(Invited) Changes in Thermal Stability of Cyclic Aged Commercial Lithium-Ion Cells

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Thermal stability is one of several factors affecting the safety properties of lithium-ion cells. The thermal stability for uncycled cells is well-documented, but the effect of cyclic ageing on thermal stability is far less studied and only for 18650 sized cells. In this paper, we describe how different temperature and current loads are affecting the thermal stability during cyclic aging. Three cylindrical lithium-ion power cells with different cathode, energy content and size were cyclic aged. Decrease in thermal stability was found in all three cyclic ageing test series as a function of relatively high current and low temperature. The decrease in thermal stability could be dangerous and should be an end of life criterion.

Introduction

It is a well-known fact that lithium-ion cells have safety issues. Several battery fire incidents have been reported. Of the more famous ones are fires in the APU battery of Boeing Dreamliner (1), fire in the Chevrolet Volt battery (2) and Samsung mobile telephone recall (2016). Many factors can make a lithium-ion cell unstable and eventually start a fire: overcharge, overload, heat exposure, external shorts, overdischarge (followed by a charge) and internal shorts. If the cell or battery system is not able to handle the heat generation caused by these factors, this could evolve into decomposition of the cell material, physical reactions like ventilation, gassing, fire and in rare cases even explosions. Figure 1 shows different factors that could make a lithium-ion cell unstable (yellow and blue circles) and the potential physical reactions (red figures). Most of these factors can be controlled by an electronic system called battery management system (BMS), and the likelihood for a fire in a lithium-ion cell is very low. However, an internal short circuit under development cannot be detected by the BMS or any other commercially available systems today (3). The internal short may be caused by defects from production (*e.g.* particles) or as a result of cyclic degradation of the cell (blue circles shown in Figure 1). The probability of a safety issue (fires and explosions) is one in 1 million to one in 10 million (4), but should not be ignored especially for large batteries or when the battery is used in challenging applications.

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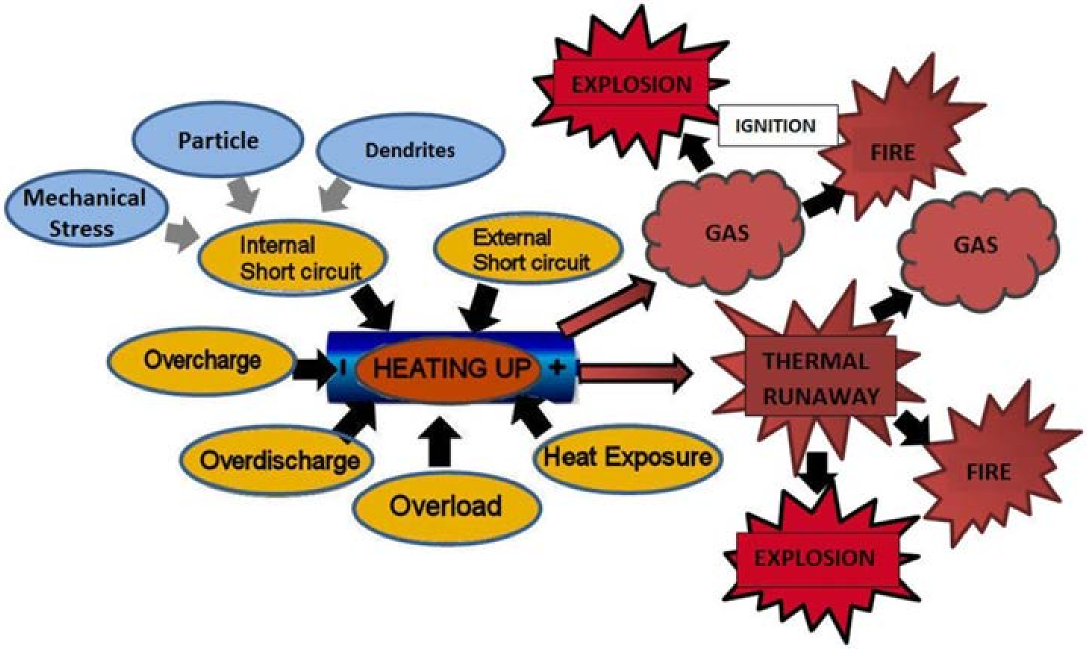

Figure 1. Overview of different factors that could affect the stability of a lithium-ion cell (yellow circles) and the reaction pattern leading to different physical reactions (red figures).

