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# Perspective – On the Safety of Aged Lithium-Ion Batteries

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## Abstract

Concerns about the safety of lithium-ion batteries have motivated numerous studies on the response of fresh cells to abusive, off-nominal conditions, but studies on aged cells are relatively rare. This perspective considers all open literature on the thermal, electrical, and mechanical abuse response of aged lithium-ion cells and modules to identify critical changes in their behavior relative to fresh cells. We outline data gaps in aged cell safety, including electrical and mechanical testing, and module-level experiments. Understanding how the abuse response of aged cells differs from fresh cells will enable the design of more effective energy storage failure mitigation systems.

## Introduction

High voltage and high energy density lithium-ion (Li-ion) batteries are increasingly used in many applications, including consumer electronics, electric vehicles, and grid-tied energy storage systems. However, with increasing energy density and installation size come heightened concerns about safety, including the risk of thermal runaway and severe fires.[1-4] Thermal runaway is traditionally defined as an accelerating release of heat inside a cell, due to a series of uncontrollable exothermic reactions, manifesting as an exponential increase in cell temperature.

To understand the risks of Li-ion battery failure, numerous studies have examined the response of fresh cells to electrical, mechanical, and thermal abuse. Specification sheets from manufacturers detail the response of fresh cells to electrical and mechanical abuse tests to satisfy reporting requirements for battery safety standards and certifications. The response of fresh cells to electrical abuse has also been examined in the academic literature to understand the impact of cell chemistry, state-of-charge (SOC), form factor, short circuit magnitude, and rate and duration of overcharge or overdischarge.[5-9] Mechanical abuse studies have examined the influence of cell chemistry, SOC, form factor, impact location, and applied force during crushing and nail penetration.[10-13] Additionally, overtemperature tests and accelerated rate calorimetry (ARC), wherein a battery is heated at a constant heating rate to a set temperature or failure, have been used to determine the onset temperatures for thermal runaway and the total heat release.[14-23]

The studies noted above were executed with fresh cells, however, given the expected lifetime of Li-ion batteries in both first and second life applications, it is critical to consider the abuse response of aged cells.[24] Aging could make cells more safe, due to reduced capacity for fueling thermal runaway. Alternatively, cells could become less safe via long-term component degradation. Cycle and calendar aging modify the morphology and integrity of the cell through processes like solid electrolyte interphase (SEI) growth, loss of active material, electrode delamination, and lithium plating. Gases such as low molecular weight hydrocarbons, $H_2$, CO, and $CO_2$ can be formed as the electrolyte in the cells decomposes or undergoes side reactions.[25] These degradation mechanisms are dependent on the aging conditions, which vary significantly with different applications.

In this perspective, we consider all available literature on the abuse response of Li-ion cells aged by different protocols and summarize critical parameters by which the safety of aged cells relative to fresh cells may be evaluated. We then identify aspects of aged battery safety that merit further exploration.

## Current Status

### *Thermal Abuse of Aged Cells*

Batteries in fielded systems can experience thermal runaway due to factors including but not limited to an external fire, inappropriate or failed electrical components, lack of appropriate safety controls, and poor thermal management. In the lab, the thermal abuse of Li-ion batteries is studied with overtemperature tests and various forms of calorimetry (e.g. ARC, cone, etc.).[26] In overtemperature tests, a cell is subjected to a prescribed heating rate, in an oven or heated fixture, until a set temperature or failure is reached. During the ARC test, a cell is placed in a heated enclosure where the temperature is increased until the onset of a pre-determined cell self-heating threshold (typically 0.02 ºC $min^{-1}$) where exothermic reactions associated with thermal runaway can be detected; then, the sample temperature and heat release rate are tracked, and the sample holder or heater temperature is adjusted to maintain adiabatic conditions. This scenario simulates a perfectly insulated cell; the measurement of interest is the rate at which the cell self-heats. It is possible to distinguish several heat-producing events using ARC, and onset temperatures are often identified as metrics for comparison.

**Table 1** summarizes the previous literature on the thermal abuse of aged cells, primarily ARC tests. The aged cells are compared to their fresh counterparts by several metrics: onset of cell self-heating, onset of thermal runaway, and peak temperature. The onset temperatures are most closely tied to kinetic effects of decomposition, while the peak temperature is tied to thermodynamic effects. Both are important for evaluating the relative safety of aged cells. An aged cell is considered safer if its onset temperature is higher or peak temperature is lower than that of its fresh cell counterpart.

