

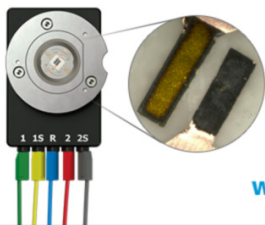
**OPEN ACCESS**

## Review—Review of Safety Aspects of Calendar Aged Lithium Ion Batteries

To cite this article: Christian Geisbauer *et al* 2020 *J. Electrochem. Soc.* **167** 090523

View the [article online](#) for updates and enhancements.

**Visualize the processes inside your battery!**  
**Discover the new ECC-Opto-10 and PAT-Cell-Opto-10 test cells!**



- Battery test cells for optical characterization
- High cycling stability, advanced cell design for easy handling
- For light microscopy and Raman spectroscopy

[www.el-cell.com](http://www.el-cell.com) +49 (0) 40 79012 734 [sales@el-cell.com](mailto:sales@el-cell.com)

**EL-CELL**<sup>®</sup>  
electrochemical test equipment





# Review—Review of Safety Aspects of Calendar Aged Lithium Ion Batteries

Christian Geisbauer,<sup>z</sup> Katharina Wöhrl, Christoph Mittmann,  
and Hans-Georg Schweiger

Technische Hochschule, Ingolstadt, Germany

Nowadays, lithium ion batteries have found their place in a various field of portable applications. With the upcoming of electrically propelled vehicles, it is mandatory to guarantee a safe and predictable behavior during the whole lifetime and not only after manufacturing during performance tests. To gain a general overview of the abuse behavior, research on the topic of abusive tests on calendar-aged cells is being investigated, split up depending on the electrode composition and lined up against each other. It can be shown, that almost all abuse experiments have been performed with external heating tests in the past, still leaving research gaps that need to be filled.

© 2020 The Author(s). Published on behalf of The Electrochemical Society by IOP Publishing Limited. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/1945-7111/ab89bf]



Manuscript submitted January 28, 2020; revised manuscript received March 26, 2020. Published April 27, 2020. *This paper is part of the JES Focus Issue on Battery Safety, Reliability and Mitigation.*

In the modern world, lithium-ion batteries are a common source of portable energy found everywhere in our daily live. From smartphones, laptops and cameras to e-bikes and e-scooters they have established their right to exist quite well. In the last years, the upcoming of electrically propelled vehicles naturally lead to a higher demand for battery systems capable of delivering the necessary power and energy needed for the vehicle.<sup>1</sup> In the year 2018, the total amount of BEVs (battery electric vehicles) was about 5.6 million cars globally, which translates to an increase of factor 10 in just five years compared to approximately 420000 vehicles back in 2013.<sup>1</sup> In the same time, the price for one kWh of storage capacity dropped massively and is expected to reach values of 84€ per kWh for 2020.<sup>2</sup> For a mid-class automotive battery system containing 50 kWh energy like e.g. Tesla's Model 3, the price of 20.000€ for manufacturing the cells in 2013 in comparison with the predicted value for 2020 of 4200€ is tremendous.<sup>2,3</sup> With the decrease in costs for battery production, EVs (electric vehicles) will become cheaper and more affordable for the consumer, leading to a wider variety of products and increasing the market share.<sup>4,5</sup> Amidst a broad EV adaptation it is absolutely necessary to have safe battery systems and to minimize the risks for the consumer and the environment. In consequence of lifetime estimations ranging up to 1.6 million km in an EV or two decades energy-buffering in the power grid, lithium ion storages need to be safe their whole lifetime and not only in pristine condition.<sup>6</sup> Current Li-ion-safety standards do not take the effect of ageing on overall safety into account when performing abusive tests.<sup>7</sup> ISO 12405-1 for example specifies a test called cycle life, which tracks the battery performance related to capacity fade and the increase of internal resistance due to charge throughput. After the procedure, no further abusive tests have to be performed at the EOL (end of life) of the system in order to pass the test.<sup>8</sup> This leads to the question of how the overall safety performance of li-ion cells during their first lifetime and towards EOL really looks like. The next paragraphs will give an overview of how and what research has been conducted in this field.

## General Ageing Concerns

Lithium ion batteries are dynamic electrochemical systems, which tend to behave differently over time. To make these changes visible, certain parameters have to be defined in order to compare different ageing states. A good way to describe the changes due to ageing is the so-called state of health (SoH), which in this paper is defined as the actual value divided by the original initial value in

pristine condition, although it might be the inverse or otherwise defined for the DC (direct current) resistance.

$$SoH_x = x_{now} / x_{init} \cdot 100\%$$

Typical physical parameters are often times the capacity and internal resistance. The second parameter can also be described as power capability, because those two values are directly correlated. In the later paragraphs when a SoH is mentioned, it refers to the capacity SoH.

When lithium batteries age, the capacity decreases while the internal resistance increases over time due to various mechanisms explained in the upcoming paragraph.<sup>9,10</sup>

To get a better understanding of the topic, ageing of lithium-ion cells can be divided into two different parts. Both parts consist of multiple processes that can overlap and thus happen simultaneously. On the one hand, there is calendar ageing. This form of ageing takes place all the time, independent of the current throughput in a lithium-ion cell. The second category of ageing is called cyclic ageing. The parasitic side-reactions taking place during this phenomena are caused by charging and discharging the battery. A common approach is to separate both mechanisms and investigate them independently.<sup>11,12</sup> Calendar ageing happens for all of the EV-lifetime, when the vehicle is stationary. Parasitic side-reactions in the electrolyte of the cells take place and the reaction rates show a correlation with storage temperature and storage state of charge (SoC), although they differ with various cell chemistries.<sup>10,13</sup>

