Abstract

Since a laptop caught fire in 2006 at the latest, Li-ion cells were considered as more dangerous than other accumulators [1]. Recent incidents, such as the one involving a BYD e6 electric taxi [2] or the Boeing Dreamliner [3], give rise to questions concerning the safety of Li-ion cells. This is a crucial point, since Li-ion cells are increasingly integrated in all kinds of (electric) vehicles. Therefore the economic success of hybrid electric vehicles (HEV) and battery electric vehicles (BEV) depends significantly on the safety of Li-ion cells.

Lithium nickel manganese cobalt oxide (NMC) and lithium nickel cobalt aluminium oxide (NCA) are two standard Li-ion cathode chemistries, which are often used for today’s HEVs and BEVs Li-ion batteries. Cells with this two cathode technologies are investigated in detail and compared to cells with the alleged save lithium iron phosphate (LFP) technology. Furthermore only commercially available and mass produced Li-ion cells were tested, in order to get as close to real end-user applications as possible. To ensure comparability, cells with the most common 18650 casing have been used. Furthermore all cells had no built-in resistor with positive temperature coefficient (PTC-device). For each abuse test at least 2 cells have been tested to get to know the statistical dispersion. The spread was in all tests for all measured values of each cell type lower than 11 %. Consequently it can be supposed, that mass produced cells show equal behaviour also in abusive test.

The performed electrical safety tests on these cells, involve overcharge, overdischarge and short circuit tests. These tests represent real abuse scenarios and are geared to established standards [15], [16], [17], [18]. To complete these measurements an accelerated rate calorimetry (ARC) test has been carried out, to determine the thermal stability of the cells. As in the literature discussed, the investigated LFP/C cells show a higher thermal stability and are therefore safer, although they do not have any overcharge buffer as the investigated NCA/C and NMC/C cells.

Keywords: battery, lithium battery, safety, reliability, short circuit, materials
1 Introduction

Because of their high energy density principally Li-ion batteries are chosen for electric vehicles. But the term “Li-ion battery” is used for all kind of accumulators based on Li-ion intercalation. So Li-ion technologies can further be distinguished according to their cathode material. Acronyms for common cathode materials are:

- LCO: Lithium cobalt oxide
- LMO: Lithium manganese oxide
- NMC: Lithium nickel manganese cobalt oxide
- NCA: Lithium nickel cobalt aluminum oxide
- LFP: Lithium iron phosphate

Usually graphite (C) is used as anode material. The various Li-ion technologies show different properties in terms of safety behaviour, energy density, electrical loading capacity and voltage level.

In this paper the safety behaviour of the NMC/C and NCA/C technologies, which are often used in electric vehicles, are investigated and compared to the alleged safe LFP/C technology. Only mass produced and commercially available cells with the most common 18650 casing (cylindrical, 18 mm diameter, 65 mm height) have been used for the safety studies. All of the cells had no built-in resistor with positive temperature coefficient (PTC). Their electrical characteristics are listed in Tab. 1.

![Figure 1: OCVs of the investigated cells](image)

<table>
<thead>
<tr>
<th>Type</th>
<th>C_N</th>
<th>U_N</th>
<th>R_i,Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 LFP/C</td>
<td>1.1 Ah</td>
<td>3.2 V</td>
<td>17 mΩ</td>
</tr>
<tr>
<td>2 LFP/C</td>
<td>1.05 Ah</td>
<td>3.2 V</td>
<td>11 mΩ</td>
</tr>
<tr>
<td>3 NMC/C</td>
<td>1.5 Ah</td>
<td>3.65 V</td>
<td>12 mΩ</td>
</tr>
<tr>
<td>4 NCA/C</td>
<td>1.5 Ah</td>
<td>3.6 V</td>
<td>24 mΩ</td>
</tr>
</tbody>
</table>

The internal ohmic resistance $R_{i,Ω}$ was determined by using the electrochemical impedance spectroscopy (EIS) on at least 15 cells of the same type. $R_{i,Ω}$ is given, by the real part of the impedance at the zero-crossing of the imaginary part in the Nyquist diagram. In Fig. 1 the open circuit voltages (OCV) of the investigated cells are shown. The lower and flatter voltage level compared to NMC/C and NCA/C is inherent for LFP/C cells. For NMC/C and NCA/C the OCV depends much more on the depth of discharge (DOD).