The environmental temperature of the aging approach had the most significant impact on cell safety and so the entries in **Table 1** are arranged from lowest to highest aging temperature. Many ARC studies of cells aged to 80% remaining capacity at -10 to 15 °C found that the onset temperatures of self-heating decreased from about 100 °C to 30-50 °C. This decrease was attributed to increased heat formation from the reaction of plated Li. A decrease in self-heating onset temperatures was apparent even in cells aged at environmental temperatures up to 25 °C. Li plating induced by other methods, such as cycling cells with a low negative : positive electrode ratio or fast charging, can also lead to a more dramatic abuse response.[27, 28] However, Li plating is not always permanent. By performing abuse experiments within 1.5 hours and 8 days of cycling, Waldmann et al. showed that resting a cell at room temperature after cold temperature aging can enable re-intercalation of reversibly plated Li and raise onset temperatures back to those of the fresh cell (see Table 1).[29] Other studies which incidentally had a long rest time after cold temperature cycling also show little difference in onset temperatures relative to the fresh cell.[30, 31] These results illustrate the value of reporting the rest time between aging and abuse experiments, a practice that is currently uncommon. For aging at elevated temperatures, higher self-heating onset temperatures were attributed to the formation of a more stable SEI layer.[32, 33] For the most part, similar aging temperature dependence trends are observed for the thermal runaway onset as for the self-heating onset.

For many studies it was not possible to evaluate thermodynamic effects such as total heat release or peak temperature because calorimetry was stopped at 250 °C or lower. Where available, the results indicate either little difference in peak temperature or a substantial decrease. The latter is consistent with a reduction in cell capacity during aging (see Remaining Capacity column in **Table 1**). Cases in which there is little difference in peak temperature despite capacity reduction point to the heat-producing role of materials that are electrochemically inactive in the operational voltage range, such as the electrolyte.

In summary, the thermal safety of aged cells relative to fresh cells depends on the aging method and the metric considered. In terms of kinetics, aging cells under conditions that can induce Li plating makes them less safe by lowering self-heating and thermal runaway onset temperatures. By thermodynamics, aged cells are often safer because their lower electrochemical capacity leads to a lower peak temperature and total heat release.

**Table 1**. Summary of studies examining thermal abuse of aged commercial lithium-ion cells (by ARC, unless otherwise noted).[a]

| Ref. | Cell Type, Capacity (Ah) | Aging Approach, Time Before Abuse[h] | Remaining Capacity | Self-Heating Onset[e] | Thermal Runaway Onset[f] | Peak Temperature |
|---|---|---|---|---|---|---|
| 34 | NMC-LMO, 1.5 | -10°C (cyc) | 81% | Lower by 50-70°C | Lower by 150°C | -- |
| 33 | NMC-LMO, 20 | -10°C (cyc) | 78% | Lower by 10-30°C | Lower by 20°C | Little difference |
| 30b | NMC622, 60 | -10°C (cyc), 5 mo | 85% | -- | Little difference | Lower by 56°C |
| 35 | NMC, 24 | -5°C (cyc) | 80-95% | Lower by 10-20°C | Lower by 20°C | Little difference |
| 36 | NMC532, 2.2 | 0°C (cyc) | 70% | Lower by 60°C | Lower by 90°C | -- |
| 37 | LCO, 2.95 | 0°C (cyc) | 70% | Little difference | Little difference | -- |
| 38 | NMC111-LMO, 2.1 | 0°C (cyc) | 75% | Lower by 35°C | -- | -- |
| 38 | NMC811, 3.5 | 0°C (cyc) | 72% | Lower by 10°C | -- | -- |
| 39 | --, 2.1 | 0°C (cyc) | 35% | Lower by 15°C | Lower by 9°C | Lower by 127°C |
| 40 | NCA, 3.25 | 0°C (cyc) | 18 cyc | Lower by 60°C | Lower by 5°C | Lower by 54°C |
| 29 | NCA, 3.25 | 0°C (cyc), 1.5 hr | 18 cyc | Lower by 40°C | Lower by 55°C | Lower by 275°C |
| 29 | NCA, 3.25 | 0°C (cyc), 8 dy | 18 cyc | Little difference | Little difference | Lower by 170°C |
| 41 | NCA, 3.25 | 0/5°C (cyc), 1.5 hr | 65% | Lower by 95°C | Lower by 100°C | Lower by 50-300°C |
| 42 | NCA, 3.1 | 1°C (cyc) | 60% | Lower by 65+°C | -- | -- |
| 43b | NMC532, 2.6 | 15°C (cyc)[c] | 20-60 cyc | -- | Lower by 47-62°C | Lower by 43-156°C |
| 32 | NMC532, 2.2 | 20°C (cyc) | 70-90% | Lower by 10°C | Little difference | -- |
| 44d | NMC442, 5 | 20°C (cyc)[c] | 80% | Little difference | Little difference | -- |
| 31b | LCO, 6.8 | 21°C (cyc), 1+ yr | 89-94% | -- | Little difference | Little difference |
| 45 | NMC532, 2 | 23°C (cyc) | 79-99% | -- | Lower by 9-32°C | Lower by 50-75°C |