The formation of the solid electrolyte interface (SEI) on the negative electrode plays a big part on the main degradation mechanisms in lithium ion batteries. The contact area between the negative electrode and the electrolyte shows a high reactivity, which builds up the SEI layer as a reaction between the electrolyte and lithium ions during the formation of the cell.<sup>14</sup> With continuous growth of this layer, e.g. due to cracks in the anode or SEI decomposition,<sup>9</sup> lithium corrosion occurs, cyclable lithium is lost and therefore the capacity decreases. The accumulation of this layer can also lead to a reduction of the power capability of the anode,<sup>14,15</sup> hence increasing the impedance. This process also takes place when the cell is at rest and the degradation is caused by the thermodynamic stability of the single components, especially the electrolyte and anode.<sup>14</sup> The SEI only forms when the voltage of the anode drops below around 1 V vs Li/Li + during cell formation.<sup>15</sup> LTO (Lithium-Titanate-Oxide) cells do not form such layer on the anode and are thus less likely to degrade.<sup>15</sup> Not only the growth of the SEI, but also the dissolution and precipitation of the SEI, exfoliation of graphite and intercalation of solvents can occur at the anode surface

<sup>z</sup>E-mail: christian.geisbauer@carissma.eu



Because of the waiting steps included every cycle, the whole experiment may take up to several hours.

Figure 1 gives an overview of the temperature trend and the key temperatures during a typical HWS external heating experiment. After a few external heating steps the cell starts to heat up on its own, followed by the meltdown of the separator. After an internal short circuit, the SHR of the cell starts to increase rapidly at  $T_{OTR}$ , releasing huge amounts of heat. This point is described as “point of no return” in this work, because the temperature increase can't be compensated by the cooling system anymore.<sup>42</sup>

Another common method is to use a thermostatically controlled oven to heat the cells.<sup>43,44</sup> This process does not include any waiting cycles and just increases the temperature over time. This means, it is faster than the aforementioned process. Because the SHR of the cell is not taken into account, the extracted thermal-runaway (TR) temperature may be a bit higher than the actual TR-temperature. The different durations of the two processes lead to a significant divergence when comparing distinct external heating research results.<sup>36</sup> The longer time spent at elevated temperatures during ARC-Tests gives room for potential side reactions of the electrolyte and possible breakdown of the solid electrolyte interface (SEI). When these reactions take place at lower temperatures, the electrolyte-electrode-reactions required for the TR may not be as energetic to be able to power the TR at higher temperatures.<sup>36</sup> Larsson et al. performed a direct comparison of two cells from the same batch. One was heated with a fixed external heating rate; the other one was put in an ARC-chamber. The TR temperature was obtained in a similar manner each time and it was found, that the two values differed by about 50 °C.<sup>36</sup> This means, it is very crucial to consider the methodology of different testing techniques when comparing studies.

**Experiments divided by electrode composition.**—In the following paragraph a short summary of various experiments on different electrode compounds on calendar aged cells is given. The composition of considered experiments are displayed in Table I.

**Cells containing Nickel-Manganese-Cobalt-Oxide (NMC) cathodes.**—Röder et al. performed calendrical ageing on 18650-cells containing a NMC (1,1,1) cathode with LMO (Lithium-Manganese-Oxide) blend (3:1) and pouch cells with the same blend, but different ratio (4:1).<sup>37</sup> They were stored at 60 °C at full SoC (4.2 V) for 36 weeks, every 6 weeks the capacity and power capability was measured. At the end of this period, the capacity decreased to about 65% of the initial capacity and the internal resistance at almost all measured SoC steps doubled to the initial value. Afterwards, the cells and both electrode materials were examined via ARC, DSC (differential scanning calorimetry) and other electrochemical processes such as slow-scan voltammetry, EIS (electrical impedance spectroscopy) or similar. The results show that the increase of the internal resistance is linked to the SEI growth and reduced conductivity of the electrolyte. Manganese deposits on the anode dissolved from the cathode also lead to an acceleration in capacity decrease. For the ARC measurement, a starting temperature of 80 °C, steps of 5 °C and a self-heating threshold of 0.02 °C min<sup>-1</sup> were used. The researchers found, that for the aged cells, the more pronounced SEI on the graphite-anode leads to a 5 °C lower OER (onset of exothermic reactions) temperature of 105 °C. According to<sup>37</sup> the voltage on the terminals for both new and aged cells increased due to the shutdown mechanism of the separator at a slightly lower temperature around 100 °C. In the same instance, the total energy released during the exothermic reaction of the anode is decreased because of less total cyclable lithium at full lithiated state, which can no longer react with the electrolyte. Interestingly, for very low temperatures below 100 °C, the fresh cells show minor exothermic reactivity (0.01–0.05 K min<sup>-1</sup>) at approx. 90 °C, whereas the aged cells show a similar reactivity already at 70 °C. In contrast to graphite, the electrolyte-reaction of the cathode shows

no major difference due to no change in the potential of the cathode with ageing, although the greater SHR above 200 °C can be attributed to cracks in the LMO particles in the positive electrode, which lead to a higher surface area and thus more reactivity for aged cells.<sup>37</sup>

Ageing does impact the safety parameters of the reviewed NMC cells, with reactions starting at lower temperatures and thus giving more relevance to a functional cooling system and an operating range at lower temperatures. When a thermal runaway is inevitable, the reaction at higher temperatures proceeds faster.