The standardized safety tests for Li-ion cells and batteries can be classified in mechanical, environmental and electrical abuse scenarios. The presented investigations focus on the electrical abuse behaviour of the named 3 Li-ion technologies. For the characterisation of the electrical abuse behaviour short circuit, overdischarge and overcharge tests were carried out. Additionally, since the thermal stability accomplishes the comprehensive investigations, each cell has been characterized by accelerated rate calorimetry (ARC).

2 Accelerated rate calorimetry

To evaluate the thermal stability of each Li-ion technology ARC tests are often performed [4], [5], [6], [7]. With an ARC the self-heating rate of a complete cell can be determined in a quasi-adiabatic environment.

In this publication fully charged cells were firstly heated up to a start temperature of 50 °C. Secondly each cell was further heated according to the heat-wait-search analysis with heating steps of 3 °C. In each of these heating steps, the cell was held at constant temperature for 30 min to reach complete thermal equilibrium with the calorimetric system (wait step). This was followed by a 10 min “seek” step, where the system tries to detect any self-heating phenomena on the cell surface. Once the self-heating rate in a seek step exceeds 0.02 °C/min, the calorimeter tracks the reaction by simultaneously adapting its temperature to the temperature measured on the cell surface. Once the self-heating rate in a seek step exceeds 0.02 °C/min, the calorimeter tracks the reaction by simultaneously adapting its temperature to the temperature measured on the cell surface. The applied ARC system can follow the temperature profile only up to a rate of 20 °C/min.

A closer look on the ARC profile of the LFP/C type 1 cell (LFP1) allows explaining the single
reactions during the test in more detail (see Fig. 2). The onset temperature is 104 °C and the temperature rate starts to rise significantly from about 120 °C on. This is mainly, because of the solid electrolyte interface (SEI) breakdown [6], [11], [14]. There are some endothermic reactions at ca. 170 °C. This is caused by the separator melting [21] and maybe also because binder in both electrodes (PVdF) melts. These endothermic phenomena could be very useful, because they hinder further thermal runaway. The thermal decomposition of the electrolyte with the negative electrode starts above 200 °C as well as the reaction of the binder with the lithiated negative material. [11]

For the two rate declines at about 250 °C and 280 °C it can be assumed, that first the safety vent of the cell and afterwards the can completely open.

The results of the ARC tests for all cells are recorded in the diagram in Fig. 3. The diagram shows only the self-heating rate dependent on the cell temperature measured at the cell’s casing.

Table 2: Important ARC values of investigated cells

<table>
<thead>
<tr>
<th>Type</th>
<th>$T_{\text{onset}}$</th>
<th>$T$ when rate $&gt;5$ °C/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 LFP/C</td>
<td>104 °C</td>
<td>287 °C</td>
</tr>
<tr>
<td>2 LFP/C</td>
<td>81 °C</td>
<td>212 °C</td>
</tr>
<tr>
<td>3 NMC/C</td>
<td>88 °C</td>
<td>212 °C</td>
</tr>
<tr>
<td>4 NCA/C</td>
<td>86.5 °C</td>
<td>183 °C</td>
</tr>
</tbody>
</table>

The LFP/C cells are from two different manufacturers and chemical details about the electrolyte, etc. are not known. Both LFP/C cells have in common, that their maximum temperature rates of 28 °C/min respectively 7 °C/min are much lower than the ones of the NMC/C and NCA/C cells. Conversely, the NCA/C and NMC/C cells show temperature rates of more than 400 °C/min. This means, that the investigated LFP/C cells show a significantly higher thermal stability. This is because the LiFePO$_4$ is a cathode material with olivine structure, which has no exothermic decomposition reaction. If the LFP cathode is overheated no gaseous oxygen is released, which could react with organic electrolyte and enhance the heat release from the cell during thermal runaway [9], [10].

