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ASPECTS OF SAFE OPERATION OF LITHIUM-BASED BATTERIES IN MARINE APPLICATIONS

ABSTRACT

The paper presents issues related to the operational safety of lithium-based batteries on vessels. In the first part of the paper the regulations of the Polish Register of Shipping (PRS), regarding the requirements for the batteries on a vessel are analysed. The next section presents the risks related to the use of lithium-based electric energy storage technology. The last part discusses the principles to be adopted during operation of lithium batteries to minimize the risk of threats.

Key words:
lithium-based batteries, safety, power supply in marine application.

INTRODUCTION

The importance and power of installed on vessels batteries increases considerably. Their share in the energy balance of the ship takes on the meaning what causes the introduction of new chemical technologies which in turn generates the emergence of new operation requirements. A relatively new method of storing electric energy and at the same time ensuring currently the highest energy density is a lithium-based cell technology. However, the introduction of this technology on

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a vessel poses new threats that did not exist in the case of lead-acid batteries. The article presents the analysis of the provisions of the Polish Register of Shipping (PRS) regarding the batteries used on vessels, analyze threats posed by lithium-based batteries and a list of rules for the use of lithium batteries to ensure their safe operation.

LEGAL ASPECTS, CLASSIFICATION SOCIETIES REQUIREMENTS FOR BATTERIES

The importance of batteries on vessels increases simultaneously with the increase of requirements concerning power supply reliability and optimization the cost of generation and storage of the electric energy at the same time. This is due to the continuously increasing usage of electric drive primarily for auxiliary devices but recently also as a main drive for vessel propulsion purpose. This implies necessity to increases not only the capacity of the installed batteries but also the use of chemical technologies of energy storage that provide greater energy density than conventional lead-acid batteries.

It should be pointed out that the accumulation of large amounts of energy in a small volume and mass, involves the risk of fire and explosion in case of its uncontrolled release. That is why the rules governing the classification principles of construction and operation of ships include chapters on the principles of installing batteries. However, analysing these regulations it cannot be noticed that they relate to lead-acid batteries and minimization of the risks associated with their operation. For example, the PRS Rules for the Classification and Construction of Sea-going Ships, Part VIII, ‘Electrical Installations and Control Systems’ [3] demonstrates several important points. Firstly, defined the requirements of the general levels of self-discharge at levels adequate for a very out-dated technology, and devoting the other three points to conditioning the safe use of corrosive liquid electrolyte in sea conditions. Hydrogen generation during the cycling operation of lead-acid batteries is also the cause of detailed determination of their positioning in sections describing a separated battery room and especially the ventilation and heating. Subsequent requirements of the analysed regulations result from direct assumption of the battery role as starter batteries for the internal combustion engines and the properties of lead-acid batteries during charging process.

The only one point which taking into account other battery technologies is the section related to the batteries supplying important and emergency appliances. However, this regulation does not contain any technical requirements, but only formal requirement to prepare a list of parameters of used batteries.

Due to the significant threat that bring modern storage technologies of electric energy, it must be emphasized that it would be desirable to take into account in the design of new or upgraded vessels, the solutions to minimize the risks described in subsequent parts of the paper.

RISKS RESULTING FROM THE APPLYING LITHIUM-BASED BATTERY TECHNOLOGY

Lithium-ion cells are able to store large amounts of energy in small mass and volumes, making them one of the most useful energy systems for vide range of applications. Unfortunately, those large amounts of energy are placed in small containers — which can be in some situations potentially dangerous. In addition, most of the materials used inside of the cell are flammable (carbon materials and low evaporation temperature organic electrolyte). Most common lithium ion cells failures can be sorted in two groups: without ignition and with ignition. As of the source of failure there are four major factors: mechanical abuse, aging abuse, electrical abuse and thermal abuse. The li-ion cell systems are pressurized, closed systems with no air or gas exchange with the surrounding. The outer cover of cells is made of steel (cylindrical), aluminium (prismatic) or metalized foil (pouch/coffee bags). Manufacturers want to store maximum energy in the outer cover volume which leads to filling nearly all of the available space inside. Each type of abuse corresponds to series of unwanted processes in the cell leading usually to ignition and fire which usually causes further cells to burn or be damaged as li-ion cells are normally placed in packs and series to fulfill the required electrical parameters.