**Cells containing Nickel-Cobalt-Aluminum-Oxide (NCA) cathodes.**—Compared to NMC cells' close relative, Roth et al. investigated the thermal performance of NCA cylindrical cells back in 2004 and categorized the occurring exothermic events into the three phases mentioned earlier. ARC, DSC and thermal ramp tests with commercial LCO (Lithium-Cobalt-Oxide), Nickel-Cobalt-Oxide and NCA cells (Gen2-Cells) were used.<sup>39</sup> This paragraph will focus on the NCA chemistry. ARC-tests were carried out on full cells and their single components, whereas DSC-tests were done on single electrodes only. Twelve cells were aged at 45 °C, 80% SoC for eight weeks until they had reached a capacity decrease of 15%. The ARC measurements were performed at 60% and 100% SoC. When both aged and unaged subjects were lined up against each other, the aged cells showed a lower heating rate (SHR = 0.1 °C min<sup>-1</sup> @ 115 °C) than their counterpart did (SHR = 0.1 °C min<sup>-1</sup> @ 105 °C). The authors explain this via a passivation layer on the anode, which slows the electrolyte reduction by the lithiated carbon. For the 60% SoC test, the results are similar, but the difference in the heating rates are less pronounced. The aged cells in both cases vented, which indicates that there was a continuous gas formation during the ageing process, which increased the initial pressure before the experiment. DSC-scans of both sets at 100% SoC showed that over the whole temperature range the reactivity of the aged negative electrode decreased. For the cathode, the reaction peak moved to a slightly lower temperature.<sup>39</sup> In this case, the initial heating of NCA cells is slower, leaving more time for the heat energy to dissipate and thus react in a safer way with increased storage duration, although the buildup of gases due to ageing needs to be taken into account when designing cell or module cases.

**Cells containing Lithium-Cobalt-Oxide (LCO) cathodes.**—Two research groups conducted experiments on the subject of aged LCO cells. The authors from<sup>39</sup> further looked into the thermal behavior of commercial 18650 cells with a cobalt-oxide cathode. The ageing process was split into the following three groups: 6 months at 25 °C, 2 weeks at 60 °C and 6 weeks at 70 °C.<sup>39</sup> The storage SoC was not mentioned. Afterwards the test subjects were put into individual ARC runs at 100% SoC. The aged cells showed lower heat rate at lower temperatures than the fresh cell. With increased ageing time and temperature, the onset of sustained exothermal output is being pushed into a higher temperature range. A possible explanation given by the authors would be, that the SEI converted partially from a metastable form into an inorganic species even at low temperatures. The aged cells also vented at low SoCs during the abuse, which can be explained by continuous gas generation during ageing and thus adding onto the gas generation throughout the abuse experiment. At high temperatures and after the decomposition of the SEI layer, the results are similar to fresh cells.<sup>39</sup>

Secondly, Larsson et al. performed external heating measurements on commercial 6.8 Ah prismatic cells. They were aged in both ways, cyclic and calendric, but for this paper, the focus will be on the calendar-aged cells. The ageing step consisted of a ten-month period at 60 °C and 100% SoC with a preceding storage span of one year at 20 °C. After this time, the voltage of both calendar aged cells dropped below 1 V and the thickness from the cells has increased. Next they were put into a thermostatic controlled oven with the other test subjects and slowly heated. In contrast to the working cyclic



aged cells, the dead cells did not show any sparks, flames or flares when undergoing thermal runaway. In comparison, the nonfunctional cells showed less reactivity with a higher TR-temperature, slower rise times and lower peak temperatures.<sup>36</sup> Because the cells were not in the normal SoC range, the results of these experiments cannot be compared directly with other findings in this review paper, yet they give information about the safety in an over discharged state after ageing. With a voltage below 1 V, the cells contained less stored energy than those with 100% SoC and thus show less exothermic reactions, which indicates that a neglected battery system stored for years without recharging naturally deactivates itself over time. To get a complete understanding of this topic, a wider range of investigations needs to be done. For the gas analysis, no calendar aged cells were directly investigated, but the other tracked test subjects showed no correlation between fire occurrence and HF generation. For all four cells that used gas measurement, HF was present during the third venting when the main vent opened.<sup>36</sup> With no dependency of fire occurrence and no online tracking for dead cells, a quantitative extrapolation for dead cells is not reasonable, but considering the fact that all other measured cells released HF it is likely that HF did occur for the dead cells as well during venting.

In conclusion, the safety performance of the first LCO cell group during the initial heating stage got better with storage time, but similar to NCA, the cells leaked gas even at SoCs below 100%. The safety risk coming from the prismatic cells in the second experiment also decreased drastically with a less pronounced thermal reactivity at higher temperatures, but this behavior cannot be traced back directly to ageing, a closer fitting explanation would be the over discharged state of the cells.

*Cells containing Lithium-Manganese-Oxide (LMO) cathodes.*—LMO pouch cells have been investigated by Zhang et al. for their thermal behavior after ageing in an ARC-chamber. 20 cells with 4.6 Ah containing an EC + LiPF<sub>6</sub> electrolyte were aged to five different ageing states. They were stored at 55 °C and 100% SoC for 10, 20, 40, 68 and 90 d.<sup>40</sup> In comparison to other studies mentioned in this article (see LFP and NMC section), the rate of capacity decrease over time is rather high. After 20 d, the cells lost 14.9% in capacity and at the end of the 90 d period a 32.0% capacity decrease can be found. The two explanations given for this phenomena are the combination of loss of reversible lithium ion and loss of active material. During the ARC-Test, every cell went through three phases consisting of a stable, a self-heating and a thermal runaway (TR) period. The temperature after the first phase (T<sub>OER</sub>) was around 115 °C for cells stored for 10 d and increased to about 150 °C after 90 d and is associated with the SEI decomposition. The second important temperature is the point at which the OCV drops to zero, which is an indicator for an internal short circuit (separator loses its function). In regards to ageing, T<sub>2</sub> did not change significantly, only after 90 d it dropped from around 140 °C to 120 °C, even though the cell was still stable at that point. The thermal runaway temperature T<sub>TR</sub> (dT/dt > 0.5 °C min<sup>-1</sup>) increased with time from almost 180 °C at 10 d to 195 °C after 90 d.<sup>40</sup> This means, that the overall safety of the cells even increased over time. The authors explained this contradiction with other sources<sup>37</sup> with a higher threshold for the SHR (0.03 °C min<sup>-1</sup>) of the ARC-system.<sup>40</sup> A higher threshold would mean that smaller temperature gradients would not be noticed and thus T<sub>OER</sub> would be higher. For the increase of T<sub>TR</sub> with increased ageing, the researchers gave the explanation that the passive film on both electrodes, which formed during the ageing process, consumed active material, which would be required as an exothermic source for the TR.<sup>40</sup> In summary, the TR risk did not vary greatly, but got shifted to a slightly higher temperature resulting in a delayed reaction.

