Li-ion cells are used in a variety of mobile and stationary applications. Their use must be safe under all conditions, even for aged cells in second-life applications. In the present study, different aging mechanisms are taken into account for accelerating rate calorimetry (ARC) tests. 18650-type cells are cycled at 0°C (Li plating expected) and at 45°C (SEI growth expected). After extensive evaluation of the electrochemical results (voltage curve analysis, capacity fade, energy fade, Coulombic efficiency), the cells are tested by Post-Mortem analysis (CT, GD-OES, SEM) to reveal the main aging mechanisms and by ARC to test the safety behavior. Besides typical ARC results such as onset-of-self-heating, onset-of-thermal runaway and maximum temperatures, as well as acoustic responses of thermal runaway are evaluated and a method is developed to compare fresh cells and cells aged until different SOHs. It turns out that the safety of aged cells is not simply a function of the SOH. However, safety is strongly affected by the main aging mechanism and to the history of operating parameters during the life-time of the cell. Unsafe behavior is indicated by certain features in the voltage curves.

In the past, failure of Li-ion cells led to product recalls which are very expensive for the manufacturers and unsettle customers, even if such incidents happen only in very few cases (ppm range).10 At the moment, safety tests have to be performed with Li-ion prototype cells before market release. In these tests, fresh cells are always used, however, aged cells are usually neglected. Even if fresh cells show an acceptable safety behavior, this can change for aged cells.7,11–15 While some authors observed decreases for certain safety properties,7,11,12 others found improvements.12,13,15

It is well known that aging mechanisms change the properties of the materials inside Li-ion cells.16–19 Operating conditions and materials have a strong influence on these aging mechanisms.12,20–23 We recently reported on a change of the aging mechanism with temperature for cycling aging of commercial 18650-type cells with graphite anodes and NMC/LMO cathodes.20 This mechanism change is expressed by a V-shape in Arrhenius plots of the capacity fade rates obtained from cycling at different ambient temperatures.20 This change of the aging mechanism is caused by the temperature dependency of the anode potential vs. Li/Li+.20,22–26

Cycling and calendar aging at elevated temperatures often leads to electrolyte decomposition and therefore to SEI growth and pore clogging on graphite anodes.7,16,18,20,25 In this case the anode potential vs. Li/Li+ is mostly positive.20,22 In contrast, critical combinations of low temperatures, high charging C-rates, and high SOCs lead to negative anode potentials vs. Li/Li+ and therefore to deposition of metallic Li on graphite anodes, often called Li plating.20,25,28–30 Due to the high reactivity of Li metal and the possibility of forming mechanically decoupled Li, cycling under Li plating conditions leads to fast capacity fade.

However, there is still a dearth of knowledge on the effect of aging mechanisms on the safety properties of Li-ion cells. Especially, the dendritic growth of Li deposition on graphite anodes is often discussed in terms of internal short circuits that can lead to thermal runaway.31–35 Furthermore, we have recently reported about strong effects of Li plating on the safety behavior in accelerated rate calorimetry (ARC) tests.11,14 For example, Li plating in commercial cells can significantly decrease the onset of self-heating (Tsh) to only 35°C11,14 whereas it is typically above 75°C for fully charged fresh state-of-the-art cells.11,12,14,34,35 An effect of mussy Li deposited on graphite anodes on ARC results was later confirmed by Winter’s group with fresh cells at different SOC by ARC.

### Experimental

The explored 18650-type NCA/graphite cells have a specified minimum capacity of 3.25 Ah and a voltage range of 2.5–4.2 V. Electrochemical tests and aging were conducted by a Basytec CTS system at 0°C, 5°C, 25°C, and 45°C inside temperature chambers (Vötisch).

After equilibration of the cells to the respective ambient temperature, the cells were charged (CC-CV, CV stopped at I<0.05C) and discharged (CC) with 0.5C with 10s breaks in between. At the end of cycling, all tested cells were charged or discharged at the respective aging temperature directly before the ARC and Post-Mortem tests.