Mechanical type of abuse usually corresponds to deformation of outer cell cover. For hard covers (metal) this cause internal short-circuits by forcing two electrodes together or tearing the separator and short-circuiting of the inner surfaces of the electrodes. If the damage is not sufficient the deformed spot can heat abnormally. This type of abuse is combined — mechanical abuse is causing the heat abuse processes to start. Mechanical damage can also lead to depressurization of the closed and sealed cell. This leads to organic compounds evaporation. Lose of the electrolyte is causing thermal imbalance leading to thermal abuse.

Depressurization is a form of mechanical abuse — causing sometimes rapid gas release. Those gases are organic compounds with low evaporation temperature — from 30° to 15°C. Like most of organic vapors they are highly flammable. That's why during the depressurization combined with a heating spot usually fire takes place.

It's as effect of flammable gas heating from short-circuited electrodes after an outer damage. Of course the State of Charge (SOC) is strongly combined with the effect — fully charged cell stores much more energy than a drain one.

Thermal abuse causes all kind of decompose process depending on the temperature — starting from electrolyte (organic evaporation) and polypropylene/ polyethylene separators (electrode surface exposition leading to short-circuit), gaskets and metalized foil outer cover(pouch type cell) to the active materials such as graphite and metal oxide spinel (fueling the flame or causing rapid oxidation). As a side effect, thermal abuse always cause increasing inner pressure as an effect of decomposition (solid and liquid state to gaseous) — this leads to rapid venting and thermal runaway.

Electrical abuse causes both thermal and decomposition effects. Depending on the SOC of cell, electrical input or drain those effects are fast and rapid or slow and stable. Both are leading to a cell failure — inner pressure rise, abnormal heat or faster aging — with all of the described effects.

When speaking about failure one cannot forget about normal process of aging. The aging of cells is irreversible process in which the capacity of the cell declines, most commonly caused by the consumption of electrode materials during normal life cycling or by improper storage. Standard cell li-ion and lithium polymer cells lose up to 20% of its nominal capacity after approx. 200 cycles of charge and discharge. The reactions on the electrodes in some part are not reversible and in the end of each cycle the cell is able to store a bit less energy. In addition, some times the cell is used in the work parameters which deviate from normal or specified by the manufacturer, causing an accelerated decline in capacity. Also, the storage cells in unsuitable conditions can cause accelerated aging. Aging is a normal process, but when forgotten it leads to exposition of cell to thermal and electrical abuse. It is a thread when cell is at the end of its work life but still exposed to normal, fresh cell parameters — both charging and discharging. This forces the cell to work in conditions that are no longer reachable by an older cell. The above-mentioned abuses and their causes and results are depicted in table 1.

The cells, which are subjected to the conditions presented in table 1 tends to fail. There are many levels of damaging a cell. From a simple voltage drop, resistance rise and capacity lose caused by losing 30% of electrolyte due to 5–10°C constant overheating to full thermal runaway while short-circuiting a high energy pouch cell with no safety devices. Not all of the cells explode or depressurise — many of cells have mechanical components preventing of further overheating (like Positive Temperature Coefficient device PTC) inner pressure rise (like Current

Interrupt Device CID) or short-circuiting (fuse type melting inner connector when high energy flow). Explosion resistant pack or cell cases, metal containers are made to rise the mechanical resistant and help with stopping the mechanical thread to the cells.

