



Failure modes, effects and criticality analysis (FMECA) of lithium-ion batteries placed in liquid silicone

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Statutory Declaration

I solemnly declare that the work presented here is my own unless otherwise stated. External sources are marked as such. This work has not been previously submitted for any other degree.

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Abstract

The abundance of lithium-ion batteries in private and professional settings calls for comprehensive knowledge regarding possible dangers arising with their use. Moreover, new and innovative ways are needed to overcome them.

By submerging stress-tested lithium-ion batteries in silicone oil, this work not only presents and assesses the effectiveness of this newly found pacifying method with the help of a failure modes, effects and criticality analysis (FMECA). Valuable knowledge is also gained about the basics of lithium-ion battery technology, as well as their safe storage.

Results show that silicone oil helps to prolong the time frame a cell can endure an overstress situation like overcharging or over-discharging and reduce the severity of a worst-case scenario like nail penetration. On the other hand, it is not suitable to prohibit cell failure altogether.

Following the recommendations proposed here, not only helps to ensure the longevity of cycled cells but also contributes to a safer work environment.

Kurzfassung

Die Allgegenwärtigkeit von Lithiumbatterien im privaten, sowie professionellen Umfeld verlangt nach umfangreichem Wissen über potenzielle Gefahrenquellen während ihrer Benutzung. Des Weiteren braucht es neue und innovative Wege diesen zu begegnen.

Mit dem Eintauchen von Batteriezellen in Silikonöl während eines Belastungstests, wird eine neuartige Methode vorgestellt und mithilfe einer Fehlzustandsart-, -auswirkungs- und -kritizitätsanalyse (engl. FMECA) bewertet. Zusätzlich gewinnt der Leser wertvolle Einsichten über die Grundlagen der Lithiumbatterietechnologie und die sichere Aufbewahrung der Zellen.

Wie die Ergebnisse zeigen, verlängert das Silikonöl während eines Belastungstests wie Überladen und Überentladen das Zeitfenster bis zum Zusammenbruch der Batterie. Die negativen Auswirkungen eines Worst-Case-Szenarios wie eine Nagelpenetration können außerdem abgemildert werden. Andererseits kann das Öl den Zellzusammenbruch nicht komplett verhindern.

Das Umsetzen der hier propagierten Empfehlungen stellt letztendlich nicht nur die Langlebigkeit der benutzten Batterien sicher, sondern leistet außerdem einen wertvollen Beitrag für die Schaffung eines sicheren Arbeitsumfelds.

Nomenclature

C	battery capacity	[Ah]
c_p	specific heat capacity	[kJ/kgK]
d	separator failure displacement	[mm]
g	gravity force	[m/s ²]
h	height	[m]
I	current	[A]
m	mass of silicone oil	[kg]
P	Ohmic/Joule heating	[W]
ΔQ	calorific energy	[kJ/Wh]
R	resistance	[Ω]
R^{nl}	nail radius size	[mm]
ΔT	heat difference	[K]
t	time	[h]
v	speed of falling object	[m/s]

Acronyms and Abbreviations

Al	aluminium
BMS	battery management system
CH ₄	methane
C ₂ H ₄	ethene
C ₂ H ₆	ethane
CO	carbon monoxide
CO ₂	carbon dioxide
Cu	copper
FMEA	failure modes and effects analysis
FMECA	failure modes, effects and criticality analysis
FMMEA	failure modes, mechanisms and effects analysis
FTA	fault tree analysis
H ₂	hydrogen
HE	hazardous element
HF	hydrogen fluoride
IM	initiating mechanism
LCO	lithium cobalt oxide
LFP	lithium iron phosphate
LiC ₆	lithiated graphite
LiPF ₆	lithium hexafluorophosphate
LMO	lithium manganese oxide
LTO	lithium titanite oxide
NCA	lithium nickel aluminium oxide
NMC	lithium nickel manganese cobalt oxide
O ₂	oxygen
PH ₃	monophosphane
RPN	risk priority number
SEI	solid electrolyte interface

SOC	state of charge
SOH	state of health
TEM	transmission electron microscopy
T/T	target and threat

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1. Introduction

Already valued at \$21.8 billion in 2019, the global lithium-ion battery market is expected to rise to a value of \$71 billion in 2025. These statistics underline the great importance this technology already has today and will have even more in the future (Research and Markets Ltd, 2020, s.p.; Wagner, 2019, s.p.).