For the voltage relaxation measurements after charging, fresh cells were charged at 0.5C (CC-CV, CV stopped at I<0.05C) at different temperatures. After each charging step, the voltage relaxation was logged for 4h.

Post-Mortem analysis was carried out according to our recent literature study.10 In particular, before disassembly, fresh cells were examined by X-ray computed tomography (CT) (v)tome(x) 300) to get more information on the internal structure and in order to determine the cutting positions for cell opening. After discharging to the end-of-discharge voltage (2.5 V) with a rate of 0.5C at the respective aging temperature, the cells were opened inside an Ar filled glove box (MBraun, 0.1 ppm O2, 0.1 ppm H2O). According to the CT measurements, the cells were cut near the upper and lower terminal as well as along the cylinder to remove the jelly roll.
Depth profile analysis of the anodes was carried out using a glow discharge optical emission spectrometer (GD-OES, Spectrumanalytical). To analyze the samples, a radio frequency (rf) method was used, while applying 550 V discharge voltage and a gas pressure of 2hPa. A gas mixture of 1 vol.-% of H₂ in Ar (both 6.0 purity) was used to improve the depth resolution and detection limits for porous carbon-based coatings. The analyzed sample had an area of ∼5 mm² (2.5 mm diameter) and the resulting crater depth was measured with a profilometer (Taylor Hobson, Form Talysurf 50). The calibration of the GD-OES was carried out using a variety of reference coatings. These graphite coatings simulated real anodes by variation of the LiH₂PO₄ content in the water based slurry preparations. This extensive calibration is necessary to avoid matrix effects. The simulated graphite based reference coatings have similar porosities and chemical compositions. The detected elements and the emission lines used are as following: P (178 nm), O (130 nm), C (156 nm) and Li (670 nm). The samples for the GD-OES study were prepared under Ar atmosphere and transferred to the spectrometer using an airtight sample holder. We note that the samples were exposed to air for transfer into the SEM (Zeiss LEO 1530VP Gemini).

The thermal runaway tests were performed with an ARC-EV (Thermal Hazard Technology). The temperature of the 18650 cells was measured on the cell surface (middle of cylinder height) during the test with a type N thermocouple. The ARC was calibrated according to the manual allowing a drift <0.01 °C/min. ARC tests were performed in the heat-wait-seek mode. The temperature was raised in steps of 5 °C followed by a wait period of 15 min and a seek period of 10 min. The cell temperature was followed if the self-heating rate (SHR) exceeded 0.02 °C min⁻¹ during the seek-period. The SHR was calculated from the temperature vs. time data by the ARC software. All cells in this study were tested in the fully charged state, however, due to different aging states, they had different charged capacities. All ARC tests were performed within <1.5h after the aging tests, since we had recently found that longer rest times after Li plating lead to chemical intercalation of Li into Li₂C₆ and thereby change the safety behavior.

A digital audio recorder (Tascam DR–05, 48kHz/16bit) located on the wall of the right upper side of the ARC blast box was put inside a vacuum cleaner bag (Kärcher 6.904-329.0) and used to record the sound of thermal runaway for several cells. The sound adsorption by the vacuum cleaner bag is negligible for this experiment. The WAV audio files were imported to Origin and their intensities were evaluated. The difference between the maximum positive and negative peak values were taken as sound levels in Figure 9b.

Results and Discussion

Electrochemical tests give hints on different aging mechanisms in 3.25 Ah 18650-type cells.—Figure 1a shows the voltage discharge curves of the 3.25Ah 18650-type cells as a function of capacity. Cells charged and discharged at 0 °C and at 5 °C feature a voltage plateau in the range of 0Ah to 0.5 Ah which is expected from experiments and simulations to be a result of stripping of plated Li from the anode. This voltage plateau is not present for charging and discharging at 25 °C and at 45 °C, indicating Li plating at these temperatures. This indicated change of the aging mechanism was also apparent from an Arrhenius analysis of capacity fade with the same cell type.