Tab. 1. Abuse of the cell and effects [own work]

Abuse type	Process caused	Result for the cell	Effect
Mechanical	Inner short-circuit	Electrode forced contact	Heat
		Electrode deformation	Heat
	Depressurization	Release of organic compounds	Toxic and flammable (mechanical damage)
		Lose of electrolyte	Heat
	Outer short-circuit		Heat
Thermal (heat)	Separator decomposition	Electrode forced contact	Short-circuit causing additional heat
	Electrolyte decomposition	Dry electrodes, voltage change	Heat
		Inner pressure rise	Rapid depressurization — flammable exhaust
	Electrode decomposition	Oxygen released	No air needed to sustain further oxidation and flame
Age and life	Electrolyte decomposition	Dry electrodes, voltage change	Heat
	Unsealing the main cell gaskets(age related)	Depressurization	Toxic and flammable (mechanical damage)
	Electrical abuse due to capacity loses of the cell	Inner short-circuit	Heat
		Inner pressure rise	Toxic and flammable (mechanical damage)
Electrical	Heating of electrodes	Inner short-circuit	Heat
	Electrolyte decomposition	Dry electrodes, voltage change	Heat
		Inner pressure change	Toxic and flammable (mechanical)

Nevertheless if the lithium cell fails fully — venting with a heat source (like short-circuited electrodes) there is a big chance or ignition. In this case flames are fuelled directly from the cell materials. Air is not needed to sustain the reaction. As the temperature rise farther materials start to decompose from electrolyte to graphite. Above 600°C active materials start to decompose delivering more oxygen and fuel. In the end copper and aluminium collector foil is starting to decompose as a termite. This thermal energy source can ignite other materials. If the cell is in pack, other cells are heated together with the cell holders and outer casts — usually made of polymer. If the pack is built in a device the heat can decompose other elements starting a fully developed fire.

To prevent electrical abuse many manufacturers use electronic modules, which ensure the proper voltage window or enforce a proper and maximal power charge and drain. When many cells are connected together a balancing unit is used. For further control BMS (battery management system) or BCM/BCU (battery control module/unit) are used. Those modules control not only energy parameters but also thermal, life and age status for further safety. Also defend chemistry's are used to address safety issues. For example evaporation exhausts from a LiFePO4 system are much less flammable than the $LiCoO_2$ or $LiNiMnCoO_2$. Also the $LiFePO_4$ systems have much wider thermal and mechanical abuse window than the $LiCoO_2$. New types of LTO ($Li_4Ti_5O_{12}$) have even more improved damage resistance.

Lithium systems are much more unstable and have less resistance than water--based systems such an acid or Ni-Cd. But storing so much energy in small volume and mass does not come without a price. Properly handled cells, with proper electronic and designed and checked outer case are safe. But forgetting or cutting costs on some aspects can lead to cell failure and then better be prepared because the lithium cells flames are not so easy to put out.

DETERMINANTS OF PROPER USE AND MAINTENANCE OF LITHIUM-BASED BATTERIES UNDER MARINE CONDITIONS

Presented in previous part of the paper threats which can occur during operation of lithium-based batteries show significant differences between threats that are related to the usage of the most often adopted on marine vessels batteries, i.e. lead-acid ones. Adopting lithium-based technology of electric energy storage to marine applications requires defining the rules of proper usage and maintenance that kind of batteries taking into account the threats which can occur as a result of technological or operational fault. It is essential to ensure the safety of people and the vessel regarding to the lithium-based batteries and their potential faults. The potential causes that may lead to dangerous battery faults are shown on figure 1.

Moreover to ensure long-lasting and reliable operation of lithium batteries it is recommended to follow so called best practices during their usage, which allow reaching nominal cycle-life of the battery or even its extension.

