time delay, and if no measures are taken to contain or extinguish the fire, the whole battery system may be lost.

7 Fire propagation in a battery pack

Battery packs may be constructed in many ways and they can be abused in many ways so a study of each combination would not be feasibly. A few simple experiments can, however, shed some light over thermal runaway propagation from cell to cell and from module to module.

7.1 Fire propagation cell to cell

A paper from Sandia National Laboratories, USA [16] suggests that a fire in a single cell may spread to adjacent cells in a thermal or an electrical way. They conducted an experiment where one cell in each of four battery modules with different configuration were ignited by driving a nail through the cell.

Table 1: Results of nail penetration experiment.

Cell type	Configuration	Result
Cylindrical	10 in series	Fire in one cell only
Cylindrical	10 in parallel	Fire in all 10 cells
Pouch	5 in series	Fire in all 5 cells
Pouch	5 in parallel	Fire in all 5 cells

Adjacent cylindrical cells shares a relatively small area whereas pouch cells share a large area. Hence, it was concluded that the heat transfer in the pouch cell module was so large that the fire spread to the adjacent cell with a delay of about 20 seconds once the first cell was ignited, due to overheating and subsequent thermal runaway. In the case of 10 cylindrical cells in series, only the cell pierced by a nail caught fire. In spite of the short circuit (the nail), almost 90% of the module voltage was preserved and the module was still working. Thus, the heat transfer between these adjacent cells seemed insufficient to trigger thermal runaway. In a similar module where the cells were arranged in a parallel configuration, however, the fire spread to all cells and the whole module was lost. The most likely reason is that when the first cell was shorted by the nail then the other nine cells powered the short circuit creating much more heat in the short circuit and internally in each cell by the excessive load. The parallel connection is therefore an example of electrical fire spread.
In addition, the wire length of the interconnections in the parallel configuration was several times shorter than in the series configuration, thus forming a more efficient heat transfer path through the cell terminals.

7.2 Fire propagation module to module

In a Chinese study [17] six modules were connected to form a battery pack in a horizontal arrangement. Each module contained two 25 Ah pouch cells connected in parallel enclosed by an aluminium shell. The cells were of NMC / graphite chemistry. A nail was used to create thermal runaway as it penetrated the middle of the first module, and the impact on the other five modules were investigated to reveal how a fire spreads in a battery pack. The experiment was carried out three times with different configurations as shown in Table 2.

Table 2: Nail penetration experiment.

Experiment	Configuration	Result
1	Modules in series	Smoke in two modules, fire in the rest
2	Modules in series	Fire in all six modules
3	Modules not connected	Fire in all six modules

All of the modules went through thermal runaway, but not all modules caught fire. In experiment 1 the first module (Module 1), which was penetrated by the nail, and its neighbour (Module 2) went through thermal runaway, they released gasses or smoke, but flames were not observed like in the rest of the modules. In spite of the lack of fire, Module 1 was able to initiate thermal runaway in Module 2, and Module 2 initiated thermal runaway in Module 3, which did catch fire. The thermal runaway propagated from one module to its neighbour with a delay of about 3 minutes and the maximum temperature during thermal runaway was in the range of 764 ^{o}C to 930 ^{o}C.

The heat, which initiates thermal runaway in the neighbour module, can follow three paths: through the shell, through the terminals (not available in experiment 3) or by fire. By analysing the heat transfer paths it is suggested that that 90 % the heat transfer passes through the shell whereas less than 10 % of the heat transfer passes through the terminals and less than 1 % is due to the fire. The fire burned at the top of the modules and if another module had been located there (see Figure 6), the fire impact would have been larger. Moreover, less than 7 % of the total heat energy created by thermal runaway is transferred to the next neighbour module.

The thermal runaway onset temperature was initially measured on a similar battery cell in an EV-ARC test (Extended Volume-Accelerated Rate Calorimetry) to be 259 ^{o}C, which is close to other findings (see section 4.5). However, in all three experiments the onset temperatures were measured in the range of 65 ^{o}C to 116 ^{o}C in the middle of the module. Since the heat transfer is horizontal, the battery cell may reach the onset temperature of 259 ^{o}C at one side, whereas the other side is less than 116 ^{o}C, and the thermal runaway is initiated at the warm side or in a hot spot.