As can be seen from Figure 1a, the cells tested at 0 °C and 5 °C show the lowest discharge capacities, while they are improved for the cells at 25 °C, and even more for 45 °C. The same trend can be observed for the discharge energy, as indicated by the higher levels of the voltage curves in combination with the higher capacities for higher temperatures. We note that the voltage plateau observed for the measurements at 0 °C and 5 °C increases the discharge energy partly since the integral in the U vs. capacity plot is increased.

Figure 1b shows voltage relaxation curves after the first charging at 0.5C at 0 °C, 5 °C, 25 °C, and at 45 °C. This experiment is suggested from the works of Uhlmann et al. who did similar measurements in half cells, by Schindler et al. who transferred this method to full cells, and by von Lüders et al. who finally correlated the voltage relaxation to Li plating by operando neutron diffraction experiments. These previous studies suggest that the shape of the voltage relaxation curves indicate Li plating in the previous charging process. This was explained by a mixed potential of the anode when both Li and Li₂C₆ are present on the anode. For charging at 0.5C at 0 °C and at 5 °C, the voltage relaxation curves show plateaus, indicating Li deposition, which is consistent with the discharge curves in Figure 1a and with literature. In contrast, for charging at 0.5C at 25 °C and at 45 °C we find an exponential decrease of the voltage relaxation curves. The absence of voltage plateaus indicates no Li deposition. This is consistent with the absence of voltage plateaus during discharging in Figure 1a.

The results of the discharge curves (Figure 1a) and the voltage relaxation measurements (Figure 1b) are consistent with the Arrhenius plot using the capacity fade rate taken from the long-term cycling tests at 0.5C with the same cell type. In the Arrhenius plot, two slopes corresponding to a change of the main aging mechanism were observed above and below 25 °C. Therefore, for 0 °C and 45 °C, clearly two different aging mechanisms can be expected from the Arrhenius plot. For the cell type under investigation, the change of the aging mechanism happens at ∼25 °C. Therefore, it is likely that both mechanisms are present around this temperature and therefore small amounts of Li are present on the anodes after extended cycling. Burns et al. investigated a very similar cell type and found an indication of small amount of Li deposition after cycling at 0.5C at 25 °C by high precision Coulometry measurements. In a previous study on the same cell type as in the present paper, we had measured negative anode potentials vs. Li/Li⁺ at 25 °C in 3-electrode full cells reconstructed.
from the electrodes used in the 18650 cells. Therefore, it has to be discussed that small amounts of Li deposited on the anode might be present at 25°C, but below the limit of detection of the stripping discharge and the voltage relaxation method. Also it is not clear at the moment if these methods are suitable for low temperatures only, due to slowed relaxation processes. All experiments in literature so far were performed below 23°C.

Figure 2 shows the aging behavior at 0°C, 25°C, and 45°C. All tests were reproduced with a second cell. The capacity fade curves are plotted in Figure 2a. In consistency with Figure 1, the capacities of the first cycles are increasing with temperature. The capacity fade is similar for 25°C and 45°C, while it is much faster for 0°C. We note that there are three jumps in the data for 45°C which correspond to shut downs of the temperature chamber for a few cycles. The temperatures changes of the cells lead to a scattering in Figures 2c, 2d, however, after restarting the temperature chambers, all data in Figure 2 continue and the results are reproducible. Therefore, we expect only minor impact of these artifacts on the results.

Figure 2b shows the energy fade at different temperatures. The energy fade is very important for automotive applications, since it reflects the driving range. The trends are very similar to the capacity fade for the tested cells.

Figure 2c shows the Coulombic efficiency (CE) at different temperatures. The CE is defined as the quotient of discharged and charged energy. As recently discussed by Meister et al., η is very important when large numbers of batteries are used. Depending on the electricity price, η is also more or less important in terms of costs. Our data for the first cycle show that η is 92.5% for 45°C, 90% for 25°C, and 82.5% for 0°C. Furthermore, it can be seen from Figure 2d that η shows a similar trend to capacity fade and energy fade. This means that the energy costs are increasing with aging. The strongest effect is observed for cycling at 0°C.