| | | | | | | |
|---|---|---|---|---|---|---|
| 39 | --, 2.1 | 23°C (cyc) | 45% | Lower by 14°C | Lower by 11°C | Lower by 66°C |
| 34 | NMC-LMO, 1.5 | 25°C (cyc)[c] | 78% | Lower by 20°C | Little difference | -- |
| 35 | NMC, 24 | 25°C (cyc)[c] | 80-95% | Lower by 10°C | Lower by 5-20°C | Lower by 30-300°C |
| 38 | NMC111-LMO, 2.1 | 25°C (cyc) | 82% | Lower by 15°C | -- | -- |
| 38 | NMC811, 3.5 | 25°C (cyc) | 79% | Lower by 6°C | -- | -- |
| 46 | NMC811, 3.5 | 25°C (105-120% OC)[g] | -- | Lower by 31-55°C | Little difference | Lower by 139-262°C |
| 41 | NCA, 3.25 | 25/45°C (cyc) | 70-85% | Little difference | Little difference | Lower by 50°C |
| 39 | --, 2.1 | 45°C (cyc) | 76% | Lower by 15°C | Lower by 5°C | Lower by 143°C |
| 30b | NMC622, 60 | 45°C (cyc) | 76% | -- | Higher by 11°C | Lower by 57°C |
| 32 | NMC532, 2.2 | 45°C (cyc) | 70-90% | Higher by 10-20°C | Little difference | -- |
| 47 | LCO, 1.2 | 25/60/70°C(cal) | -- | Higher by 25-40°C | -- | -- |
| 35 | NMC, 24 | 55°C (cyc) | 80-95% | Little difference | Little difference | Little difference |
| 35 | NMC, 24 | 55°C (cal) | 80-95% | Higher by 15-25°C | Little difference | Little difference |
| 48 | LMO, 4.6 | 55°C (cal) | 68-93% | Higher by 14-38°C | Higher by 4-19°C | -- |
| 49 | NMC-LMO, 2 | 60°C (cal) | 55% | Lower by 20°C | Little difference | -- |
| 30b | NMC622, 60 | 60°C (cal) | 94% | -- | Little difference | Little difference |
| 50 | LFP, 2.3 | 60°C (cal) | 70-90% | Higher by 10°C | Lower by 20°C | -- |
| 51b | NCA, -- | 60°C (cal) | 80% | Little difference | Little difference | Lower by 150°C |
| 52b | NMC, 1.3 | 60°C (cal) | 94% | -- | Higher by 50°C | Lower by 104°C |
| 53 | LCO, 2.6 | 60°C (cal) | 6-16wk | Higher by 17-40°C | -- | -- |
| 53 | LFP, 2.3 | 60°C (cal) | 6-16wk | Higher by 15-22°C | -- | -- |
| 52b | NMC, 1.3 | 20°C (cyc) + 60°C (cal) | 95% | -- | Higher by 26°C | Lower by 54°C |
| 54 | LCO, 2.55 | 80°C (cal) | 56% | Higher by 10-15°C | Little difference | -- |
| 53 | LFP, 2.3 | 80°C (cal) | 2-16wk | Higher by 32-52°C | -- | -- |
| 33 | NMC-LMO, 20 | 80/90/100°C (brief ARC) | 73-95% | Higher by 15-35°C | Higher by 15°C | Lower by 30-45°C |