Furthermore the test results reveal that thermal stability of the NMC/C cell is higher than of the NCA/C cell. All these results are in line with other reported tests [4], [7], [8].

3 Short circuit

In case of an electrical short circuit the most dangerous consequence is, that the cell heats up due to the high current. This is in close relation to the already discussed thermal stability. In this investigation a resistance of 8 mΩ has been chosen for short circuiting the Li-ion cells. The current, temperature and voltage curve over time for the short circuit test at the LFP1 cell are shown in Fig. 4. The cells are short circuited at exactly 10 s. All cells were in a fully charged state at the beginning of the short circuit test.

At the beginning the current shows a peak of 122 A. The maximum is set by the conductivity of the electrolyte and solid-phase materials [12]. The peak value can be estimated with formula (1). For the measurement shown in Fig. 4. with $U_{\text{start}}=3.34$ V and $R_{\text{i},\Omega}=17$ mΩ (see Tab. 1) a peak current of 134 A can be calculated.
The peak is very short in time and within 4 s after the short circuit started the current decreases to 98 A. This is due to limitations in mass transport. After 4 s the current starts to rise again, because the temperature inside the cell is rising and accelerates diffusion and all other electrochemical processes. At about 20 s the current declines again, because the cell is rapidly discharged. [12]

The sharp cut of the current at 35 s can be due to separator melting (~125 °C for polyethylene and ~155 °C for polypropylene [21]) or CID opening (see Chap. 5). [12], [13]

The short circuit tests have been performed on all 4 cell types (see Tab. 1). Every test has been carried out on 3 single Li-ion cells of the same type. The measured value with the greatest statistical dispersion was the temperature. The maximum spread in the measured values was usually as low as 6 % and only for the LFP2 cells, where the safety vent at 2 cells opened, 11 %. The following statement can be supposed: Mass produced cells show only slight differences also in their abuse behaviour.

The current profiles for the different types are shown in Fig. 5, the voltage and temperature behaviour in Fig. 6. It can clearly be seen, that the safety mechanism of the NCA/C cell is activated much earlier than those of the NMC/C, LFP1 and LFP2 cell. Although the temperature of the NCA/C cell, measured at the casing, in Fig. 6 is much lower it can be assumed, that the internal temperature or the gas production of the NCA/C cell was higher and therefore the separator melted or the CID opened (see Chap. 5).

There is also a step in the NMC/C current profile at ca. 25 s. Here some safety mechanism as for example a partial melt down of the separator is activated. The characteristic test results are listed in Tab 3. The order in which the safety mechanisms are activated – NCA, NMC, LFP2 and LFP1 – reflects the thermal stability of the ARC tests. Whereas the succession of the maximal currents is reflected by formula (1), thus by the starting voltage and the internal resistance.

### Table 3: Important values of short circuited cells

<table>
<thead>
<tr>
<th>Type</th>
<th>t_safety</th>
<th>I_max</th>
<th>U_start</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP/C</td>
<td>35 s</td>
<td>122 A</td>
<td>3.34 V</td>
</tr>
<tr>
<td>LFP/C</td>
<td>32.5 s</td>
<td>150 A</td>
<td>3.4 V</td>
</tr>
<tr>
<td>NMC/C</td>
<td>ca. 23.5 s</td>
<td>176 A</td>
<td>4.0 V</td>
</tr>
<tr>
<td>NCA/C</td>
<td>11.7 s</td>
<td>120 A</td>
<td>4.0 V</td>
</tr>
</tbody>
</table>

### 4 Overdischarge

In the data sheet of every Li-ion cell a minimum voltage is defined. For the investigated LFP/C and NMC/C cells it is 2.0 V and for the NCA/C cell...
2.5 V. There are several potential failure causes, which can lead to discharging the cell below this minimum voltage. Self-discharge can be one cause, but since the self-discharge rate of Li-ion cells is only a few per cent of the nominal capacity per month [19], only long storing periods can seriously overdischarge the cells. On the other hand, connected electronic circuitry, other electronic loads or even a wet battery container can overdischarge a Li-ion cell. Furthermore, several cells connected in series can lead to a forced overdischarge, when the voltage of one cell is significantly lower than the others and single cell voltages are not monitored. An example is shown in Fig. 7, where one cell is completely discharged, whereas the other cells are nearly fully charged. If the battery pack is then discharged, this will lead to a forced overdischarge of the empty cell.