When the cell pouch ruptured, gasses from the electrolyte were released to the shell chamber and from here to the surroundings. The electrolyte accounts for about 15 % of the module weight, but about 28 % of the weigh was lost during thermal runaway. Hence, other battery material must account for the residual 13 % of weight loss.

8 Gasses from a cell fire

Most substances in a lithium battery cell are harmless to humans unless they are swallowed. Electrolytes like ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) are poisonous but no more than methanol (wood alcohol). However, during thermal runaway the electrolyte decomposes and react with other parts of the battery. Two products of these processes should be mentioned here.

Carbon monoxide (CO) is colourless, odourless, and tasteless, but highly toxic. It bonds to haemoglobin that normally carries oxygen in the blood. CO concentrations as low as 670 ppm may cause heart attack, coma and even death as the amount of useful haemoglobin reduces to 50 %.

Many electrolytes contains fluorine, which immediately combines with water including moisture in human tissue forming hydrofluoric acid, which is a colourless solution that is highly corrosive. Hydrofluoric acid penetrates easily human tissue and may cause serious skin burns, bronchitis, pulmonary edema (water in the lungs), cardiac arrest and other injuries.

In conclusion it is not recommendable to approach a lithium fire without wearing appropriate protection equipment and in addition assure sufficient ventilation in the battery compartment

{See the qualitative study, section 3.2.2 and 3.2.3, for descriptions on the separate ventilation systems}

9 Fire accident analysis

To prevent failures and fire accidents in the field, laboratory tests based on a risk assessment and international standards are normally performed when new products involving a large battery pack are introduced. However, fire incidents still occur in the field, and it seems appropriate to learn from these incidents in an attempt to avoid repetitions of already recognized hazards.
Fortunately, only few marine battery fires are registered, but useful knowledge can also be derived from other battery fire incidents.

9.1 Fire in a tug boat – Campbell Foss

On 20th August 2012, the Campbell Foss tugboat was at work in the Long Beach Harbour of Los Angeles when the crew heard a loud bang and observed black smoke coming from the engine room vents.

Campbell Foss was propelled by a hybrid system including a diesel generator and an electrical engine. The latter was supported by a large high voltage battery pack. The battery pack consisted of 10 Corvus AT6500 battery modules with a voltage of 48V and a capacity of 135 Ah. The modules were connected in series to form a 480V / 135Ah battery pack. In the Battery Re-installation Report [2], it was stated that the battery cells in these modules were arranged in a parallel configuration, so 3 or more cells were arranged in parallel to gain 135Ah and 13 of these parallel connections were arranged in series to gain 48V, since each cell had a nominal voltage of 3.7V (NMC cells from Kokam). In the following the cells arranged in parallel is called the series element.

The fire investigation report [1] concluded that the fire was caused by a chain of events. The root cause was overcharging. This was due to the charging method leading to rupture and fire in one or two battery cells inside one of the battery modules. The battery system was equipped with a BMS and a Pack Controller. The BMS was monitoring the series element voltages and the temperature of each module. The Pack Controller estimated the SOC (State of Charge) based on the voltage over the series element with the lowest voltage, which means that other cells would be at higher SOC during charging. When the battery was charged to 90 % SOC, the controller would change to trickle charge, and at 92 % SOC, the charging would be terminated. When the battery cells are new, they can be well matched, but as the cells are aging, the mismatch in capacity between cells increases. Hence, other cells than the one used for the SOC estimation may be at higher voltage than assumed by the SOC figure monitored. No over voltage limit for the battery pack was implemented, although a 500VDC limit was specified in the design phase. Fortunately the pack controller was designed to open the main contactor in case the BMS reported an over voltage on one of the serial elements or an over temperature in one of the modules. Unfortunately, an error in the pack controller prevented it from opening the main contactor and thereby terminating the charge. The pack controller did report numerous failures and alarms about this and many other problems, but the large number of these failure and alarm messages and the fact that the Alarm and Monitoring System masked out detailed information from the pack controller prevented the crew from perceiving the right information at the right time.