Today's omnipresence of lithium-ion batteries can be seen as a two-edged blade, though. On the one hand, life as we know it would not be possible without them. The battery found its way into an abundance of everyday objects reaching from electronic devices like smartphones and laptops to electric cars. On the other hand, the manifoldness of lithium-ion powered products has led to a surge of accidents involving them (Tomboy, 2018, 3; Bilton, 2016, 2).

Pictures of burning Teslas or mobile phones raise concerns in private, as well as professional settings, and call for clarification regarding the safe handling and possible dangers of lithium batteries, as well as their countermeasures. Here, the work at hand sets in.

A detailed description of the working principle, built-in safety features and possible sources of danger first familiarizes the reader with this technology. In the future course, a failure modes, effects and criticality analysis is carried out to investigate the effects of submerging batteries experiencing a variety of overstress situations in silicone oil. Furthermore, advice is given concerning the safe storage of the cells.

The results are incorporated in future test set-ups done by the University of Natural Resources and Life Sciences Vienna as part of the MEGAWATT-Logistics project. Goal of this project is to find solutions for logistic companies to switch from normal to e-trucks successfully. Within this scope, the University examines the cycle life of the used lithium-ion batteries subjected to different levels of stress, creating ageing models from the findings. To do so, a battery testing unit is set up where cells are cycled in a silicone bath. The liquid silicone acts hereby as a pacifier in potentially dangerous situations. Since errors during testing cannot be ruled out completely, this work shows the consequences one has to expect and possible countermeasures. Goal is to provide valuable knowledge for creating a safer workspace (Klima- und Energiefonds, 2019, 13).

2. Background

2.1 State of knowledge and key objectives

When Sony released the first commercially available lithium-ion battery in 1991, the world was at the beginning of a transformative change named globalization. It meant highly increased competition and allocation of production around the globe. Lithium battery production was no exception and moved from Japan to South Korea and China. That led to an estrangement of electronics and battery producers. Ever-increasing computing power demanded more power, which meant thinning out separators to create room for more reactive material. This came at the cost of safety, whose results can be seen in the notebook battery fire crisis of 2006. Dell, for instance, had to recall 4.1 million notebook computer's Sony batteries because of fire hazards (Eisler, 2016, s.p.; Mauger and Julien, 2017, 1933).

These incidents would have been avoidable, though. As soon as 1991 and meant as support data for failure modes and effects analyses (FMEAs) and failure modes, effects and criticality analyses (FMECAs), the Reliability Analysis Centre (RAC) released a document containing failure distributions on parts and assemblies. Listed here are failure mode probabilities of lithium batteries like manufacturing defects (RAC, 1991, 42).

FMEAs are widely accepted as a supporting tool in reliability programs. According to a survey of 500 reliability professionals across the globe, an FMEA is even the single most important tool in their reliability programs (Carlson, 2012, 4). Therefore, an abundance of papers and scientific books published about FMEAs comes as no surprise. A general overview of existing hazard analysis gives Ericson with "Hazard Analysis Techniques for System Safety". FMEAs are discussed in length by Carlson (Ericson, 2005; Carlson, 2012).

The entry of lithium batteries in our daily life fuelled, among others, by portable electronics, gave birth to countless scientific essays, especially in recent years. They examine every stage of the batterie's life cycle, from production (Mauger and Julien, 2017) to recycling (Diekmann et al., 2018). Safety aspects play a critical role hereby (Mauger and Julien, 2017, 1933). Basics of lithium batteries are illustrated in Reiner Korthauer's "Lithium-Ion Batteries: Basics and Applications" (2018).

But what about the combination of hazard analysis and lithium batteries? As Bubbico et al. state, there are only a few papers published in that area (2018, 73). Most rely on the fault tree analysis (FTA), a certain kind of hazard analysis, which breaks down all failure modes "into a series of discreet [sic] events linked together through logic gates" (Fouchard and Lechner, 1993,

1193). Its accuracy makes it a powerful tool to identify failure paths. On the other hand, this makes it too specific to be used for a whole typology of systems. Examples can be found in literature from Tabaddor and Fouchard and Lechner (Bubbico et al., 2018, 73).

Scientific documents found about lithium battery FMEAs, often focus on particular aspects of this technology. Schlasza et al., for example, give a comprehensive overview of aging mechanisms of lithium batteries using said method (2014). The rather general approach of an FMEA, which makes it easily adaptable to different systems, is underlined in Ashtiani's work, who uses the technique in the electric vehicle sector to examine the risk posed by batteries in case of a mishap (2008). Valuable insights of failure modes were gained by Hendricks et al. via an failure modes, mechanisms and effects analysis (FMMEA), a technique first proposed by Ganesan and team (2015; 2005).