In conclusion, electrochemical tests (voltage plateaus and relaxation, fast capacity/energy/energy efficiency fade, and low CE values) show that cycling at 0°C at 0.5C very likely leads to Li plating for the tested 3.25 Ah cells. In order to proof Li plating under these conditions, Post-mortem analysis of aged cells is performed in the next section.

Post-Mortem analysis reveals different aging mechanisms in 3.25 Ah 18650-type cells.—Figure 3 shows CT cross-sections, giving insight into the architecture of the fresh 18650 cells. A cross-section through the center of the jelly roll is depicted on the left hand side of the graph. The jelly roll has 17 windings which are stabilized between the center pin and the housing.

The right side of Figure 3 shows a detailed view on the different safety devices at the positive terminal. This terminal is directly connected to the PTC (positive temperature coefficient) resistor. The PTC device protects the cell from overheating caused by high currents, since its ohmic resistance increases with rising temperature. In this study the PTC has no importance, since no currents are applied to the cell during thermal runaway. The PTC device is directly followed by the CID (current interruption device), which acts as a burst disc. If

![Figure 2](image_url)

Figure 2. a) Capacity fade, b) discharge energy, c) Coulombic efficiency, and d) energy efficiency during cycling at different ambient temperatures. Capacities were measured at the respective temperatures. The inset of c shows the mean values and standard deviations of the CE for the tests at 0°C. Filled and open symbols represent reproduced results with a second cell, respectively. The legend in (d) is valid for the whole Figure.
the pressure inside the cell increases significantly, the CID / burst disc bulges and thus loses contact to the current collector disc below. With further increasing gas pressure inside the cell the CID will further bulge until the cell is vented. We note that liquid electrolyte is visible in the CT cross-section. Therefore, it is likely that evaporating electrolyte will contribute to the pressure rise at elevated temperatures. The last safety device is the insulator disc which separates the jelly roll from the tab and the other security devices.

Figure 4 shows Post-Mortem results (GD-OES and SEM) of anodes from fresh and aged 3.25 Ah 18650 cells. In Figure 4, all cells were opened after discharging to the end-of-discharge voltage of 2.5 V. The cycled cells were opened directly after the end of aging. We note that the photographs were taken inside the glove box. The samples were transported from the glove box to the GD-OES by an air tight chamber without exposure to air. In contrast, the samples for SEM investigations were transferred through air, however, experience showed that the microstructure does not change significantly, i.e. particles and (oxidized) Li dendrites are usually still visible in SEM observations.

Figure 4a shows the GD-OES measurement of the fresh cell. The O and P peaks show a nearly constant distribution through the anode. The Li depth profile shows a peak at the anode surface. This peak has a maximum of \( \sim 19 \) wt.-% and decreases within the first \( 5 \) μm from the anode surface. The Li peak reaches a nearly constant level after a depth of \( \sim 5 \) μm. The peak maximum of the Li peak is typical for the initial SEI and in consistence with our previous findings for 1.5 Ah and 16 Ah cells with different graphite anodes.\(^27,47\) The inset of Figure 4a shows a photograph of the anode inside the glove box. As expected, for a graphite anode from a discharged fresh cell, a black color was observed. Figure 4b shows a typical SEM image of the anode surface revealing the graphite particles. The SEM images are in agreement with the GD-OES measurements and the photograph in Figure 4a and with literature on fresh cells.\(^20,44,47\) As expected, no aging effects are visible in the fresh cell from optical inspection, GD-OES, and SEM measurements.