In [16] and [18] discharging with a 1 C rate is demanded. Accordingly, in this paper the fully loaded Li-ion cells were discharged with a 1 C rate for 3 hours. The current as well as the resulting voltage and temperature of the LFP1 cell over time are shown in Fig. 8. The voltage curve shows for the first 3400 s the normal discharge characteristic. When the voltage drops below the allowed minimum voltage, the temperature rises because of the SEI break-down and electrolyte reduction [20], [21]. When the anode’s voltage reaches about 3.4 – 3.5 V the copper foil starts to oxidize [20], [22]. These processes cause the rise of the cell temperature. Since the cell is further discharged, the voltage is reversed and gets negative. The dissolved Cu²⁺ ions can penetrate through the separator and cause shunts between the cathode and the anode. This might lead to the second temperature rise at about 6000 s.

After the cell is internally short circuited and no further chemical reactions take place, the cell behaves like an ohmic resistance. Than the negative terminal voltage of the cell results solely from the IR drop [21].

For each cell type only 2 cells have been overdischarged, because the 2 curves each showed very good resemblance. The terminal voltages over time are presented in Fig. 9.

All cells reached their minimum voltage at DOD=1.05 – 1.15. Subsequently, the voltages were reversed. The lowest voltage reached for each cell is listed in Tab. 4. It can clearly be seen, that the lowest voltage is reached for the NCA/C cell. While the NMC/C cell shows a broader peak of the first voltage decline, the LFP1, LFP2 and NCA cells show a second voltage decline (see Fig. 9). This behaviour is reflected in the temperature diagram (see Fig. 10). The second voltage decline leads to a second temperature rise.

The highest temperature is reached by the NMC/C cell. An interesting observation can be made: the higher the temperature of the cell casing, the earlier the second voltage decline respectively second temperature increase occurs.
Table 4: Important values of overdischarged cells

<table>
<thead>
<tr>
<th>Type</th>
<th>(U_{\text{min}})</th>
<th>(T_{\text{max casing}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 LFP/C</td>
<td>-0.87 V</td>
<td>37 °C</td>
</tr>
<tr>
<td>2 LFP/C</td>
<td>-1.0 V</td>
<td>41.5 °C</td>
</tr>
<tr>
<td>3 NMC/C</td>
<td>-0.92 V</td>
<td>47.5 °C</td>
</tr>
<tr>
<td>4 NCA/C</td>
<td>-1.6 V</td>
<td>42.5 °C</td>
</tr>
</tbody>
</table>

This leads to the conclusion that a certain heat output triggers the second reaction, which might be caused by the internal copper short circuit.

![Figure 10: Temperature over time for the overdischarged Li-ion cells](image)

Summing up, for all cells no dangerous temperatures arose and the cells showed no damage at the casing, let alone electrolyte leakage. The 2 LFP/C cells showed a relatively low voltage decline and the lowest maximum temperature in the comparison.

5 Overcharge

Overcharging a Li-ion cell is one of the severest failures to occur. Therefore a very effective safety device, the current interrupt device (CID), is usually implemented in cylindrical Li-ion cells. In Fig. 11 the functionality of the CID is illustrated. The CID is a diaphragm made of metal at the top of the cell, which opens, when too much gas pressure is produced inside the cell. When it opens, it disconnects one electrode from the cell terminal and no further current flow is possible [23], [24].

The voltage and temperature behaviour of the NMC/C cell, when overcharged with a constant 1 C rate is shown in Fig. 12. The NMC/C cell shows the most typical overcharge behaviour for Li-ion cells. At the beginning the cell was completely discharged and reaches at 3300 s 4.2 V, the maximum voltage permitted by the manufacturer.