In contrast to the specific approach of these papers, Soares et al. analysed the whole life cycle of a lithium battery to find situations most hazardous and how to avoid them (2015). By conducting an FMEA targeting unwanted interactions between the environment and lithium batteries, Bubbico et al. also do not focus on certain internal reactions (2018).

Hong and Binbin try to combine FTA and FMEA in their work, to obtain the best of both worlds. This approach is also taken up by NASA, a popular advocate of FMEAs due to their well-planned space missions (2009; Lanzisero and Fernando, 2009).

The scientific publications presented here show that lithium batteries, as well as FMEAs, are well studied, especially on their own. Research combining both is present, but not in relevant numbers. The work at hand tries to close this gap. For this, an FMECA focusing on lithium batteries is carried out. Adding criticality allows a better judgement of the severity by developing an RPN-severity matrix. More precisely, the question it tries to answer is:

“By deploying an FMECA, can the hazard potential of stress-tested lithium-ion cells be reduced by submerging them in liquid silicone?”

Answering this question provides guidance for University employees and students, who will carry out future tests at a University battery testing unit with similar conditions. In an effort to answer this question, the batteries are overcharged, over-discharged, and mechanically damaged. The stress test results are then classified according to criteria set by the FMECA.

Since the batteries are not only cycled but also stored at the University, another key objective is to work out a set of rules for safe storage of them. This set of rules is not only based on results of the stress test though but also on findings in relevant scientific literature.

2.2 Development and operating principle of lithium-ion batteries

The following three chapters are set out to familiarize the reader with lithium-ion technology and show up potential dangers during their use, as well as measures to avoid them.

The development of lithium-ion batteries dates back to 1912 when Gilbert Newton Lewis became a professor of physical chemistry and dean of the College of Chemistry at the University of California, Berkeley and launched research in this field. It took till the 1970s, though, to get the invention ready for the market and another two decades to introduce it to a broader public. In the 1990s, Sony took a patent for the first rechargeable lithium-ion battery, built into one of the company's newest camcorders. This marks the starting point of this technology's triumphal march into as many products as it can be found in today (Mauger and Julien, 2017, 1933; Sony, 2018, s.p.).

Figure 1 demonstrates the operating principle of a rechargeable lithium-ion battery. An ion-conducting electrolyte is situated between two electrodes. A porous membrane electrically isolates the two electrodes hereby. During charging and discharging, single lithium-ions migrate between the two electrodes and are intercalated into the active materials. Aluminium plays the role of a positive, copper the one of a negative current collector. During discharging, lithium is deintercalated at the negative electrode. This sets free electrons, which migrate through an outer electrical connection to the positive electrode, whereas the lithium-ions travel through the electrolyte and separator to the positive electrode. Once arrived there, they are again intercalated into the positive electrode's active material, namely mixed oxides. At the negative electrode, on the other hand, the active material is graphite and amorphous carbon (Leuthner, 2018, 14).

During charging, electrons are forced from the positive to the negative electrode. Lithium-ions then migrate from the positive electrode through the electrolyte and separator to the negative electrode, where they are intercalated into the active material once more. It has to be stated that for the course of this work the cathode will always refer to the active material of the positive current collector, whereas the anode will refer to the active material of the negative one (Leuthner, 2018, 14; Weber and Roth, 2018, 78).

Going into more detail, the (dis-)charging process makes use of the different electrochemical potential between the electrodes. Aluminium (Al) and copper (Cu) are hereby chosen as current collectors due to their high conductivity and stability, also at the high potentials found at the electrodes (Vuorilehto, 2018, 23).

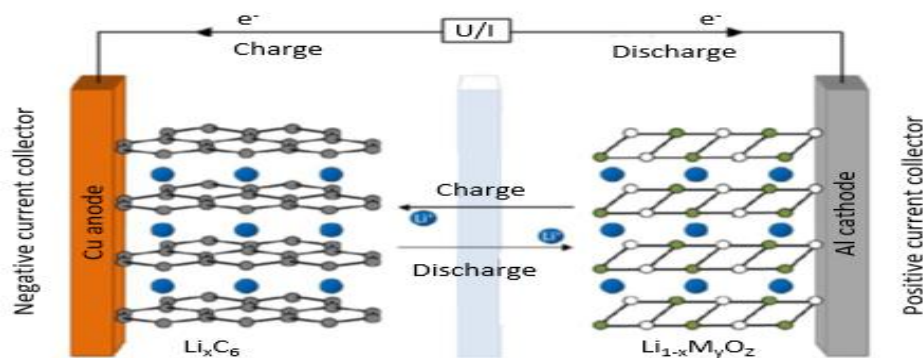


Figure 1: Set-up of a lithium-ion battery (Buchberger, 2016, 4)

Coming to the electrolyte, it is made up of a solvent, lithium conducting salt and additives. To live up to today's high standards regarding safety, function, ecology and economy, these materials must fulfil a number of requirements to form an adequate electrolyte (Hartnig and Schmidt, 2018, 60).