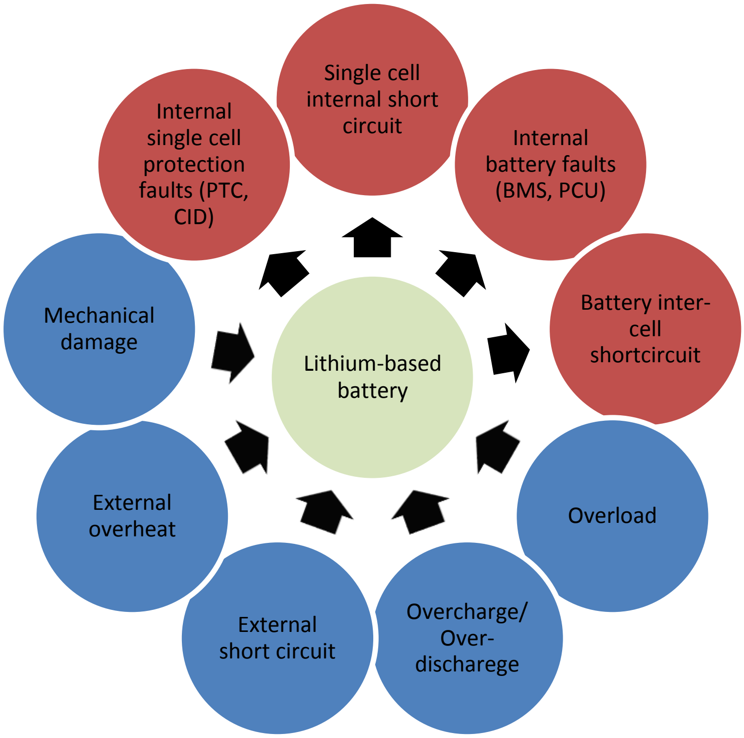

Fig. 1. Internal faults and improper handling that may be the cause of the threats associated with usage of lithium based batteries [own work]

Figure 1 presents possible situations, which potentially can lead to dangerous situations. Events in red circles indicate internal faults of the battery or cell, while blue circles present external events being dangerous for the battery. The most dangerous fault of the lithium battery is so called 'thermal runaway', which could lead to [2, 5]:

- oxidation of the electrolyte at the cathode;
- gas formation;
- reaction of the anode active materials with the electrolyte;
- thermal decomposition of the cathode;
- oxidation of the anode, separator and electrolyte.

The thermal runaway starts when the temperature inside a battery reaches specific value. The temperature may increase as a result of:

- overcharge;
- overload;
- exposing the battery to high temperature;
- internal or external short circuit.

It is also possible the temperature rises above the critical temperature during charging the battery with to high current. The thermal runaway could lead to potentially dangerous situations such as: pressure increase inside the cell, violent burst of the cell, leakage of irritant and corrosive electrolyte, flammable and/or toxic and irritant gas generation and finally, if the temperature is high enough, fire.

Despite these intrinsic threats, modern lithium-based batteries are safe energy sources due to adopting into their construction multilevel protection devices. They prevent the battery, the battery user and powered device against faults caused by technological defects and improper usage or maintenance of the battery. The protection devices are present at the single cell level as well as at the battery level. Depending on the cell manufacturer it may be protected by [1, 2]:

- current interrupt device (CID), disconnecting the cell when the current drawn from battery or the temperature exceeds specified value; generally non-resettable device;
- positive temperature coefficient device (PTC) — disconnects the cell or increases its internal resistance if the temperature or current drawn from a cell is to high;
- shut down separator — in case of thermal runaway electrically separates electrodes of the cell preventing internal short-circuit of the electrodes;
- safety vent — releases gases produced in a cell when the internal pressure rises above specified value and prevents violent rupture of a cell;
- safety fuse — disconnects the cell if the current drawn from the cell or charged into cell exceed specific value (similar to the CID).

At the battery pack level the protection is generally provided by battery management system (BMS) [4] (sometimes called protection circuit board — PCB, protection circuit module — PCM etc.). The BMS is a real-time system controlling many functions vital to the correct and safe operation of the lithium battery pack. This includes monitoring of temperatures, voltages and currents, maintenance scheduling, battery performance optimization, failure prediction and/or prevention as well as battery data collection/analysis [4]. The BMS prevents the battery against short-circuit, overload, overheating, overcharge and to deep discharge.

Despite the use of the multi-level safety device of lithium batteries, their use should be carried out in a way to prevent potentially dangerous situation that could lead to damage to the battery. These situations may occur at any stage of the battery life. Table 2 summarizes the activities related to the operation of the battery, and the potential damage to the battery and the rules to counteract them.