Figure 4c shows the GD-OES analysis of the cell cycled at \( 0^\circ \) C. The P peak shows a nearly constant distribution through the anode. The O and P peaks show a nearly constant distribution through the anode. Both, the Li and O depth profiles show peaks at the anode surface.
The Li peak has a maximum of ~35 wt.-% and decreases within the first 2.5 μm from the anode surface. The Li peak reaches a nearly constant level after a depth of ~15 μm. A similar accumulation of Li on the anode surface (between anode and separator) was recently reported by simulations from Hein and Latz.\textsuperscript{29} In contrast to the depth profile of the fresh cell (Figure 4a), the Li peak of the anode cycled at 0 °C is much higher and broader which is typical for Li deposition.\textsuperscript{57,58} Indeed, an estimation based on the Li and O depth profile\textsuperscript{47} revealed that Li metal is present in this sample. This fits to the optical appearance of the anode which is shiny and metallic (see inset of Figure 4c). Figure 4d shows a typical SEM image of the anode surface revealing no graphite particles, but a thicker film. The inset of Figure 4d shows dendritic structures which are typical for Li metal deposition on graphite anodes.\textsuperscript{35,49,50}

Figure 4e shows the GD-OES analysis of the cell cycled at 45 °C. The P depth profile shows a peak near the anode surface, which is absent in the anodes from the fresh cell and from the cell cycled at 0 °C. The level of the O depth profile is higher compared to the other measurements. For Li, a peak is observed on the anode surface. The Li peak is lower compared to the other samples. The GD-OES measurement of the anode from the cell cycled at 45 °C does not indicate Li metal, instead the increased Li and P peaks are consistent with an increased SEI growth involving decomposition of LiPF\textsubscript{6}.\textsuperscript{16,27,47,51} This fits to the optical appearance of the anode which is black (see inset of Figure 4e). We note that the adhesion of the anode coating from the cell cycled at 45 °C is lower as indicated by material which is detached during disassembly. Figure 4f shows a typical SEM image of the anode surface from the cell cycled at 45 °C which looks very similar to that of the fresh cell (Figure 4b). SEM does not indicate SEI growth in this case, since it is most likely too marginal to be observed by this method.

The SEM images, GD-OES measurements, and optical appearances of the anodes are in agreement with each other and show that Li plating is present on the anode surface after cycling at 0 °C but not at 45 °C. These Post-Mortem results together with the electrochemical evaluation in Figure 1 substantiate the findings by Uhlmann et al.\textsuperscript{40} Schindler et al.\textsuperscript{30} and von Lüders et al.\textsuperscript{41} However, it must be critically discussed here that temperature might play a role in the shape of the voltage relaxation behavior, which was not investigated in detail yet. The finding that cycling at 0 °C and at 45 °C leads to different aging mechanisms furthermore substantiates the change in the slope of Arrhenius plots constructed from capacity fade data of the present\textsuperscript{26} and other cell types.\textsuperscript{30}

In contrast to the cells discussed above, the data in Figure 5 originates from a cell which was disassembled after 8 days of rest time at 25 °C after it had been cycled at 0 °C. It can be seen from Figure 5a that the maximum of the Li peak is lower compared to that of the cell disassembled directly after cycling at 0 °C (Figure 4c). The optical appearance of the anode (inset of Figure 5a) is not shiny as in the inset of Figure 4c, but light gray and less homogeneous. Figure 5b shows a SEM image of the anode taken from the cell opened after 8 days rest time. The structure of the deposited Li is not dendritic in this case. The reasons might partly be chemical intercalation of Li into Li\textsubscript{x}C\textsubscript{6} and reaction of Li with electrolyte during the rest time.

The Post-Mortem results presented in Figure 5 clearly show that the amount of Li plating on anodes decreases during the rest time of 8 days at 25 °C. This can be explained with chemical intercalation of Li metal into adjacent graphite particles and is in agreement with experiments utilizing Li atoms evaporated onto the surface of a graphite single crystal in ultrahigh vacuum by Mandeltort et al.\textsuperscript{52} with neutron diffraction experiments with 18650-type Li-ion cells,\textsuperscript{41,53} with operando measurements of the thickness of pouch cells\textsuperscript{24,53} from other groups, and with ARC experiments with the same type of 18650 cells in the present paper after different rest times from our group.\textsuperscript{14}