{The ability to make the right decision and distinguish between relevant and irrelevant information among enormous amounts of input and data in critical situations is found to be crucial among the crew in the qualitative study, section 3.2.3.}

As a result of overcharge, one or more cells in one of the modules ruptured and caught fire. The heat from this thermal runaway ignited the neighbouring cells and eventually all cells in the module were burned. Eight of the remaining nine modules showed a high voltage up to 540VDC, but none seemed to be damaged by the fire. The open circuit voltage of 540VDC measured after the fire would have been somewhat higher during charge depending on the maximum voltage of the charger. 540VDC corresponds to a cell voltage of 4.16V, which is about the maximum specified voltage limit during charging for this chemistry.

During the fire, the battery compartment was overheated and the ventilation ducting made of PVC melted so the hot gasses were vented into the engine room where combustibles were ignited. Activation of the fire suppression system put out the fire in the engine room.

Some constructive learning can be extracted of the unfortunate incident:

- Charging of a lithium-ion battery should always be terminated when the upper voltage limit is reached by a battery cell or before. If balancing is performed by the end of charge all other battery cells will be fully charged at that occasion. A lithium-ion battery can be operated and charged by many different methods, but voltage, current and temperature must always be kept within the specified SOA.
- As mentioned in section 7.1, parallel connection of battery cells is an architecture causing concern for safety reasons.
- The BMS is mostly a complex piece of electronics with an even more complex software. A high degree of self-test and self-diagnostics should therefore be integrated in the BMS. The BMS interacts with many other parts of the safety system and the control system, so these systems should be part of the tests and diagnostics as well. Moreover, the BMS should inform the crew about the battery status in an appropriate way. Alarm and error messages should be fully understandable for the crew and acknowledged messages should not be repeated every minute.
- Critical components such as the main contactor should be redundant and/or diagnosed by the BMS.
- As a fire incident might occur, the battery room should be constructed to cope with it. Combustibles should be avoided and only materials with a high melting point should be applied. Automatic fire extinguish equipment should be installed.

9.2 Fire in a ferry boat - Sweden

In 2015 there was a fire incident in the battery on a hybrid ferry boat in Sweden. The boat is a series hybrid with a 480V / 180kWh NiMH Battery pack consisting of a number of strings in parallel each with 100 single cells in series. When fully charged a contactor controlled by the BMS disables the charger from each string in the battery.
The battery was charged during the night when the boat was at the dock, and when fully charged the BMS deactivated the contactors to disconnect the charger. One of the contactors was welded in the close position and therefore it could not open when deactivated by the BMS. Charging of the particular string persisted and the cells were overcharged.
The overcharge resulted in a minor fire where polymer material surrounding the modules caught fire and damaged the adjacent modules and some of the cables. The fire did not sustain, so no fire extinguishing equipment was brought in use.

NiMH batteries react much less violently to overcharge than lithium-ion batteries. When a NiMH is overcharged, oxygen is evolved at the positive electrode accompanied by an increase in pressure and heat. If the pressure exceeds a certain limit, the safety valve will open releasing the oxygen. In the case above, overheating may have ignited the polymer without releasing oxygen, but this information is not available.

The root cause, the welded contactor, could occur in a lithium-ion battery system as well, so a redundant contactor and an electronic check of the contactor status is highly recommendable.

9.3 Fire in vehicles and aircrafts

Some of the fire incidents involving lithium-ion vehicle batteries that were reported in the years 2008 to 2016 are listed in Table 3.

Table 3: List of lithium-ion fires.

No.	Date	Location	Accident	Possible cause
01	2008-06	Columbia, USA	The lithium-ion battery pack of a modified Prius caught fire during highway running.	Connection loose led to battery overheat near bolt [3].
02	2010-03	Nr. Sundby, Denmark	A Nissan Qashqai burnt out during charging.	The cable for charging was shorted to ground and thereby the battery was shorted.
03	2011-05	Burlington, USA	A Chevy Volt, which had side-pole impact test 3 weeks ago, caught fire and destroyed adjacent cars.	The side-pole impact damaged the coolant system and the battery module. Conductive coolant formed external short circuit and ignited flammable gas leaked from cells [4].
04	2012-04	Connery, USA	A Chevrolet electric vehicle was on fire when it was charging.	Overcharge caused the lithium-ion battery pack on fire.
05	2012-05	Shenzhen, China	A BYD E6 taxi was collided from rear end by a Nissan GTR at extreme speed. The taxi caught fire after hitting a tree, killing 3 occupants.	High speed collision deformed the high voltage circuit. Arc was triggered from the damaged high voltage circuit, ignited 25% cells and the whole car.
06	2012-05	Texas, USA	A Fisker electric vehicle is on fire after parking.	High external temperature led to the LIB pack fire.
07	2012-10	Seattle, USA	A Fisker electric car was on fire when it was driving	External short circuit caused by sea-water led to LIB to catch fire.
08	2013-01-07	Boston, USA	The APU battery pack caught fire and filled the cabin of a Boeing 787 Dreamliner with smoke.	Internal short circuit [5].
09	2013-01-16	Takamatsu, Japan	The Main battery pack caught fire during a Boeing 787 flight from Yamaguchi-Ube to Tokyo.	Internal short circuit [6].