*Cells containing Lithium-Iron-Phosphate (LFP or LiFePO) cathodes.*—Experiments with LFP cells have been conducted by

Abada et al. in order to gain input information for and to validate their physical thermal runaway model.<sup>34</sup> The researchers not only wanted to model the TR in simulation via chemical and physical equations, but also take the effect of ageing into account. For this intent cylindrical LFP cells with a capacity of 2.3 Ah were aged for two different time spans:

The first group was aged for 75 d at 60 °C/100% SoC and the second one at the same conditions but for 340 d. The capacity loss of the 75 day cells was around 10 ± 3%, whereas the 340 day cells lost about 30 ± 3%. To parametrize the model, an external heating experiment with a heat wire was set up with cells at 100% SoC. The procedure was analogue to a HWS-setup consisting of a start temperature of 30 °C and incremental steps of 5 °C, with a self-heating detection threshold of 0.02 °C min<sup>-1</sup>. The OER of the cells was found to be at 107 °C, the separator melting, resulting in a slight endothermic phase, was at 137 °C and the OTR itself started at 173 °C. In a second external heating experiment, the model was validated in a more real-life based scenario with no adiabatic conditions in an oven. Overall, the OER temperature increased with ageing duration, the same goes for the separator melting temperature, which might be linked to mechanical stress. In contrast, the OTR temperature did decrease over time. The authors do limit the possibility to draw conclusion from the positive effects of ageing, i.e. the shift of OER and separator melting towards higher values, because of the delayed self-heating stage in the HWR-setup. The computational model showed a correlation between the delay of the OER for the aged cells because of a thicker SEI film and the resulting diffusion limitations.<sup>34</sup>

Del Corso et al. performed abuse tests with fresh and new cells in the EU project HELIOS (High-Energy-Lithium-Ion-Storage-Solutions). NCA, NMC, LMO-NCA (LMO-blend) and LFP cells were aged and compared, although this was not the only focus of the project. The four types were stored at 60 °C and 100% SoC. In this study, the LFP cells lost about 50% of their initial capacity after 24 weeks. The LMO and NMC test subjects still had 70% capacity after 48 weeks. In contrary, the NCA cells performed the best and had about 92% after 48 weeks. The authors explain this huge difference with a rather short improvement period for the LFP, NMC and LMO chemistries (they were self-produced), whereas the NCA cells were commercially available and therefore longer optimized. A nail penetration test and thermal stability test was carried out with pristine and aged 40 Ah (for LMO: 28 Ah) cells.<sup>45</sup> The thermal abuse test was only conducted with cycle-aged cells and not with calendar-aged subjects. The nail penetration test was performed on two fresh cells and on one aged cell of each category, where a 3 mm conductive nail was pushed through the radial side of the cylindrical cell with 3 mm s<sup>-1</sup>. The results of all the tests were evaluated according to the EUCAR hazard levels.<sup>46,47</sup>

Table II gives an overview of the safety rating for the tested cells. The LFP cells get a rating of level 4 (venting, no fire/rupture) for the initial and the aged state. For the nail penetration test, the LMO-NCA cell's safety decreased from level 4 to 5 (fire/flame, no rupture/explosion) with ageing, where on the other hand the NMC cells even improved from level 6 (rupture, no explosion) to level 4. The NCA cells stayed consistent with a rating of level 5.<sup>45</sup>

Without additional factors like key-temperatures for the ARC tests and detailed behavior on single tests, no further conclusion can be drawn except that LFP cells have the best overall rating in this comparison and NMC cells even improved with the state of ageing opposed to LMO and NCA in the case of an intruding nail. For the first test, a higher OER and separator melting temperature could be observed, but was linked with a lower TR temperature. Due to a delayed period at lower temperatures, a reasonable conclusion in terms of hazard development can't be drawn.

*Cells containing Lithium-Titanate-Oxide (LTO) anodes.*—The literature for cyclic<sup>48-51</sup> and especially calendar<sup>10,48,49</sup> lifetime performance of LTO cells is relatively scarce. To the authors'

**Table I. Comparison of calendar ageing procedures considered in this work.**

Source	Ageing temperature	Duration	Chemistry	Tests
37	Calendar, 60 °C	252 d	NMC/LMO	ARC, DSC, EIS
39	Calendar, 45 °C, 55 °C for DSC	56 d, 140 d for DSC (single electrodes)	NCA	ARC, DSC
39	Calendar, 60/70 °C	14/42 d	LCO	ARC
36	Calendar/Cyclic, 60 °C	240 d	LCO	ARC, external heating, Gas analysis
40	Calendar, 55 °C	10, 20, 40, 68, 90 d	LMO	ARC
45	Calendar/Cyclic, 60 °C	336 d	LMO, NCA, LFP, NMC	Nail penetration
34	Calendar, 60 °C	75/340 d	LFP	ARC, external heating

**Table II.** Comparison of EUCAR hazard level rating change caused by ageing during nail penetration from Ref. 45.

	Rather safe		Less safe		Unsafe
Initial	LFP (4)	LMO/NCA (4)	NCA (5)	x	NMC (6)
48 weeks @ 60 °C	LFP (4)	NMC (4)	LMO/NCA (5)	NCA (5)	x

knowledge, no safety abuse tests for calendar aged LTO cells have been reported and thus no statement about their safety performance can be drawn.