One criterion for a proper solvent is hereby a high permittivity achieved through the ability to dissolve high concentrations of lithium salts. A low viscosity on the other hand, provides a sufficient migration speed of ions, especially needed for high-voltage applications and low-temperature scenarios. Furthermore, inertness towards all other cell components provides electrochemical stability for today's 4 V and tomorrow's expected 5 V charging potentials. The wide range of applications lithium-ion batteries are used for, also calls for a wide liquid range of the solvent. Therefore, not only a low melting point but also a high boiling point is favourable. Last but not least, economic and ecological aspects like toxicity must be taken under consideration (Hartnig and Schmidt, 2018, 60f.).

Complying to all these aspects has led today's researchers to two classes of organic solvents: Ethers and esters, including organic carbonates. While ethers exhibit high conductivity, their low boiling point between 65-84 °C excludes them from use at a higher electric potential. With a melting point down to -84 °C (methyl butyrate), a boiling point up to 249 °C (ethylene carbonate, "EC") and moderate viscosity, Esters are the current state of the art. Most deployed hereby are ethylene carbonate and propylene carbonate (Hartnig and Schmidt, 2018, 62).

One task of additives, like the just mentioned ethylene carbonate, is the establishment of the solid electrolyte interface (SEI) layer, which are displayed in Figure 2. It is formed during the first charging cycle between the electrolyte and the negative electrode and is of paramount importance to the performance and service life of the battery. Additives are chosen according to their reduction potential, which makes EC the first choice. In this organic carbonate, hardly

soluble lithium alkylcarbonates are formed, which accumulate on the electrode and the outer layers of graphite, forming the passivation layer (Hartnig and Schmidt, 2018, 67f.).

Being permeable for lithium ions, but rather impermeable for other electrolyte components, the layer protects the electrolyte compounds from further reduction and the charged electrode from corrosion (Vetter et al., 2005, 271).

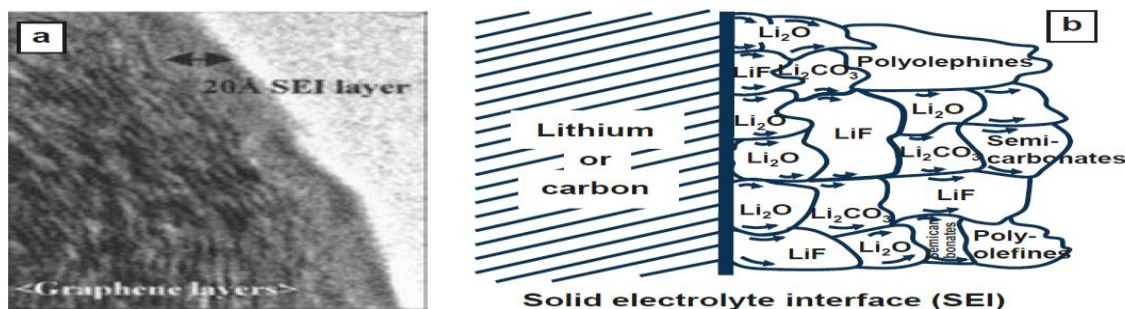


Figure 2: TEM picture (a) and schematic diagram (b) of an SEI (Wurm et al., 2018, 49)

Coming to the conducting salt, as has already been stated, this component requires a maximum solubility in the solvent to guarantee high lithium-ion mobility. Also, in compliance with the solvent, is the compatibility towards other cell components, since the lithium salt can affect the reaction between electrolyte and electrode. From a chemical point of view, high chemical stability towards the solvent, as well as high electrochemical anion stability is needed. These requirements, combined with reasons of costs, processing and stability, boil the list of useable salts down to mostly complex anions with their negative charge distributed widely across them. The so gained reduced charge density causes a low attraction between the lithium cation and the anion, which permits free movement of the cation (Hartnig and Schmidt, 2018, 62).