**Effect of differences of aging mechanisms on thermal runaway behavior of 3.25 Ah 18650-type cells.**—Figure 6 shows a typical ARC result with marked regions of interest. In heat-wait-seek mode of an ARC experiment, the temperature is increased until exothermic reactions are detected at the onset-of-self-heating temperature T\textsubscript{SH} (see inset of Figure 6 on left hand side). The condition to detect T\textsubscript{SH} is SHR < 0.02 °C/min. The ARC then changes to the exothermic mode in which the temperature of the cell is followed adiabatically, i.e. the temperature of the cell increases until the thermal runaway occurs. During this stage, the pressure inside the cell rises due to evaporation of electrolyte and due to formation of gaseous decomposition products, which leads to activation of the burst disc and venting of the cell (see Figure 3 and discussion above). After the venting, the conditions change from isochoric/adiabatic to isobaric/adiabatic conditions and diffusion of O\textsubscript{2} and H\textsubscript{2}O into the cell become possible and increase
Figure 7. a) Temperature curves (1,2) 0°C/0.5C 1.91Ah/1.62Ah, (3) 5°C, 0.5C, 2.50 Ah, (4) 45°C/0.5C, 2.66 Ah, (5,7) fresh cells 3.27 Ah, and (6) 45°C/0.5C, 3.17 Ah. b) SHR as a function of temperature during ARC tests with 3.25 Ah cells. The data in (b) was smoothed with a moving average filter over 5 data points.

Figure 8. a) Self-heating rate for 35°C, b) onset of self-heating, and c) onset of thermal runaway for fresh and cycled 3.25 Ah cells. The fresh cells (black filled circles) were charged to SOC levels of 0%, 80%, and 100%. The cycled cells (red triangles, white circles, dark blue squares, and light blue diamonds) are fully charged and have different SOH levels. The dashed line in (a) represents the threshold for detection of TSH, whereas the dashed lines in (b), (c) are linear fits to the data points of the fresh cells.

the reactivity. Due to evaporation of electrolyte, often a drop in the temperature curve is observed (see inset of Figure 6 on right hand side). In cases of a more rapid temperature change, the time of venting is not observable in the temperature profile, however, it can be determined by audio recording during the ARC test.

Figure 7a shows the temperature curves of the ARC tests for 3.25 Ah cells aged under different conditions. Curves (1,2) correspond to cells cycled at 0°C/0.5C, (3) 5°C/0.5C, (4,6) 45°C/0.5C, and (5,7) fresh cells.

Figure 7b shows the SHR, which is the derivation of the exothermic part in the curves shown in Figure 7a. It can be seen, that the SHR curves are very similar for the fresh cells at 100% SOC and for the cells cycled at 45°C. In contrast, the cells cycled at 0°C show an earlier TSH and a higher SHR for lower temperatures. The data shown in Figure 7 are evaluated in the following.

Figure 8 shows different results occurring during the ARC tests as a function of capacity for the 3.25 Ah 18650-type cells. Figure 8a shows the SHR at the temperature step of 35°C (SHR@35°C). The fresh cells at different SOC, as well as the cells cycled at 25°C/0.5C and at 45°C/0.5C are below the threshold for detection of exothermic reactions in the ARC experiment (SHR < 0.02°C/min, dashed line in Figure 8a). In contrast, the SHR@35°C for the cells cycled at 0°C/0.5C are reproducibly in the range of 0.0842 ± 0.007°C/min. This is in good agreement with our previous measurements on the same cell type. The SHR@35°C value for 5°C/0.5C (0.091°C/min) is in a similar range like the measurements at 0°C/0.5C. This shows that the safety behavior for cells cycled at low and high temperature, i.e. with different aging mechanisms can be very different although they have similar SOHs.

The black filled circles in Figure 8b show the TSh for fresh 3.25 Ah cells with different charged capacities corresponding to SOCs of 0%, 80%, and 100%. As expected from literature, TSh is decreased with higher charged capacity. Therefore, the safety of the cells decreases with higher charged capacity, i.e. with higher electrochemical energy content. However, for the fresh 3.25Ah 18650 cell in this study, TSh is still in an acceptable range, as expected for a commercial cell. The observed decrease of TSh with capacity is linearly correlated with the charged capacity as can be seen from the high R2 value of 0.98. Börner et al. found a similar trend for different cells, however, in their tests the dependency was less linear.
In the following, the linear fit to the fresh cells with different SOC (dashed line in Figure 8b) is used for comparison with differently aged cells at different SOH.