[a] All temperatures are given in reference to those of fresh cells in the same study. Outcomes that make a cell less safe or more safe are highlighted in red and blue, respectively. A dashed line indicates that the specified information was not available. All values were taken directly from the publications, without raw calorimetry data available for reference. Thus, it is possible that some of the values may have been determined by slightly different methods of analysis. Reporting the metrics as the relative values of the aged and fresh cells eliminates some of these discrepancies because there is at least self-consistency in the measurements from each publication.
[b] Overtemperature test.
[c] Cycling involves fast charging (C-rate > 1C)
[d] Non-commercial cells.
[e] First exothermic event detected by ARC. Typically defined as 0.02-0.05 °C min$^{-1}$
[f] Defined differently in different studies, typically 1-5 °C min$^{-1}$
[g] Aged by overcharge
[h] Time before abuse indicates the amount of time that passed between the end of the aging experiment and the execution of abuse experiments (rest time). Only a few publications note this.

### *Electrical Abuse of Aged Cells*

Electrical abuse typically covers overcharging, overdischarging, and external shorting of cells and batteries. Overcharging adds excess electrical energy into the battery whereas external short circuits can be considered an electrical shock to the system.[5, 55] There are few studies of these two abuse methods and no studies of overdischarge for aged cells. The critical parameters to evaluate the safety characteristics of batteries during overcharge and external short circuit tests are: 1) the thermal runaway behavior (i.e. the occurrence of venting, smoke, and fire) and the ability of the internal safety devices to prevent these occurrences, and 2) the temperature response.

Juarez-Robles *et al.* overcharged 18650 NCA cells with a 1C current to 12 V for a period of six hours or until an off-nominal event occurred.[56] The internal current interrupt device (CID) was effective in preventing the occurrence of thermal runaway for both fresh and cycle-life-aged cells. The fresh cells experienced maximum temperatures of 80 °C and the aged ones remained below 55 °C after CID activation. The CID activated earlier for aged cells due to a build-up of gaseous electrolyte degradation products during aging, but no major relationship between the time of CID activation and the capacity loss was observed. The CID activation was, however, affected by the environmental temperature of cycling. For cells aged at 10 °C and 25 °C to 20% capacity fade using an electric vehicle (EV) drive cycle, CID activation occurred earlier, whereas the cells aged at 40 °C could be overcharged to a similar capacity as a fresh cell before CID activation.[56]

Juarez-Robles *et al.* have also conducted overcharge tests on cycle-life-aged pouch cells without internal safety devices. The overcharge response was affected by the magnitude of the overcharge current: fresh NCA pouch cells experienced thermal runaway and fire when exposed to a 1C overcharge current but only swelled at a C/3 current.[57] However, beyond 15% capacity fade, the cells did not experience thermal runaway even at the 1C overcharge current. For cells aged to less than 15% capacity fade, thermal runaway occurred earlier compared to fresh cells, but the maximum temperatures reached (around 360 °C) were significantly lower than for fresh cells (above 900 °C) due to reduced energy and active material available for adverse reactions.

Feng *et al*. aged commercial NMC-LMO/C-$SiO_x$ pouch cells through cycling at a slight overcharge condition (0.3 V above manufacturer-recommended limit) and subsequently performed extreme overcharge tests at various rates.[58] Under 2C overcharge, all cells went into thermal runaway and the cell with 10% capacity fade showed a higher maximum temperature (803 °C) compared to fresh cells and cells at 20% capacity fade (630–682 °C). However, the authors reported uncertainty in the maximum temperatures. They also measured a reduced time to thermal runaway for aged cells, attributed to Li deposition and loss of anode active material.