In Norway, there are economic incentives for changing from fossil fuel to electrical power in maritime applications. Fires in maritime applications are challenging, but the Norwegian Maritime Authority (NMA) rules require that a battery powered propulsion system should be as safe as a conventional propulsion line. Since the development of an internal short in a lithium-ion battery cannot be detected, the physical reactions of a lithium-ion battery must be managed by a robust battery design. The battery design needs to be approved in propagation tests as a verification of the design (5). During a propagation test, one or several lithium-ion cells are forced into fire either by heating, overcharge or nail penetration. The acceptance criterion is; no spread of fire between cells in a module or between modules.

The degradation effects of cyclic ageing of lithium-ion cells are complex and not fully understood (6, 7). If the thermal stability and physical reaction of the cell change, it could also affect its ability to pass a propagation test. The thermal stability for uncycled cells is well-documented (8-18), but the effect of cyclic ageing on thermal stability is far less studied (15, 19-21). Fleischhammer *et al.* conducted cyclic ageing at -10 °C, with decreased thermal stability as a result. However, the cycling was outside the specification given in the datasheet and lithium plating was found during post-mortem analysis. Friesen *et al.* reported a similar change in thermal stability for 18650 lithium-ion cells cyclic aged at 0 °C. The cells were cyclic aged to 70% of new capacity and post-mortem studies found evidence of lithium plating on the anode. Börner *et al.* on the other hand reported unchanged thermal stability and lithium plating after cyclic ageing at 20 °C on the same cell. These results indicate that lithium plating could be the cause of decreased thermal stability, but also that more work is needed in order to understand the conditions where lithium plating could reduce thermal stability of lithium-ion cells.

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Cyclic ageing reported in the literature were performed on small cylindrical 18650 cells. Literature on cyclic ageing of larger format lithium-ion cells has not been found. The 18650 cell is normally not used in larger energy storage systems for the maritime industry due to increased complexity and cost. There is a strong need to understand the safety aspects of cyclic aged large format power capable lithium-ion cells in the field of marine applications.

This paper addresses how different temperature and current loads affect the thermal stability of cyclic aged cylindrical lithium-ion power cells.

Experimental

Three cylindrical lithium-ion power cells with different cathode chemistries, energy content and size were cyclic aged as described in Table I. The cells were cycled at two different current rates: standard cycle (SC) or high-rate cycle (HC). The rates were all within the data sheet limits of each cell and all cells were cycled in the full state-of-charge window. Every 100-300 cycles all cells were characterized at 25 °C measuring remaining capacities at C/10 discharge rate. The measured discharge capacity during each cycle was normalized with respect to the nominal capacity of each cell type. The cumulative sum of these normalized cycles gave the total number of normalized cycles used in Tables II, III and IV. The thermal stability of the cells was determined using an EV+ accelerating rate calorimeter (ARC) from Thermal Hazard Technology. The ARC measures the thermal response of the cells as a result of controlled heating with a heat, seek and wait procedure. Heating is conducted in 5 °C steps. At each step the instrument waits for a certain number of minutes depending on the cell size, before entering a seek mode looking for exothermic reactions. When the cell starts to self-heat (0.02 °C/min), the temperature of the ARC follows the temperature of the cell, *i.e.* adiabatic conditions. If the exothermic reaction inside the cell halts, the controlled heating phase starts over. This continues either to the occurrence of the next exothermic response, or to the maximum achievable temperature of the ARC (250 °C).

TABLE I. Overview of the tested lithium-ion cells and the cyclic ageing conditions for each cell. SC is standard cycling and HC is high-rate cycling.