The filled red triangles in Figure 8b represent ARC tests with cells cycled at 45 °C/0.5C. As these data points are in the range of the line for the fresh cells, the involved aging mechanism at this temperature (SEI growth and adhesion loss of anode active material) does not compromise the safety properties in this case. The reason is that for this cell type cycling at 45 °C leads to loss of cyclable Li by SEI growth on the anode surface. Therefore the electrochemical energy is lowered for the aged cells. Our results are difficult to compare to literature since different types of plots were used. For different cells cycled at 45 °C, TSH was shifted to higher temperatures in the experiments by Börner et al. A similar trend was found by Zhang et al. for calendar aged 4.6 Ah pouch cells using a calorimeter (not ARC). The authors stored the cells at 100% SOC at 55 °C and found an increase of TSH with longer aging time and with lower cell capacity. This is in agreement with our results on cycled cells at 45 °C since the main aging mechanism of SEI growth during calendar aging can be expected to be similar.

In contrast, the cells cycled at 0 °C/0.5C (dark blue squares in Figure 8b) reproducibly showed a strong decrease of TSH below 40 °C. A similar observation was made for an exemplarily cycled cell at 5 °C/0.5C (light blue diamond in Figure 8b).

We note that additional cells cycled at 25 °C/0.5C (white circles) showed similar TSH values which were in a similar range like the fresh cells. However, all these cells showed very similar TSH values instead of increased values with stronger capacity loss. Recently, Börner et al. showed that TSH is slightly decreased in the case of mossy Li on graphite anodes produced by cycling at 20 °C which is similar in our case.

Figure 8c shows the onset temperature of thermal runaway (TTR) for cells aged at 45 °C, 0 °C, and 5 °C as a function of capacity. The other aged cells were not measured until the occurrence of thermal runaway. Just as TSH, the TTR data for the fresh cells at different SOCs agreed well with a linear fit (R² = 0.93), i.e. higher SOCs, lead to lower temperatures of thermal runaway.

Again, the cells cycled at 45 °C/0.5C show a similar behavior for TTR like the fresh cells. This result shows a similar trend like for calendar aged cells by Zhang et al. In contrast, the cells cycled at 0 °C/0.5C showed a significantly lower TTR value (126.1 ± 3.2 °C) compared to the fresh cells (208 ± 2 °C, estimation from linear fit in similar capacity range) and the cells cycled at 45 °C/0.5C (185.3 ± 5.2 °C). Börner et al. who cycled their cells at 20 °C and 45 °C reported similar values for both cases. The difference in our experiments is that the cells with Li plating were cycled at significantly lower temperatures.

Figure 9 shows the results from the end of thermal runaway as a function of capacity for the 3.25 Ah 18650-type cells. Figure 9a shows the maximum temperature (Tmax) measured on the cell surfaces. For the fresh cells, Tmax correlates linearly with the capacity (with a certain scattering, R² = 0.72). The reason is most likely the higher electrochemical energy content of cells at higher SOC. The cells cycled at 45 °C/0.5C, 0 °C/0.5C, and 5 °C/0.5C show a scattering around the linear fit for the fresh cells (dashed line in Figure 9a). Therefore, the correlation of Tmax with capacity is also valid for the cycled cells. In contrast to the results shown in Figure 8, this correlation is independent from the aging mechanism.

Figure 9b shows the correlation of the audio level during thermal runaway with the cell capacity. We note that the audio level is not an absolute value since it depends on the geometry of ARC blast box and on the microphone position and orientation. For example, the left and right microphone channels give slightly different audio levels. However, for the same microphone position and orientation, the relative audio levels can be compared. It can be seen from Figure 9b that the maximum audio levels of fresh and cycled cells correlate approximately linearly with the cell capacity (R² = 0.81). Therefore, like the maximum temperature, this correlation is independent from the aging mechanism. However, the maximum audio level (and likely the strength of the explosion) is correlated with the charged capacity.