### Discussion

Even though there has been lots of research conducted in the field of cyclic and calendar ageing, it was more dedicated towards the electrochemical performance, i.e. the mechanisms of impedance growth and capacity loss, and less directed towards the changes in safety and hazard analysis. The latter still has to be taken serious, because it could be shown that there is an observable change during abuse scenarios for calendar aged cells over time. The changes of the key temperatures are shown in Fig. 2, where the arrows display the changes of the key temperatures during ageing from new to aged.

Except for one mechanical nail test, the available research was concentrated on the thermal behavior above standard operating temperatures of lithium ion cells.

**Initial exothermic behavior during thermal abuse.**—As Fig. 1 illustrates, the first heating phase is initiated by the decomposition of the SEI, followed by electrolyte reactions with the anode, resulting in a temperature ramp until the separator melts.<sup>40,42</sup>

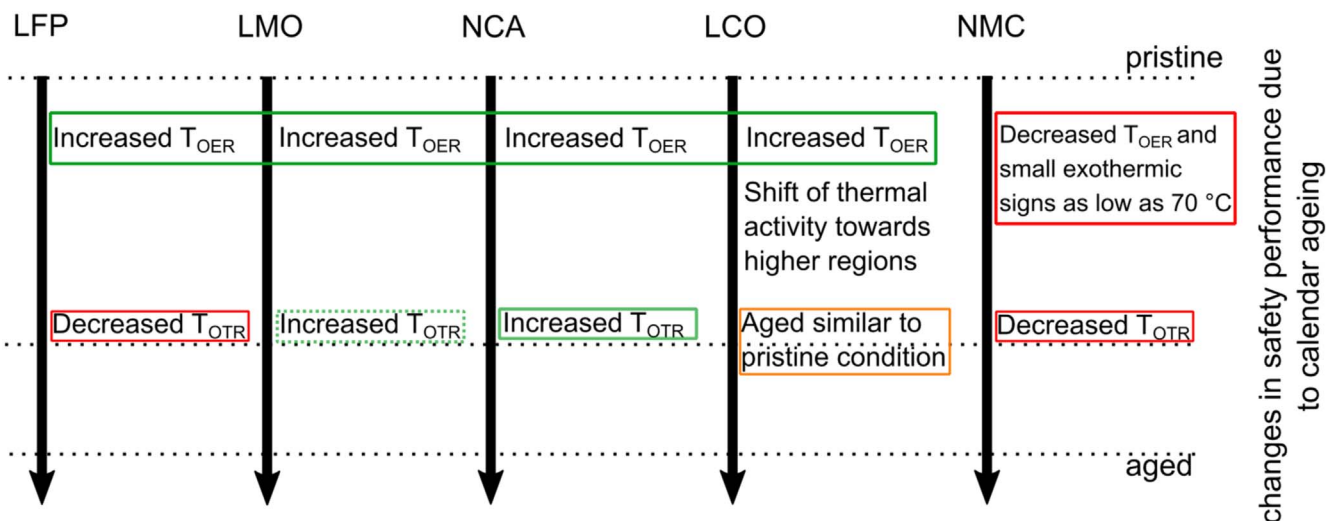
Findings on commercial LFP cells showed an increase of OER temperatures with ageing, which can be traced back to the increased thickness of the passivation layer on the anode and hindered diffusion reactions. A similar trend was observed for LMO cells that also used graphite as anode material. The increase in  $T_{OER}$  for aged LMO cells was rather high with a delta of 80 d leading to a difference of 35 °C, whereas the change for LFP cells, which also used a graphite electrode, was about 13 °C after 340 d. The OER also occurred at much lower temperatures for LFP cells (80 °C–92 °C), resulting in a delta of 35 °C between fresh LFP and LMO cells and approximately 45 °C for both aged cells respectively. Even though both experiments lead to the conclusion of a shift of the initial exothermic behavior towards higher temperatures, the absolute discrepancy in temperatures can be explained with a lower SHR-detection limit for the LMO setup of 0.03 °C min<sup>-1</sup> instead of 0.02 °C min<sup>-1</sup>. This alteration leaves less pronounced exothermic reactions undetected at lower

temperatures and thus leads to a higher  $T_{OER}$ . In accordance with the first two findings, NCA cells also did show an increase in  $T_{OER}$  of 10 °C after eight weeks of storage at 45 °C and characterized at full SoC. The measurement at 60% SoC shows less deviation between the aged and the pristine cells with less total energy in the system.

The available data for LCO cells, which also contained graphite anodes, shows an increase of  $T_{OER}$  with ageing and storage temperature. Even though the storage duration was comparatively short with a length of two weeks at 60 °C for the first group and six weeks at 70 °C for the second, a shift of the exothermal activity to higher temperatures can be observed. Unfortunately, the LCO cells stored for eight months by Larsson et al. did show voltage below the operational limit and were therefore described as dead cells.

In contrast to the previous results, research on Graphite/NMC cells shows a slightly decreased OER temperature with ageing. Because the onset temperature range around 100 °C is dominated by the anode reaction and the corresponding SEI dissolution<sup>52–54</sup> both appearances of the temperature rise are in correlation with the anode reaction. In direct comparison of both cases where a SHR threshold of 0.02 K min<sup>-1</sup> was used, i.e. LFP and NMC, a slight contradiction of an increase and decrease of the OER with calendar ageing for both instances containing a graphite electrode occurred. This is explainable with differences in the whole measurement setup, such as the heating-method via heat wire for the LFP cells or the atmospheric argon environment for the NMC ARC setup. In addition, the possibility of different additives in the electrolytes and resulting differences in the SEI composition may be a reason. Also, the additional 90 d of ageing for the LFP cells could have led to a more pronounced SEI, which further hindered the diffusion process during SEI decomposition and therefore increased the onset temperature. Interestingly, the NMC/LMO blend showed first signs of exothermic behavior at temperatures as low as 70 °C, demonstrating the importance of research on the safety behavior during ageing.