Cell nominal capacity		**1.5 Ah**	**6 Ah**	**30 Ah**
Cycle Temperature	**Cycling condition**	**Discharge/Charge rate**	**Discharge/Charge rate**	**Discharge/Charge rate**
5 °C	SC	1C/1C	1C/1C	1C/1C
5 °C	HC	2C/2C	3C/1.5C	
25 °C	SC	1C/1C	1C/1C	1C/1C
25 °C	HC	2C/2C	3C/1.5C	
45 °C	SC	1C/1C	1C/1C	1C/1C
45 °C	HC	2C/2C		

Results and discussion

The effect of cyclic aging on thermal stability was evaluated for three different cylindrical lithium-ion power cells. The remaining capacity is given as State of Health (SoH). This is the cell's remaining capacity relative to the cell's capacity as new. The results for each cell type are described in the following sections.

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Thermal stability and cyclic ageing of 6 Ah cylindrical cell

Electrical Energy. The capacity losses of the cyclic aged 6 Ah cells are presented in Table II.

TABLE II. Capacity loss (SoH) and normalized cycles for the 6 Ah cells under different cyclic ageing conditions. Standard condition (SC): discharge 1C and charge 1 C. High current cycling (HC): discharge 3C and charge 1.5 C.

Temperature	Cycling Current	Normalized Cycles	SoH
5 °C	SC	2280	79%
5 °C	HC	650	65%
25 °C	SC	4540	82%
25 °C	HC	4600	77%
45 °C	SC	3270	81%

Thermal stability. ARC tests were conducted on one cell from each cyclic aged test series and the results were compared with results from ARC tests of uncycled cells. Figure 2 presents the results from the ARC test of uncycled and cyclic aged 6 Ah cells.

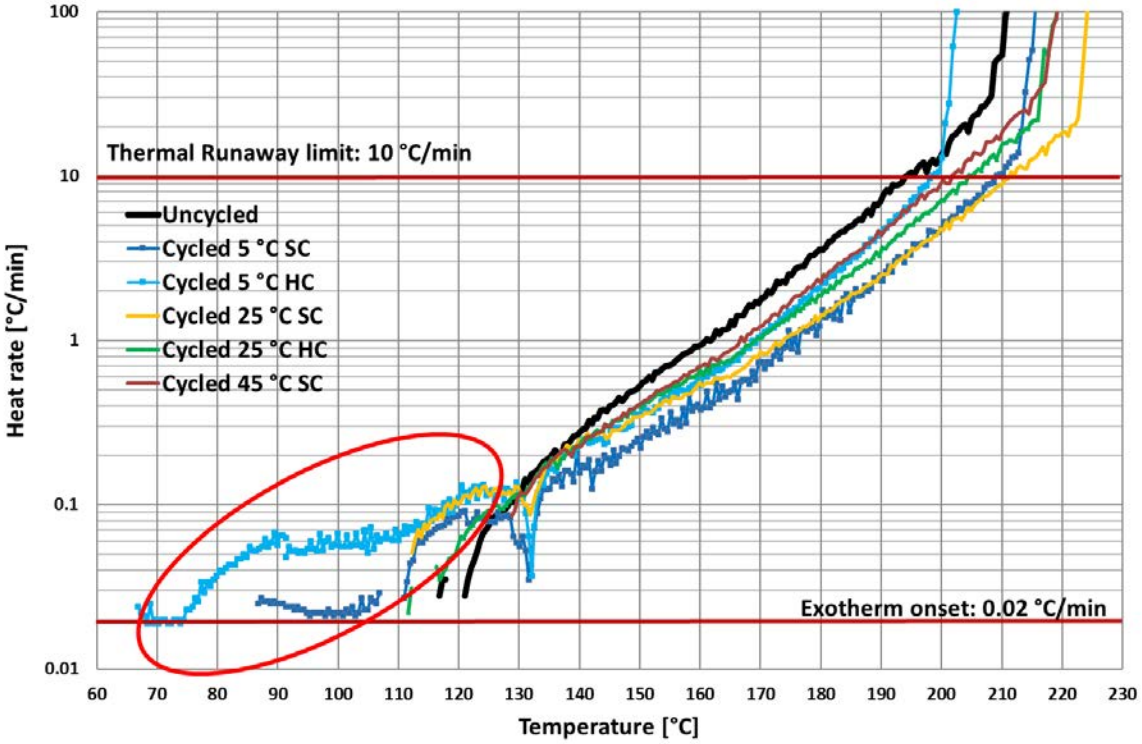

Figure 2. Heat rates as a function of temperature for uncycled and cyclic aged 6 Ah cells. Red ellipse presents changes in heat rates in the 60-120 °C area for some of the cyclic aged cells.