The few publicly reported external short circuit tests of aged cells have shown little impact on safety relative to fresh cells. In tests with cycle-life-aged 18650 NCA cells, no difference was observed due to similar protection provided by the positive temperature coefficient (PTC) device for both fresh and aged cells.[56] Wu *et al*. reported that a capacity fade of roughly 13% had no effect on the safety behavior of laboratory-made LCO pouch cells under external short circuit, with neither fresh nor cycled cells going into thermal runaway.[59]

To summarize, present results on the overcharge of 18650 cells suggest that aged cells might be safer than fresh cells due to reduced capacity for fueling thermal runaway, and internal safety devices provide cell-level protection even in the aged condition. By contrast, in some pouch cell designs, capacity fade did not reduce the hazards associated with overcharge and external shorts. This indicates that the abuse response of aged cells is highly dependent on the aging conditions, the cell design, and the overcharge current value and duration, although the number of studies currently published is too small to make general conclusions.

## Mechanical Abuse of Aged Cells

The mechanical abuse of Li-ion batteries has been investigated using an array of tests, including nail penetration [60, 61], crush [62], indentation [63], pinch [64], three-point bend [65], and lateral compression [66]. The results of a mechanical insult to the battery are influenced by battery chemistry (including electrolyte), SOC, and the anisotropic nature of the cell stack (different for pouch, prismatic, and cylindrical formats). The loading direction of the mechanical insult is most significant since it could make the difference between a catastrophic thermal runaway and a graceful failure (such as self-discharge without fire or single cell thermal runaway without propagation).

Critical parameters to evaluate safety during mechanical abuse, illustrated in Figure 1, are: 1) strain or displacement at the inflection point, 2) maximum applied force to rupture/crack the outer shell of the cell, generally observed as a sudden drop in the applied force, 3) strain or displacement required for a voltage drop >500 mV, generally associated with the initial short circuit of the cell, 4) overall temperature response, and 5) thermal runaway behavior. Kovachev et al. used most of these parameters to investigate the effects of 60 °C cycle aging on the mechanical abuse response (10 mm diameter indenter) at 100% SOC of 41 Ah NMC-LMO/graphite pouch cells.[67] The aged cells required greater mechanical intrusion to create the internal short circuit, as evidenced by the indenter depth and applied force required to initiate failure, likely due to electrolyte dry-out.[68] The fresh cells also showed more violent thermal runaway behavior due to the greater stored energy.[69]

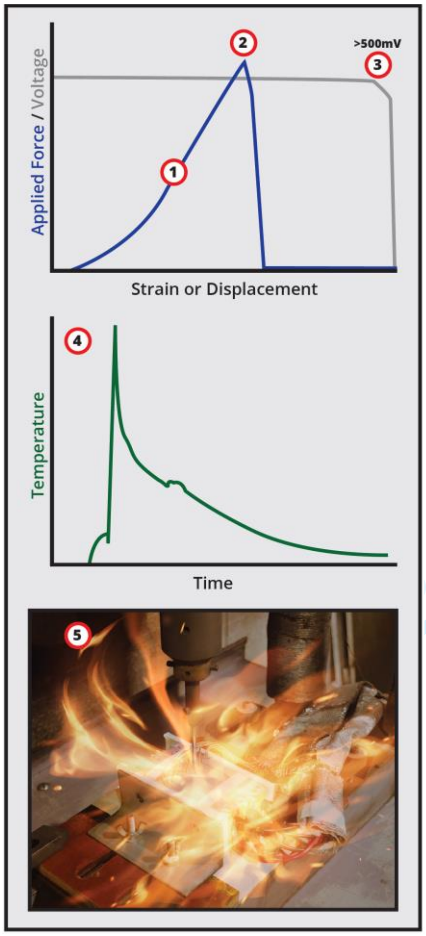


*Figure 1. Parameters to evaluate the safety characteristics during mechanical abuse: 1) inflection point, 2) applied force for rupture, 3) onset strain for >500 mV drop, 4) temperature, and 5) thermal runaway behavior. The two plots represent two different concepts each under different conditions.*

Liu et al. reported the mechanical abuse (25 mm indenter diameter) of 25 Ah NMC/graphite pouch cells aged by 0 °C cycling to 90%, 80%, and 70% remaining capacity.[70] Similar to Kovachev et al., the authors showed an increase in applied force to trigger the short circuit and higher displacement values for the aged cells. Differing from the observations by Kovachev et al., the aged cells displayed a rapid voltage decay compared to the fresh cells. We hypothesize this behavior results from insufficient energy of the aged cells to support the short circuit current. The results also highlight the sensitivity of mechanical abuse tests to conditions such as available stored energy, chemistry, and form factor.