**Onset of thermal runaway (OTR).**—The OTR is the last point before a steep temperature ascent in a short period of time, oftentimes preceded by the meltdown of the separator and the



**Figure 2.** Comparison of key temperature changes of external heating experiments conducted on calendar aged cells.

following internal short circuits releasing a huge amount of thermal energy. The exothermic reaction at higher temperatures ( $>150\text{ }^{\circ}\text{C}$ ) is generally associated with the cathode reaction and further electrolyte decomposition<sup>40</sup> leading to the TR.

For both LFP and NMC cells the temperature needed for the TR decreases with storage duration, resulting in an earlier thermal runaway onset and potential hazards. LFP decreased by about  $20\text{ }^{\circ}\text{C}$  at a SoH of 70%, whereas NMC only decreased by  $5\text{ }^{\circ}\text{C}$  at 50% SoH. Even though the temperature, at which the separator melted, did increase with storage duration for LFP cells, the corresponding  $T_{\text{OTR}}$  decreased. The explanation given by the authors is possible ageing of the PP (Polypropylene)-separator by mechanical stress. The shut-down-effect of the NMC cell separator took place at the same temperature for new and aged cells, but was made of PP-PE (Polyethylene)-PP and the absolute melting temperature was lower than for LFP cells. Depending on which derivate of PP was used, the melting point for PE is typically a bit lower than for PP,<sup>40</sup> giving a shutdown effect at lower temperatures in comparison with pure PP. As mentioned by the authors of,<sup>34</sup> the ageing effect of the separator itself is not fully understood yet. The PE-separator melting temperature for the LMO cells only changed significantly for the 90 d aged cell and dropped by about  $20\text{ }^{\circ}\text{C}$ .

In contrast to LFP and NMC, LMO cells showed an increase for the OTR temperature with storage time and the exothermic rate at this temperature region also reduced. The detection limit for exothermal events was set to  $0.03\text{ }^{\circ}\text{C min}^{-1}$  in comparison with  $0.02\text{ }^{\circ}\text{C min}^{-1}$  for both previous findings, which may lead to higher detected values for both  $T_{\text{OER}}$  and  $T_{\text{OTR}}$  and although the exothermic rate in the upper range also decreased, it is not safe to conclude that the overall safety increased.

LCO cathodes, with generally the lowest side reaction temperature of the aforementioned materials,<sup>40</sup> showed no big changes during the process of ageing. In a different investigation it was shown, that LCO cells with less than 1 V OCV had a slight increase in the OTR temperature of  $10\text{ }^{\circ}\text{C}$ – $15\text{ }^{\circ}\text{C}$  and the maximum average temperature was slightly lower than for fresh cells and cells cycled up to 300 cycles. The reason for the  $T_{\text{OTR}}$  increase of both dead cells may just simply be less electrochemically stored energy which could be released in order to start the TR process quickly. This claim can be supported by the fact, that the cells had a lower  $T_{\text{TR}}$  peak temperature than fresh and working cycle-aged cells and that no signs of sparks, flames and gas explosions were present. Unfortunately there was no reference cell, which was calendar aged and not dead to compare the influence of the voltage loss during ageing on safety. With this result, one can only conclude that aged cells that self-discharged during storage tend to show a decreased risk during external heating, but still undergo TR when enough activation energy is present. All working cells that had gas monitoring released HF (hydrogen fluoride) during the biggest venting and the presence of HF did not correlate with a fire/flame occurrence. Therefore it is plausible that the calendar aged dead cells also released HF, which is highly toxic and harmful in direct contact with skin tissue. A dependency on ageing state for neither cyclic or calendar aged cells could be found.

The fully charged aged NCA cell showed less steep heating rates in the lower temperature range up to  $150\text{ }^{\circ}\text{C}$  during external heating experiments. The cells tested at 60% SoC behaved more similar to fresh cells at the same SoC, although they had a slight lower heating rate overall. Those findings were confirmed by DSC of both single electrodes, which indicates less heat flow for the calendar aged anode, which was also shifted into a higher temperature region. With increased ageing up to 20 weeks, the exothermal reactivity further decreases. The cathode reactivity increases and shifts slightly towards higher temperatures and decreases drastically after 20 weeks at  $55\text{ }^{\circ}\text{C}$  storage. The divergent exothermic behavior at 100% SoC can be explained with the loss of cyclable lithium, which reduces the absolute stored electrical energy at full charge. At 60% SoC, dependent on the SoC definition itself, the difference may not be as powerful to alter the abuse performance significantly.