All the cyclic aged cells show decreased heat rates in the temperature interval 135-200 °C. The decrease in heat rates could be explained as a loss of cathode material and electrolyte during cyclic ageing (22). Some of the cyclic aged cells have an increase in heat rates in the 60-120 °C range. This is normally attributed to changes in the anode material (20, 23, 24). The increased heat rates seem to be related to cycling at low temperatures and high current rates. The cells with increased heat rates also give a new endothermic signal at 131-132 °C. A ventilation of a cell could give endothermic signals due to electrolyte

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evaporation, but all tested cells ventilate between 91 and 120 °C. The signal could be a combination of separator melting and evaporation of electrolyte. However, the origin of the endothermic signal need more investigations to be explained.

Thermal stability of cyclic aged 1.5 Ah 18650 cylindrical cell

Electrical Energy. The capacity losses of the cyclic aged 1.5 Ah cells are presented in Table III.

TABLE III. Capacity loss (SoH) and normalized cycles for the 1.5 Ah cells under different cyclic ageing conditions. Standard condition (SC): discharge 1C and charge 1C. High current cycling (HC): discharge 2C and charge 2C.

Temperature	Cycling Current	Normalized Cycles	SoH
5 °C	SC	800	65%
5 °C	HC	590	70%
25 °C	SC	940	81%
25 °C	HC	1100	71%
45 °C	SC	930	74%
45 °C	HC	880	68%

Thermal stability. ARC tests were conducted on one cell from each cyclic aged test series and the results were compared with results from ARC tests of uncycled cells. Figure 3 represents the results from the ARC test of new and cyclic aged 1.5 Ah cells.