It is noted that the audio recording inside the ARC blast box has the additional advantage that the time of cell venting can be determined. This is useful when the temperature drop in the T vs. t diagram of the ARC tests is not visible (see inset on right hand side of Figure 6) and if a camera is not possible in the ARC setup. We found that such “hidden ventings” do often occur in tests with Li plating.

![Figure 9](https://example.com/figure9.png)

**Figure 9.** a) Maximum temperature and b) maximum audio level at the end of thermal runaway for fresh and cycled 3.25 Ah cells. The dashed lines correspond to linear fits to the data points of the fresh cells.

### Conclusions

In the present paper, we observed the effect of different aging mechanisms on the thermal runaway properties in ARC tests. As an example, commercial 3.25 Ah 18650-type cells with graphite anodes and NCA cathodes were investigated in detail by electrochemical analysis, Post-Mortem analysis, and ARC tests. Post-Mortem analysis of 18650 cells revealed that the main aging mechanisms for cycling at a rate of 0.5C at 0 °C is homogeneous Li plating. In contrast, cycling at 45 °C at 0.5C leads to SEI growth and adhesion loss of the anode active material. These results are consistent with electrochemical tests.

The ARC tests showed that:

1. The onset temperature is linearly lowered with increasing SOC for fresh cells. The SOC of fresh cells can be used to compare aged cells with SOHs lower than 100%.
2. The main aging mechanism of SEI growth on graphite anodes after cycling at 45 °C/0.5C does not lead to a decrease of safety properties. Cells cycled at 45 °C are comparable with fresh cells with similarly charged capacities.
3. The main aging mechanism of Li plating on graphite anodes after cycling at 0 °C/0.5C leads to a drastic decrease of safety properties. Cells with reduced capacity due to aging under Li
plating conditions are not comparable to fresh cells. The same trend was found for exemplary cells cycled at 5°C/0.5°C.

4) The decrease of the safety properties during Li plating in this paper is not connected to Li dendrites but most likely to exothermic reactions of Li metal with electrolyte and the fact that there is no possibility of heat dissipation under the quasi-adiabatic conditions of the ARC tests. Additionally, Li becomes liquid above 180.5°C.

5) Both, the maximum cell temperature \( T_{\text{max}} \) and the maximum audio level during thermal runaway correlate linearly with the cell capacity of fresh and cycled cells. These properties are correlated to the charged capacity and not to the aging mechanism.

6) Potentially unsafe behavior in ARC tests correlates with features in the voltage curves (voltage plateau during discharge, shape of voltage relaxation after charging).

Our study has shown that the aging history of Li-ion cells can have a strong influence on their safety behavior in ARC tests. For a given cell type, the aging history is mostly affected by the operating parameters, such as charging C-rate, temperature, and SOC range, which have a large influence on the main aging mechanism. The results show that safety behavior is not simply a function of SOH, but of the involved aging mechanisms.

Plated Li is much more reactive compared to SEI layers and therefore leads to a drastic decrease of cell safety in ARC tests. We stress that in case of ARC tests, the thermal runaway is not induced by Li dendrites but most likely due to the stronger exothermic reactions of metallic Li with electrolyte in combination with lack of heat dissipation. In applications with sufficient cooling this might not be as critical as in lab tests, however, our results clearly show a decrease of the safety properties when Li plating is present in contrast to SEI growth.

In order to achieve a safe operation in second-life applications, our findings demonstrate that the aging history of batteries in the first-life application has to be very well known. This is usually not the case for cells that are received from an application. Therefore, the next step would be the development of a method to determine if a cell from a first-life application is safe for use in other second-life applications. In this paper it was already demonstrated that certain features in the cell voltage curves indicate a potentially unsafe behavior of Li-ion cells. In case these features are detected for a cell, safety tests are clearly indicated. Further studies in this direction are ongoing in our lab.

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