At last, the short overview of four cathode chemistries given by Del Corso et al.<sup>45</sup> compares the safety performance during nail penetration. The EUCAR safety rating during nail penetration is shown in Table II. An external heating experiment was also conducted, but not with calendar aged cells. Unfortunately no key parameters are available for each test, therefore any conclusions will be derived from the hazard rating. Apparently the storage at elevated temperatures did not show any relevant changes for LFP and NCA cells considering their safety, whereas the safety performance of NMC cells improved from signs of fire, flames and rupture to only gas venting. In contrast, after ageing the LMO/NCA test subjects showed decreased safety performance with appearance of flames. Compared with the results from the previous findings on external heating research, the results from the nail penetration deviate. Where NMC cells showed a decreased  $T_{\text{OTR}}$  after 36 weeks ageing, the hazard rating in a nail penetration setup resulted in a more safe behavior after 48 weeks storage. A comparable effect for LMO can be found in the opposite direction, where  $T_{\text{OTR}}$  increased with ageing, but the hazard rating for nail penetration worsened with ageing. The intruding nail, resulting in internal short circuits, possibly started the exothermic reactions inside the cell much quicker than heating the cell from the outside in small increments, therefore reaching temperatures higher than the required  $T_{\text{OTR}}$  shortly after nail impact. On another note, the SEI decomposition reaction, which appears at lower temperatures than  $T_{\text{OTR}}$ , has enough time to take place during the longer waiting and heating steps in an external heating experiment and thus release part of the total chemical energy of the system early on. During the nail experiment there is no such time, so the ongoing reactions could behave differently. This on the other hand is by far an insufficient explanation and further research is needed in order to get a more in depth look on the differences between different ageing and abuse cases and the consequences for the safety behavior. A last important aspect is to take the gas generation due to ageing into account.<sup>55</sup> The gases released during venting can generally lead to fire and even explosions<sup>36</sup> and the additional gases due to SEI buildup might lead to a different gas mixture when undergoing TR. The gas generation for cells with a fixed volume, e.g. cylindrical cells with a metal housing or multiple pouch cells packed together in a metal container as a module, leads to an increased pressure buildup over time. When the safety vents open and the gases are inside their flammable limits, an ignition source could lead to a fire and further accelerate the OER or in the worst case, lead to an explosion.

In summary, the aforementioned facts and findings ultimately highlight the necessity for a wider in depth look on the differences in safety rating and accompanied performance losses in order to detect failures early on. With more information about the ongoing abuse processes for a wide variety of current and upcoming cell materials, a full comparison of safety parameters caused by ageing can be determined and compared. For now, such study still has to be conducted in order to fill the research gaps.

## ORCID

Christian Geisbauer  <https://orcid.org/0000-0002-0481-8438>

Hans-Georg Schweiger  <https://orcid.org/0000-0003-0184-1322>

## References

1. ZSW, (2019), Weltweite Bestandsentwicklung von Elektroautos in den Jahren 2012 bis 2018.
2. Horváth & Partners, (2018), Weltweite Preisentwicklung für Lithium-Ionen-Batterien von 2013 bis 2020 (in Euro/kWh).
3. F. Lambert, (2017), Tesla Model 3: Exclusive first look at Tesla's new battery pack architecture.
4. E. Bannon, (2019), Electric surge: Carmakers' electric car plans across Europe 2019–2025 Electric surge: Carmakers' electric car plans across Europe –2025.
5. T&E, (2019), Anzahl angebotener Elektroautomodelle in Europa nach Herstellern in den Jahren 2012 bis 2025.
6. J. E. Harlow et al., *J. Electrochem. Soc.*, **166**, A3031 (2019).
7. V. Ruiz, A. Pfrang, A. Kriston, N. Omar, P. van den Bossche, and L. Boon-Brett, *Renew. Sustain. Energy Rev.*, **81**, 1427 (2018).



