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 safe 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.

Table 1: Electrical characteristics of investigated cells

<table>
<thead>
<tr>
<th></th>
<th>Type</th>
<th>C_N</th>
<th>U_N</th>
<th>R_{iΩ}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LFP/C</td>
<td>1.1 Ah</td>
<td>3.2 V</td>
<td>17 mΩ</td>
</tr>
<tr>
<td>2</td>
<td>LFP/C</td>
<td>1.05 Ah</td>
<td>3.2 V</td>
<td>11 mΩ</td>
</tr>
<tr>
<td>3</td>
<td>NMC/C</td>
<td>1.5 Ah</td>
<td>3.65 V</td>
<td>12 mΩ</td>
</tr>
<tr>
<td>4</td>
<td>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_{iΩ} was determined by using the electrochemical impedance spectroscopy (EIS) on at least 15 cells of the same type. R_{iΩ} 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).

![OCV of investigated cells](image)

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. 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.

Self-heating occurs already at temperatures around 80 °C but temperature rates higher than 5 °C/min do not appear before 180 °C is reached on the cell casing. Tab. 2 summarizes these values for the investigated cells.

<table>
<thead>
<tr>
<th>Type</th>
<th>T_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 LiFePO₄ 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_start=3.34 V and R_0=17 mΩ (see Tab. 1) a peak current of 134 A can be calculated.
Figure 4: Current, temperature and voltage curves for an overcharged LFP1 cell

\[ I_{\text{peak}} = \frac{U_{\text{start}}}{R_{\text{ohmic}} + R_{\text{short, ext}}} \]  

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 early 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_{\text{safety}} )</th>
<th>( I_{\text{max}} )</th>
<th>( U_{\text{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
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 loaded. 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 Cu$^{2+}$ 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</td>
<td>-0.87 V</td>
<td>37 °C</td>
</tr>
<tr>
<td>2</td>
<td>-1.0 V</td>
<td>41.5 °C</td>
</tr>
<tr>
<td>3</td>
<td>-0.92 V</td>
<td>47.5 °C</td>
</tr>
<tr>
<td>4</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.

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.

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]

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.

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.
References


[7] J. Jiang, J. R. Dahn, ARC studies of the thermal stability of three different materials: LiCoO2; Li[Ni0.1Co0.8Mn0.1]O2; and LiFePO4 in LiPF6 and LiBoB EC/DEC electrolytes, Electrochemistry Communications, 6 (39-43), 2004


[9] M. Roscher, Zustandserkennung von LiFePO4-Batterien für Hybrid- und Elektrofahrzeuge, Dissertation, RWTH Aachen, 2010


[16] Standard, Secondary lithium-ion cells for the propulsion of electric road vehicles – Part 2: Reliability and abuse testing, IEC 62660-2, 2010

[17] Standard, UN Transportation Testing for Lithium Batteries, UN 38.3


[25] R. Spotnitz, J. Franklin, Abuse behavior of high-power lithium-ion cells, Journal of Power Sources, 113 (81-100), 2003

Authors

**Dipl.-Ing. Martin Brand**
 wrote his diploma thesis at the BMW group on the project MINI E and received the diploma degree in electrical engineering from TU Munich in 2010. At the moment he is a Ph.D. student at the Institute for Electrical Energy Storage Technology at the TU Munich. At the institute he is leading the team “battery systems technology”.

**Dipl.-Ing. Simon Gläser**
 received his diploma degree in electrical engineering from the TU Munich in 2012. He works at the TÜV SÜD Battery Testing GmbH, specialized in abuse and environmental testing of Li-ion cells. At the moment he is sub-project manager at the project ExZellITUM, which aims on developing new methods for production and testing of energy storage systems.

**Dipl.-Ing. Jan Geder**
 graduated in chemical engineering from University of Ljubljana, Slovenia, in 2010. He gained experience in his field working for the Siemens AG and the Forschungszentrum Jülich. In 2011, he started Ph.D. studies at TUM CREATE in Singapore, where his research focuses on the influence of structure and composition of battery electrode materials on thermal stability and safety.

**B. Sc. Sebastian Obpacher**
 is studying electrical engineering at the TU Munich. Before that, he graduated in business administration at the University of Regensburg. His practical experiences contain different activities in the hydrogen fuel cell industry and in the battery industry. Currently he is researching on battery safety at the TÜV SÜD Battery Testing GmbH.

**Prof. Dr.-Ing. Andreas Jossen**
 earned his doctorate, dealing with management of photovoltaic plants using energy storage systems at the University of Stuttgart. Since 1994 he was group leader for different battery related topics at the ZSW in Ulm. Since 2010 he is full professor at the Institute for Electrical Energy Storage Technology at the TU Munich.

**Dipl.-Ing. Daniel Quinger**
 worked in different positions for 3M, BMW, EVA and ENAX. He received his diploma degree in mechanical engineering from TU Munich in 2009. He is founder of LION Smart GmbH and currently CTO of the TÜV SÜD Battery Testing GmbH, which is a joint venture between the LION Smart GmbH and the TÜV SÜD AG.

**B. Sc. Stefan Menacher**
 is student of electrical engineering at the TU Munich since 2008. He gained his Bachelor of Science, dealing with the characterisation of organic light emitting diodes. At the moment he is working on his master thesis about abuse tests and safety of lithium ion batteries.