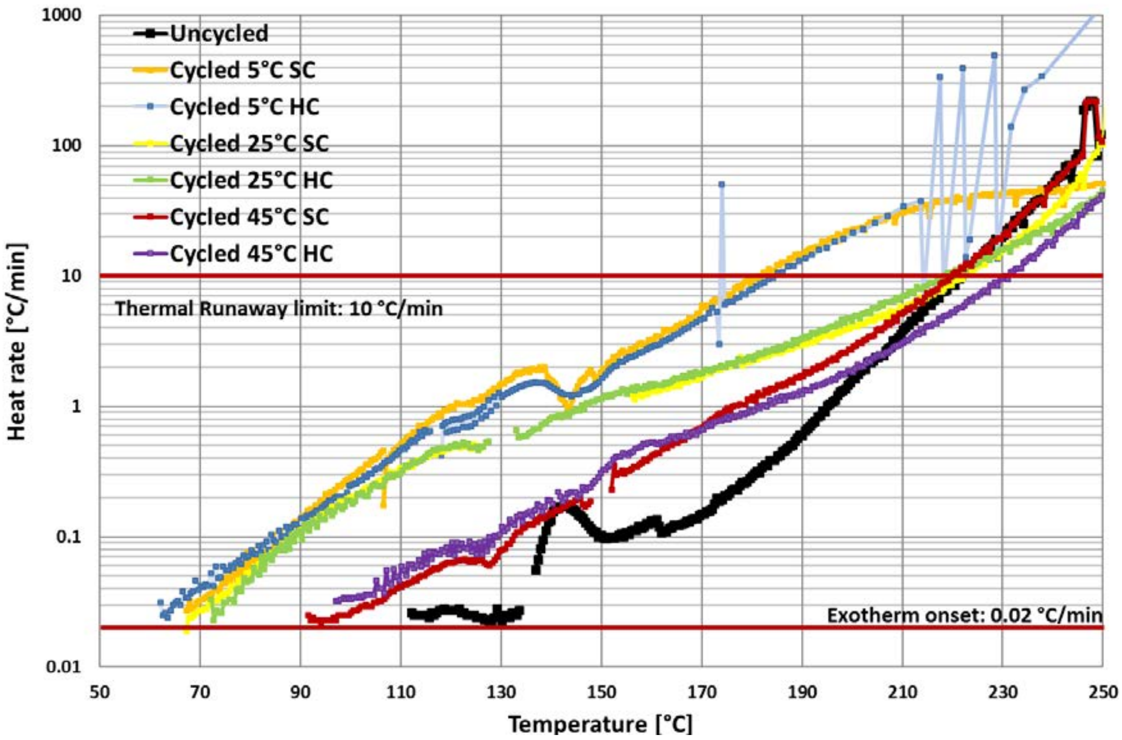

Figure 3. Heat rates as a function of temperature for uncycled and cyclic aged 1.5 Ah cells.

All the cyclic aged cells have an increase in heat rates in the 90-200 °C interval. For cells cycled at 5 and 25 °C accelerated self-heating starts at 66-75 °C, while uncycled cells are stable up to 110 °C. For the cell cycled at 45 °C there is an increase in the heat rate up to 200 °C, but the rate is much lower compared to cells cycled at 5 and 25 °C. Larger heat rates for cells cycled at 5 and 25 °C could increase the consequences of an internal short compared to an internal short in an uncycled cell. However, the amount of electrical energy that could be released into the short is less compared to an uncycled cell. If this amount of electrical energy is sufficient to initiate thermal decomposition of the cell there could be an increased risk of failing a propagation test when the cell is cyclic aged at 5 and 25 °C. The cyclic aging current rates do not seem to have any effects on the heat rates in the different temperature series.

Thermal stability and cyclic ageing of 30 Ah cylindrical cells

Electrical Energy. The capacity losses of the cyclic aged 30 Ah cells are presented in Table IV.

TABLE IV. Capacity loss (SoH) and normalized cycles for the 30 Ah cells under different cyclic ageing conditions. Standard condition (SC): discharge 1C and charge 1C.

Temperature	Cycling Current	Normalized Cycles	SoH
5 °C	SC	2910	72%
25 °C	SC	4900	81%
45 °C	SC	2900	77%

Thermal stability. ARC tests were conducted on one cell from each cyclic aged test series and the results were compared with results from ARC tests of uncycled cells. Figure 4 presents the results from the ARC test of uncycled and cyclic aged 30 Ah cells.