10	2013-03	Japan	A Mitsubishi electric car was on fire when driving.	High external temperature led to the LIB pack fire.
11	2013-10	Seattle/ Tennessee USA	Two Tesla Model S ran over large metal objects at highway speed and caught fire.	The battery pack was pierced and deformed by the metal objects. Short circuit occurred and ignited some cells.
12	2014-02	Los Angeles, USA	A Tesla electric vehicle was on fire spontaneously when it was parking.	High external temperature led to the LIB pack fire.
13	2015-03	Zhangzhou, China	A Greenwheel EV bus was on fire when it was driving.	External short circuit of battery pack occurred, leading to the bus fire.
14	2015-03	Henan, China	A Tang Jun (BYD) electric car combust spontaneously	High external temperature led to the battery pack fire.
15	2015-04	Shenzhen, China	Wuzhou Dragon EV bus caught fire during charging in a garage.	The BMS failed in stop charging, the battery pack was overcharged until TR and fire.
16	2015-09	Hangzhou, China	The battery pack of an HEV bus caught fire.	The battery pack was out of warranty after 7-year service.
17	2016-01	Gjerstad, Norway	A Tesla Model S caught fire while fast-charging at a Supercharger Station.	Short circuit during charging
18	2016-04	Shenzhen, China	A Wuzhou Dragon EV bus caught fire.	Short circuit caused by wire deterioration.
19	2016-05	Zhuhai, China	A Yinlong electric bus caught fire when it was charging.	External short circuit of battery pack occurred, leading to the bus fire.
20	2016-06	Beijing, China	An iEV5 caught fire before the landmark of Sanlitun.	Might be overheat caused by wire connection loose.
21	2016-07	Nanjing, China	The battery pack of an EV bus caught fire after heavy rain.	Water immersion brought short circuit.
22	2016-07	Rome, Italy	An EV police car caught fire on the street.	Unknown.

Although maritime battery pack systems may differ from those listed in Table 3, some details may be educational. In Table 4 the fire incidents are ranked after the root cause. Since only few of the original accident reports were available, the references [3, 4] are applied.

Table 4: Fire incidents ranked after root cause.

Root cause	Number	Vehicle
External short	7	3 cars & 5 busses
Over temperature	4	4 cars
Loose connection	2	2 cars
Internal short	2	2 Boeing 787
Unknown	2	1 car & 1 bus
Short by metal object	2	2 cars
Overcharge	1	Car
BMS failure (Overcharge)	1	Bus

Collision	1	Car
Impact test	1	Car

External short circuits were concluded to be the most common root cause in these 23 accidents. In most cases these short circuits can be prevented by different safety devices, but two of the seven short circuits were created by water intrusion. The conductance of tap water and water from raining is low, whereas seawater has a high conductance due to its content of salts. An open battery pack would face a number of parallel short circuit paths in the magnitude of 20 Ohm (0.05 S/cm) if submerged into seawater. A high power battery pack would be discharged fast, but it should be able to handle such a discharge without triggering thermal runaway however, other failure mechanisms (light arcs) may initiate a battery fire.

In October 2012 the hurricane named Sandy caused a car of make Fisker Karma to catch fire as the car was partly submerged into sea water for several hours. The Vehicle Control Unit, which was powered by the 12V battery, caught fire due to a short circuit in the unit caused by corrosion as a consequence of the salty seawater. Hence, the 20kWh lithium-ion high voltage battery pack did not cause the fire, and Fisker claimed that it did not even contribute to the fire, that spread to other vehicles parked nearby.
In another case, the external short circuit was created by wire deterioration and in two cases loose connections overheated one or more battery cells by increasing the contact resistance, which is critical in high power connections.