The form factor is significant since it will determine the impact of cell degradation on the physical integrity of a cell's outer shell. In pouch cells, gas generation affects the strain or inflection point. Cells with a can outer-shell (e.g., 18650, 26650) may not experience physical changes that affect the mechanical data, so abuse studies typically report only thermal data. Friesen et al. evaluated the mechanical abuse (3 mm indenter diameter) of 2.2 Ah NMC/graphite 18650 cells by cycling at 0 °C to 70% remaining capacity.[36] The aged cells experienced sustained self-heating before the thermal runaway event, while the thermal runaway of fresh cells was triggered immediately after the nail penetration. Hildebrand et al. encountered similar trends with 2.6 Ah NMC-LCO cells cycle-aged at 20 °C or 40 °C to 70%, 80%, and 90% remaining capacity.[71] The sustained self-heating prior to thermal runaway was more prominent for cells aged at 40 °C.

Based on the available literature, aged cells appear safer than fresh cells during mechanical abuse. Aged pouch cells require greater mechanical intrusion to trigger a short circuit and aged cylindrical cells experience a several minute delay to thermal runaway following nail penetration. However, mechanical abuse tests are complex, and, due to anisotropy, the results are dependent on cell design. It is of paramount importance to evaluate the thermal and electrical response along with the mechanical data to provide a complete story of the mechanical failure. Despite the importance of this subject, data in the literature is limited.

*Module and Battery Level Testing*

Most of the experiments conducted so far to understand the abuse behavior of Li-ion systems have been performed on single cells. The main concerns when scaling up from the single-cell level to modules and batteries are the hindered heat dissipation, the possibility of thermal runaway propagation, and the ability of the cell-level safety devices to protect the larger systems. When modules and batteries are tested, the thermal runaway propagation behavior is a critical parameter to evaluate the safety of the systems, in addition to the parameters listed in the previous sections for each abuse method on the single-cell level.

Cell-level internal safety devices often do not protect at the larger module and battery scale.[5, 56, 57, 72, 73] Juarez-Robles *et al.* showed that while the CID prevents fresh 18650 NCA single cells from experiencing thermal runaway during overcharge, a fresh module of the same cells in a 3P9S configuration experienced a thermal runaway with fire.[56] Explanations include the difference in heat dissipation and the limitations of internal safety devices in the high-voltage environment of a module.[56, 72, 73] However, a cycle-life-aged module (20% capacity fade) showed improved safety with sequential CID activation and no thermal runaway (attributed to the earlier CID activation observed for aged single cells as well as to the significantly reduced energy, electrolyte dry out, and degradation of the electrodes observed in the aged cells).[56]

By contrast, another study conducted on modules of NCA pouch cells in a 5P5S configuration showed that even 20% capacity loss did not increase the safety under an overcharge event.[57] Both fresh and aged modules went into thermal runaway with fire under C/3 overcharge current and reached similar high temperatures. In cell-level testing, no thermal runaway took place when fresh and aged cells were overcharged at the C/3 rate. In external short testing of the modules, the lower energy content of the cycle-aged module (20% capacity fade) appeared to improve the safety, as a fresh module went into thermal runaway and experienced fire, whereas the cycle-aged one did not.[57]

Wang *et al*. studied the effect of cycle-life aging (capacity fade 0–95%) on thermal runaway propagation in modules consisting of three commercial 18650 NMC cells in an enclosed environment.[74] They used a resistance wire heater to trigger one of the cells into thermal runaway and concluded that aging had a negligible effect on the propagation behavior. A high aging rate was reported for the cells (over 90% capacity fade after 500 cycles) but details on the cycle aging protocol were not given. Considering the small size of the modules and the excessive capacity fade observed in the work, more testing is needed to confirm the propagation trend.

The limited available data show that the safety trends for aged modules depend on many factors including cell formats, the internal design of the cell (e.g. quantity of flammable electrolyte), the number of cells, thermal environment, and the effect of aging on the internal components of the cell, especially the electrodes and the electrolyte.