8. (2011), Electrically propelled road vehicles - Test specifications for lithium-ion traction battery packs and systems, 43.120(ISO 12405-1:2011(E)).
9. C. R. Birkl, M. R. Roberts, E. McTurk, P. G. Bruce, and D. A. Howey, *J. Power Sources*, **341**, 373 (2017).
10. M. Dubarry, N. Qin, and P. Brooker, *Current Opinion in Electrochemistry*, **9**, 106 (2018).
11. J. de Hoog, J.-M. Timmermans, D. Ioan-Stroe, M. Swierczynski, J. Jaguemont, S. Goutam, N. Omar, J. van Mierlo, and P. van den Bossche, *Appl. Energy*, **200**, 47 (2017).
12. J. Schmitt, A. Maheshwari, M. Heck, S. Lux, and M. Vetter, *J. Power Sources*, **353**, 183 (2017).
13. S. Ma, M. Jiang, P. Tao, C. Song, J. Wu, J. Wang, T. Deng, and W. Shang, *Progress in Natural Science: Materials International*, **28**, 653 (2018).
14. M. Broussely, P. Biensan, F. Bonhomme, P. Blanchard, S. Herreyre, K. Nechev, and R. J. Staniewicz, *J. Power Sources*, **146**, 90 (2005).
15. A. Jossen and W. Weydanz, *Moderne Akkumulatoren richtig einsetzen* (Neusäß) (Ubooks-Verlag) (2006).
16. J. Vetter, P. Novák, M. R. Wagner, C. Veit, K.-C. Möller, J. O. Besenhard, M. Winter, M. Wohlfahrt-Mehrens, C. Vogler, and A. Hammouche, *J. Power Sources*, **147**, 269 (2005).
17. J. Henschel, F. Horsthemke, Y. P. Stenzel, M. Evertz, S. Girod, C. Lürenbaum, K. Kösters, S. Wiemers-Meyer, M. Winter, and S. Nowak, *J. Power Sources*, **447**, 227370 (2020).
18. A. Friesen, F. Horsthemke, X. Mönnighoff, G. Brunklaus, R. Kräft, M. Börner, T. Risthaus, M. Winter, and F. M. Schappacher, *J. Power Sources*, **334**, 1 (2016).
19. M. Winter, *Z. Phys. Chem.*, **223**, 1395 (2009).
20. Y. Liu, K. Xie, Y. Pan, H. Wang, Y. Li, and C. Zheng, *Solid State Ionics*, **320**, 126 (2018).
21. T. Matsushima, *J. Power Sources*, **189**, 847 (2009).
22. M. Naumann, M. Schimpe, P. Keil, H. C. Hesse, and A. Jossen, *Journal of Energy Storage*, **17**, 153 (2018).
23. E. Sarasketa-Zabala, I. Gandiaga, L. M. Rodríguez-Martinez, and I. Villarreal, *J. Power Sources*, **272**, 45 (2014).
24. R. Mathieu, I. Baghdadi, O. Briat, P. Gyan, and J.-M. Vinassa, *Energy*, **141**, 2108 (2017).
25. J. Schmalstieg, S. Käbitz, M. Ecker, and D. U. Sauer, *J. Power Sources*, **257**, 325 (2014).
26. M. Broussely, S. Herreyre, P. Biensan, P. Kaszejna, K. Nechev, and R. J. Staniewicz, *J. Power Sources*, **97-98**, 13 (2001).
27. M. Ecker, N. Nieto, S. Käbitz, J. Schmalstieg, H. Blanke, A. Warnecke, and D. U. Sauer, *J. Power Sources*, **248**, 839 (2014).
28. P. Keil, S. F. Schuster, J. Wilhelm, J. Travi, A. Hauser, R. C. Karl, and A. Jossen, *J. Electrochem. Soc.*, **163**, A1872 (2016).
29. D.-I. Stroe, M. Swierczynski, S. K. Kar, and R. Teodorescu, *IEEE Trans. on Ind. Applicat.*, **54**, 517 (2018).
30. W. Waag, S. Käbitz, and D. U. Sauer, *Appl. Energy*, **102**, 885 (2013).
31. A. Eddahech, O. Briat, and J.-M. Vinassa, *Energy*, **84**, 542 (2015).
32. A. E. Mejdoubi, H. Gualous, H. Chaoui, and G. Alcicek, "Experimental investigation of calendar aging of lithium-ion batteries for vehicular applications." *IV International Electromagnetic Compatibility Conference*, (EMC Turkiye), Ankara24.09.2017 (IEEE) p. 1 (2017).
33. P. Svens, R. Eriksson, J. Hansson, M. Behm, T. Gustafsson, and G. Lindbergh, *J. Power Sources*, **270**, 131 (2014).
34. S. Abada, M. Petit, A. Lecocq, G. Marlair, V. Sauvans-Moynot, and F. Huet, *J. Power Sources*, **399**, 264 (2018).
35. M. Börner, A. Friesen, M. Grütze, Y. P. Stenzel, G. Brunklaus, J. Haetge, S. Nowak, F. M. Schappacher, and M. Winter, *J. Power Sources*, **342**, 382 (2017).
36. F. Larsson, S. Bertilsson, M. Furlani, I. Albinsson, and B.-E. Mellander, *J. Power Sources*, **373**, 220 (2018).
37. P. Röder, B. Stiaszny, J. C. Ziegler, N. Baba, P. Galaly, and H.-D. Wiemhöfer, *J. Power Sources*, **268**, 315 (2014).
38. E. P. Roth and D. H. Doughty, *J. Power Sources*, **128**, 308 (2004).
39. E. P. Roth, C. C. Crafts, D. H. Doughty, and J. McBrean, *Thermal Abuse Performance of 18650 Li-Ion Cells SAND2003-3106J* (2003).
40. J. Zhang, L. Su, Z. Li, Y. Sun, and N. Wu, *Batteries*, **2**, 12 (2016).
41. M. Fleischhammer, T. Waldmann, G. Bisle, B.-I. Hogg, and M. Wohlfahrt-Mehrens, *J. Power Sources*, **128**, 432 (2015).
42. D. H. Doughty and E. P. Roth, *Interface Magazine*, **21**, 37 (2012).
43. F. Larsson and B.-E. Mellander, *J. Electrochem. Soc.*, **161**, A1611 (2014).
44. F. Larsson, P. Andersson, and B.-E. Mellander, *Batteries*, **2**, 9 (2016).
45. F. Del Corso, H. Mettlach, M. Morcrette, U. Koehler, C. Gousset, C. Sarrazin, G. Binotto, D. Porcellato, and M. Vest, *Electric Vehicle Batteries: Moving from Research towards Innovation*, ed. E. Bricc and B. Müller (Springer International Publishing, Cham) p. 1 (2015).
46. D. Doughty and C. Crafts, *FreedomCAR Electrical Energy Storage System Abuse Test Manual for Electric and Hybrid Electric Vehicle Applications SAND2005-3123* (2006).
47. H. Mettlach, F. Del Corso, A. Warm, H. Bryngelsson, G. Binotto, and S. Boyanov, (2011), Abuse test procedures for high energy Li-ion battery cells.
48. A. Farmann, W. Waag, and D. U. Sauer, *Energy*, **112**, 294 (2016).
49. M. Rogge, D. Müller, and D. U. Sauer, "Lithium-Titanate Cells for Fast Charging Battery Buses - Results of a Performance and Aging Analysis." *Kraftwerk Batterie 2015/Advanced Battery Power Conference 2015*, Aachen, April-2015 (2015).
50. A.-I. Stroe, V. Knap, and D.-I. Stroe, *Microelectron. Reliab.*, **88-90**, 1251 (2018).
51. A.-I. Stroe, D.-L. Stroe, V. Knap, M. Swierczynski, and R. Teodorescu, "Accelerated Lifetime Testing of High Power Lithium Titanate Oxide Batteries." *2018 IEEE Energy Conversion Congress and Exposition (ECCE)*, Portland, OR23.09.2018 - 27.09.2018 (IEEE) p. 3857 (23.09.2018).
52. G.-H. Kim, A. Pesaran, and R. Spotnitz, *J. Power Sources*, **170**, 476 (2007).
53. H. Maleki and J. N. Howard, *J. Power Sources*, **137**, 117 (2004).
54. Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun, and C. Chen, *J. Power Sources*, **208**, 210 (2012).
55. J. H. Seo, J. Park, G. Plett, and A. M. Sastry, *Electrochem. Solid-State Lett.*, **13**, A135 (2010).