![Figure 11: CID at top of cylindrical battery cell before and after opening (according to [24])](image)

When the cell is further charged, nearly all Li-ions are pumped from the cathode to the anode. For the NMC/C cell at about 4.5 V the cathode is mostly discharged. When the anode is fully loaded lithium metal may be deposited on the carbon and hereby reduces the thermal stability of the cell. Up to now no serious heat output can be observed. [21], [25], [26]

![Figure 12: Voltage and temperature behaviour of NMC/C cell when overcharged with a constant 1 C rate](image)

The resistance of the nearly discharged cathode increases and therefore Joule heat is generated. Furthermore the electrolyte oxidizes at the cathode and produces further heat. The deposited lithium at the cathode can form dendrites and they can cause a soft short circuit. With the increasing temperature also the anode starts to react exothermically. This can lead to further heat output and finally result in a thermal runaway. [11], [21], [25], [26]

The oxidation of the electrolyte produces gas. The gas pressure inside the cell opens the CID and thereby disconnects one electrode from the cell terminal. The sharp voltage step to the maximum voltage of the power supply is the consequence.

For every cell type 3 cells have been tested. The statistical dispersion of temperatures between the single cells was lower than 7%. This is also
because of the different start temperatures and can be comprehended by Fig. 13. For the other cell types the spread of the measured values was also much lower than 10%. Consequently the results and findings are at least representative for the investigated cells.

Figure 13: Comparison of overcharge behaviour of 3 NMC/C cells of the same type

In Fig. 14 the overcharge behaviour is shown over the SOC for the different cell types. The onset SOC of the temperature rise and the temperature rate over the SOC are listed in Tab. 5.

Table 5: Overcharge values of investigated cells

<table>
<thead>
<tr>
<th>Type</th>
<th>SOC onset</th>
<th>T rate after onset</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 LFP/C</td>
<td>1</td>
<td>0.8 °C per % SOC</td>
</tr>
<tr>
<td>2 LFP/C</td>
<td>1.05</td>
<td>0.77 °C per % SOC</td>
</tr>
<tr>
<td>3 NMC/C</td>
<td>1.35</td>
<td>1.02 °C per % SOC</td>
</tr>
<tr>
<td>4 NCA/C</td>
<td>1.3</td>
<td>1.74 °C per % SOC</td>
</tr>
</tbody>
</table>

It can clearly be seen, that both LFP/C cells start to react exothermally as soon as they reach SOC=1, whereas the NMC/C and NCA/C cell show some overcharge buffer. This is because the LiFePO₄-cathode is almost completely discharged at SOC=1 (x~0.0 respectively Li₀.₀FePO₄). For NMC/C at 100% SOC the remaining Li content is x~0.48 and for NCA/C x~0.36. [4].

From the performed overcharge test it can be concluded, that LFP/C cells show no overcharge buffer. If this type of cell is charged a little above SOC=1, the cell is irreversibly damaged. Furthermore all investigated cells contained a CID, so that no dangerous situation or even thermal runaway occurred.

6 Conclusion

Electrical abuse tests, namely short circuit, overcharge and overdischarge, have been performed and evaluated. Additionally ARC tests gave information about the thermal stability. The cells’ safety features effectively prevented a dangerous situation. For each Li-ion battery type at least 2 cells have been investigated. Because the statistical dispersion is very low, it can be suggested, that mass produced cells show similar behaviour even in abuse conditions.

The presented results show that the LiFePO₄/C cells have a higher thermal stability and therefore are safer for all kinds of thermal abuse or electrical abuse, where the heat generation is the critical point. Nevertheless, when overcharging a LFP/C cell the cathode does not have an overcharge reserve as the NMC/C and NCA/C cells and therefore is earlier irreversibly damaged. Furthermore both investigated LFP/C cells showed sometimes electrolyte leakage when short circuited. It can be noted that apart from the chemistry also the concrete design of each cell is crucial for its safety.

Figure 14: Comparison of overcharge behaviour of 3 NMC/C cells of the same type
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