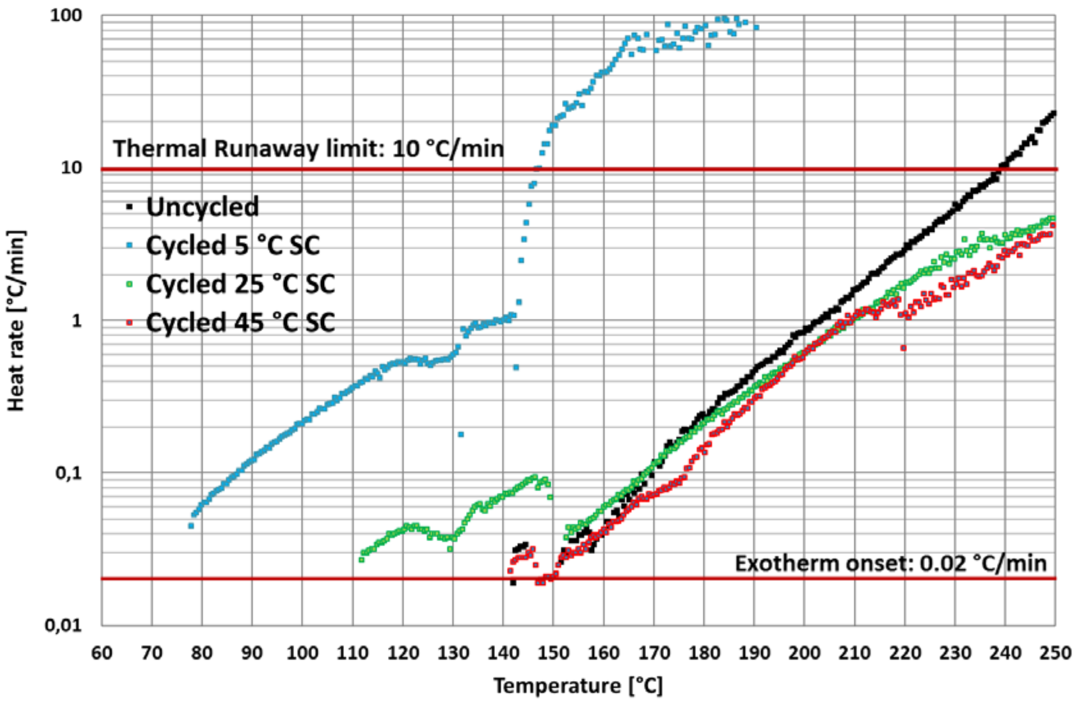

Figure 4. Heat rates as a function of temperature for uncycled and cyclic aged 30 Ah cells.

The cells cyclic aged at 45 °C SC and 25 °C SC show similar heat rates between 150 and 167 °C and a decrease in heat rates in the temperature region between 167-250 °C

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compared to uncycled cells. The decrease in heat rates could be explained as a loss of cathode material and electrolyte during cyclic ageing. The cell aged at 25 °C SC starts self-heating at 111 °C and shows higher heat rates up to 150 °C compared to an uncycled cell. The cyclic aged cell at 5 °C SC shows higher heat rates at all temperatures compared to uncycled cells. The onset temperature is reduced from 139 to 77 °C and the thermal runaway temperature drops from 238 to 147 °C. The accelerating response of the heat rates between 142 and 150 °C could be due to a short circuit inside the cell. The cell cycled at 5 °C SC experienced severe disintegration at the end of the ARC test. Figure 5 shows a picture of this cell after the ARC test.

Figure 5. Picture of the ARC interior after ARC test of the 30 Ah cell, cycled at 5 °C SC conditions.

An evaluation of physical reaction demands at least three parallel sessions and the results from this test does not fulfill this requirement. However, the combination of these findings could indicate that under certain conditions the cyclic aged lithium-ion cells loses thermal stability and might disintegrate totally during a thermal runaway.

Conclusion

Lithium-ion safety properties are well documented for uncycled cells. However, there is little literature on how cyclic degradation affects the safety. There is a strong need to understand the safety properties of aged, large, and power capable lithium-ion cells in the field of marine applications. This paper investigates how different temperature and current loads during cycling affect the safety properties of three cylindrical lithium-ion power cells with different sizes.

New and potentially dangerously safety aspects have been found in cyclic aged lithium-ion batteries. Decrease in thermal stability was found in all three-test series with high current and low temperature cycling even if the cells have been tested within the limits of the data sheet. The thermal stability decrease was minor for the 6 Ah cells but rather large and potentially dangerous for the 1.5 Ah and 30 Ah cells. As a result, one of

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the cells with decreased thermal stability experienced severe disintegration of the cell can cylinder during ARC test.

The decrease in thermal stability could be dangerous and should be an end of life criterion. An uncycled cell in a battery module may withstand the heat from a neighboring thermal runaway cell, while a cycled cell may be driven into thermal runaway. It is of vital importance to develop new diagnostic tools capable of detecting and possibly avoiding a dangerous drop in thermal stability in cyclic aged lithium-ion cells.

Acknowledgments

The authors want to acknowledge the funding received for the SafeLiLife project (project no. 228739) and BattMarine project (project no. 281005) from the Research Council of Norway. We also want to acknowledge MoZEES, a Norwegian Centre for Environment-friendly Energy Research, co-sponsored by the Research Council of Norway (project number 257653) and 40 partners from research, industry and public sector.

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