Tab. 2. Preventing dangerous situation during different activity related to battery operation [own work]

Activity	Threat	Prevention
Transportation	Mechanical damage	- secure during transportation to prevent spontaneous movement, - during manual transfer not to allow to fall on a hard surface, - do not throw, - not to allow other heavy objects fall on the battery, - prevent excessive vibrations during transport (positioning on vibration isolating base)
	Electrical damage	- protect against external short-circuit, - it is recommended to transport lithium batteries charged to the 30% of nominal capacity
	Heat damage	- isolate from external heat sources, - avoiding direct sunlight
	Battery internal fault	- isolate the battery to prevent the spread of fire, - extinguish burning battery with D class extinguisher, - cool down the battery (water, compressed CO_2 etc.), - shipping container should be made of materials which do not spread fire
Installation and place of installation	Mechanical damage	- fasten to the base with original mounts or according to the manufacturers instructions in a way reducing excessive vibrations, - secure against spontaneous movement or fall, - protect against the possibility of the fall of other heavy objects on the battery, - place of installation should provide protection against accidental mechanical damage caused by human and other items
	Electrical damage	- protect against external short-circuit during installation (use covers of the battery terminals), - connecting batteries of the same type in series or parallel only if the battery supplier provides for such a possibility, - not connect different types of batteries in series or parallel, - place of installation should provide protection against accidental external short-circuit (with external electrically conducting items)
	Heat damage	- avoid using welding, soldering or other heat-generating methods during installation or isolate the battery from the heat source, - place of installation should guarantee thermal insulation from external heat sources such as IC engines, flues, direct sunlight etc.
	Internal faults	- place of installation should be equipped with proper extinguisher or extinguishing system, - place of installation should not spread the fire and isolate the fire from the rest of the vessel, - gases generated in case of battery fault should be immediately removed from the vessel

Activity	Threat	Prevention
Charging	Electric damage	- the battery must be charged only by the charger delivered by battery producer or from an energy source with parameters specified by battery producer (for smart batteries)
Discharging	Electric damage	- the current drawn from the battery should not exceed the maximal current specified by the producer, - minimal discharge voltage of the battery must not drop below minimal value specified by the producer
Maintenance	Electric an thermal damage	- during usage the battery temperature, voltage and current must be continuously monitored, - battery real capacity must be continuously monitored
Batteries storage	Mechanical damage Heat damage	- the same as in transportation and installation activities, - mechanically damaged battery must be replaced and secured, - batteries can be repaired only by qualified personnel
	Electrical damage	- the same as in transportation and installation activities, - the battery should be stored partially charged (up to 50% of nominal capacity), - the battery must not be stored totally discharged

Above listed prevention activities are mandatory for ensuring safety during usage of lithium-based batteries. It is also possible to specify a list of rules for the operation of lithium-based batteries, which will allow their long and reliable operation. Below the 'best practices', which allow for cycle-life extension, are listed:

– if it is not necessary avoid 100% charge and total discharge;
– avoid fast charging (with high current value);
– avoid high discharge currents;
– avoid operation of the battery in high temperature (above 40°C);
– storing the battery in low temperature (between 0 and 20°C).

SUMMARY

The above presented information shows that modern technologies which allow to store in a small volume and weight large amounts of energy generate new threats and operational requirements that should be taken into account when designing the new vessels and the training of crews.

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ASPEKTY BEZPIECZNEJ EKSPLOATACJI BATERII LITOWYCH W ZASTOSOWANIACH MORSKICH

STRESZCZENIE

W artykule przedstawiono zagadnienia związane z bezpieczeństwem eksploatacji akumulatorów litowych na jednostkach pływających. W pierwszej części dokonano analizy przepisów PRS dotyczących wymagań w stosunku do akumulatorów stosowanych w okrętownictwie. W drugiej przedstawiono zagrożenia wynikające z zastosowania technologii magazynowania energii elektrycznej opartej na ogniwach litowych. Ostatnia część omawia zasady, jakie należałoby przyjąć podczas eksploatacji baterii litowych, aby zminimalizować ryzyko wystąpienia zagrożeń.

Słowa kluczowe:
akumulatory litowe, bezpieczeństwo, źródła zasilania dla jednostek pływających.