## Future Needs and Prospects

The number of studies on battery aging and safety in the open literature is limited. However, as Li-ion battery lifetimes lengthen and the demand for repurposing them grows significantly, more data is required to understand the safety of aged systems. In the following section, we lay out areas for further investigation in cell-level and module/pack-level studies.

### *Cell Level Studies*

To date, most studies of aged cell safety have relied on ARC (Table 1) and enough data has been collected to reveal clear impacts of cell aging temperature on the kinetics and thermodynamics of adiabatic heating-induced thermal runaway. Yet, most of the cells in Table 1 are under 6 Ah and the field would benefit from additional data on the thermal abuse response of cells of various sizes that have larger capacities (which are common in many Li-ion battery applications). We cannot yet draw conclusions from electrical and mechanical abuse tests due to the lack of a statistically significant number of studies. Future studies of aged cell safety should focus on the latter two abuse categories for all electrode chemistry combinations (e.g., metal oxide and olivine cathodes, graphite and advanced anodes) and cell formats. These studies should also consider the impact of the cell's thermal environment during aging as well as exposure to vibration and shock using field-relevant protocols. For all three categories of off-nominal abusive conditions, cells should be examined at various stages of capacity loss. Earlier studies by Juarez-Robles et al. suggest that safety metrics do not always monotonically change with capacity loss.[57]

Complementing abuse tests with disassembly and characterization of a cell aged under the same conditions will provide critical details on the degradation of cell components and help explain changes in safety metrics. For example, disassembled cells have shown that Li plating is the cause of significantly lower thermal runaway onset temperatures in ARC tests.[41]

*Module and Battery Pack*

Extensive studies at the module and battery pack/system level are needed to characterize the safety trends for various levels of aging. The influence of many factors including cell design (e.g., form factor and internal safety device), battery configuration (e.g., S-P versus P-S, number of cells), aging protocol (e.g., field-relevant conditions with calendar aging, varying current rates, and vibrations), level of capacity fade, and abuse protocol (e.g., rate of overcharge and short circuit magnitude) is worth exploring as, to date, fewer than five studies on the safety of aged modules have been reported in the open literature.

Beyond the cells, it is imperative to understand the impact of aging on the degradation of the accessories used for building modules and battery packs. These include interconnecting tabs and busbars, wires and cables, conformal coatings, and the containers. The integrity of these connectors should be examined with environmental testing protocols such as vibration (uneven roads as with EVs) and extreme thermal conditions. Damage to these components can initiate thermal runaway and influence subsequent propagation. For example, the disconnect of one electrical connection by excessive vibration can alter current flow such that a set of cells is overcharged or cause interconnects to dislodge, leading to short circuits across terminals or between a terminal and the cell container.

Previous studies have shown that even single cells from reputable manufacturers degrade at different rates due to manufacturing tolerances.[75] These differences are exacerbated by thermal gradients across a battery assembly, which cause an uneven increase in internal resistance as well as larger voltage deviations between cells. Large deviations in voltage can place a higher load on the battery management system (BMS), with more frequent balancing needed than in a fresh battery. Hence, more research is required to understand how the operation of a BMS should change over a battery's lifetime and how long the electronic components used for voltage and current sensing remain properly calibrated. The characterization proposed above builds on UL1974 (Standard for Evaluation for Repurposing Batteries), which requires module-, bank-, or string-level and cell-level safety tests for the module with the worst thermal exposure in the first life application.

## Conclusions

We summarized all open literature on the thermal, electrical, and mechanical abuse response of aged Li-ion cells and modules relative to their fresh counterparts. A majority of the studies have relied on thermal abuse via ARC; key conclusions are that aged cells generally have a lower peak temperature than fresh cells, although aging cells under conditions that induce Li plating can lower thermal runaway onset temperatures by over 50 °C. There have been just a handful of studies on the electrical and mechanical abuse response of aged batteries, so it is difficult to draw broad conclusions. Based on this analysis, we lay out several research areas that merit further exploration. It is important to understand how the failure modes of aged cells differ from fresh cells (e.g., lower thermal runaway onset temperature, more vulnerability to vibration) to design more effective battery qualification procedures and failure mitigation systems for second-life applications.

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