Four cars caught fire due to high external temperatures. As mentioned in chapter 4 the chemical reactions that heat up the cell to thermal runaway is initiated by high temperature. Thus, the cooling system must be able to handle extreme ambient temperatures in warm regions on the earth. Direct sunlight, heating system failures and other unexpected incidents in the battery room may enhance the demands for cooling. Often the cooling must persists long after the battery is shut down and during charge.

An example of an internal short circuit in a battery cell was given in the two spectacular cases of fire in a Boing 787 Dreamliner. After the fire, the safety was confirmed to be as specified. No traces of abuse, mal function or mistreatment was discovered and it was concluded that the fire was started as a result of self-ignition in one of the cells most likely due to impurities from the manufacturing process.

Some of the incidents mentioned in the above tables may as well take place in a maritime high power battery pack. Hence, the following learning may be extracted:

- In maritime applications, seawater is a threat due to its high conductance and its corrosive properties. Therefore, the battery pack as well as the safety system should be well protected against seawater and salty mists.
- The interconnections in the battery pack should be verified as part of the regular maintenance to avoid short circuits and overheating in plugs and screw connections.
- Sufficient cooling of the battery cells is mandatory to keep the cells within the SOA limits and prevent thermal runaway.
- In spite of a comprehensive test program of all cells at the battery manufacturer to detect flaws, which can result in an internal short circuit, a few cell flaws would leave the factory anyway. The risk of spontaneous self-ignition is not yet eliminated, although methods to spot these internal short circuits before self-ignition may be applied. As the failure is very difficult to detect post mortem, unknown failures may be of this sort.

- All electronics components including the BMS, sensors, contactors and other safety components may fail. Hence, regular diagnostics of these components should be performed to identify and repair such failures before they develop to catastrophic failures.
- In several cases the fire was initiated by other components than the lithium-ion battery pack and the fire then spread to high voltage battery pack as in the fire incident with the Fisker Karma mentioned above. Therefore, fire protection also comprises equipment and materials near the battery pack.
- Not all risks can be eliminated, so the battery pack and the battery compartment should be designed to minimize the consequences of a fire in a cell or other components near the

10 Conclusion

The key to a safe battery pack is the design of a safety system, which always secure that all the battery cells are operated well inside their safe operation area (SOA) with regard to voltage, current and temperature. The key components to keep all battery cells within the SOA is the battery management system (BMS) plus the thermal management system (TMS), and a robust risk assessment including the learning from previous fire accidents as presented in this report is vital when designing the battery safety system. Comprehensive knowledge about lithium-ion battery hazards and a large number of recommendations to reduce the risks when applying lithium-ion batteries are given throughout this report.
The risk assessment for a propulsion battery installed on board a vessel should include:

- Hazards which are detected by the safety (BMS and TMS) system and the response from the safety system on such hazards should be well-defined.
- Hazards which may not be detected by the safety (BMS and TMS) system and the consequences for the safety.
- Hazards caused by BMS or TMS failures and the need for self-diagnostics and/or redundant safety components.

Furthermore it is important to make the behaviour of safety system known to the crew and to make sure that all alarms and alerts are fully understandable to the crew.
Acceptance test and maintenance test of the BMS, the TMS and the whole safety system should be performed and international test standards for such tests are desirable.
The SOA is given by the choice of cell chemistry and operating all cells well inside the SOA keeps the battery safe and prolongs the battery lifetime.

In spite of all protective measures the battery may still catch fire by a spontaneous internal short circuit in a single cell, unintended abuse such as mechanical damage due to a collision or extreme ambient temperatures. Hence the battery compartment should be designed to handle a battery fire and a firefighting strategy should be integrated in the battery pack design and the battery compartment design in an early stage in the design process.

Although a great deal of knowledge about the lithium-ion technology has been gained from research, some obvious questions still remain.
The mechanism that ignites the electrolyte when released during thermal runaway is yet to be elucidated.
The fire propagation and the heat transfer paths in large battery packs such as maritime batteries is not yet mapped and fully understood. If a battery fire can be contained to a few cells in a battery module without transferring heat to other modules, then the damaged module can be cut out and the vessel can continue to power the engine with only some battery capacity lost.
Several fire extinguish medias are available on the marked, but very little documentation of their effect can be found and very little research in this area, if any, has been published.

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