Today, most lithium-ion batteries are equipped with lithium hexafluorophosphate (LiPF_6). The reason for this is the unique combination of advantages found in this salt. With 8-12 mS/cm (room temperature, 1 mol/l), LiPF_6 , in combination with organic carbons, not only forms a highly conductive electrolyte. Its electrochemical stability up to almost 5 V vs. Li/Li^+ and prevention of the corrosion of the aluminium positive current collector above potentials of 3 V vs. Li/Li^+ renders this material useful for present and future applications. The limited chemical and thermal stability can be seen as a downside, though. The disintegration of LiPF_6 into lithium fluoride (LiF) and phosphorous pentafluoride (PF_5) occurs at a highly pure form of the salt already at room temperature. However, in combination with organic solutions, this process can be prevented up to a temperature of 70 °C. Another disadvantage poses the high susceptibility of the P-F compound to hydrolysis with slightest amounts of water, forming hydrofluoric acid (HF) (Hartnig and Schmidt, 2018, 62f.).

By having one more look at Figure 1, another battery component of great importance strikes the eye: The separator. This porous membrane made of PE or PP prevents physical contact and thereby a short circuit between anode and cathode while enabling enough lithium-ions to pass between the electrodes. To be able to perform this task, the separator must fulfil a number of requirements. According to their field of application, separators are between 25 and 40 μm thick. A porosity of 40 % uniformly distributed and with holes small enough to hinder loose electrode particles from travel through causing a short circuit, guarantees longevity. Of utter importance regarding a long service life is also the dimensional stability of the separator since too big shrinkage can lead to direct contact between the electrodes. Finally, to prevent uncontrolled discharging of the cell, the separator must withstand some particle puncture as it can happen during the production and cycling of the cell (Weber and Roth, 2018, 75ff.).

Even though Sony revolutionised the market for electrical equipment with the introduction of the first rechargeable lithium-ion battery, camcorders catching fire due to defective lithium batteries soon enough showed up the flaws still existing with that, by then, new technology (Sony, 2018, s.p.; Mauger and Julien, 2017, 1936).

Lithium batteries of the first generation were equipped with a lithium cobalt oxide (LCO) cathode and a graphite anode, as listed in Table 1. The previously mentioned safety risk of these batteries fuelled research to improve their thermal stability. As a result, lithium nickel aluminium oxide (NCA) cathodes were introduced, an advancement of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, which is beset with capacity fading and the evolution of dangerous gases at an advanced age due to the strong oxidizing features and the subsequent decomposition of the liquid electrolyte. Even though Al doping reduces this risk, NCA cathodes still experience strong thermal reactions at relatively low temperatures of 200-250 $^{\circ}\text{C}$ (Mauger and Julien, 2017, 1936).

Cathodes with manganese followed. Batteries with a nickel manganese cobalt oxide (NMC) cathode combine the high capacity of lithium nickel oxide with the thermal stability and low costs of lithium manganese oxide and the good rate capability of lithium cobalt oxide, which explains its high commercial success. Especially in the electric vehicle sector, this battery is in high demand, supplying amongst others BMW i3 and Nissan Leaf with energy (Chen et al., 2019, 1; Miao et al., 2019, 6).

The mix of the various metals varies by manufacturer and is geared to the field of application. Nickel is the active material, switching from a Ni^{2+} to a Ni^{3+} and upon lithium extraction to a Ni^{4+} state. A higher Ni content offers higher capacity at the cost of stability, cobalt avoids Ni

cation mixing and its increase means more rate capability at higher costs, whereas a higher Mn content stabilizes the lattice, which leads to better thermal stability at lower costs. Besides lower thermal stability compared to lithium manganese oxide (LMO) and lithium iron phosphate (LFP), this cathode also experiences active oxygen formation released by the transition metal of higher oxidation state, which causes side reactions of the anode with the electrolyte. A relatively low discharge voltage of around 3.7 V compared to 3.9 V reached by LCO, for example, can be seen as another disadvantage (Chen et al., 2019, 1; Mauger and Julien, 2017, 1937; Graf, 2018, 33).

With lithium batteries finding their way more and more into our daily life, the materials used and their origin are brought to the public's attention. The first three cathodes presented here, all use cobalt. Cobalt is not only toxic but also partly mined by children under inhuman conditions in the Republic of Congo. An LMO cathode avoids this conflict resource altogether. This is not the only advantage it has over the previous cathodes, though. Its spinel structure gives it better thermal stability compared to the former lamellar structures. Nevertheless, its instability towards acids gives it poor cycling stability. These can be formed by traces of water reacting with the conducting salt and decrease the reversible capacity notably (Balakrishnan et al., 2006, 410f.; Graf, 2018, 35; Kara, 2018, s.p.).

The olivine structure of the LFP cathode is yet another advancement. The little reactivity with the electrolyte gives it remarkable thermal stability with no heat generated below 200 °C. Furthermore, the passing of all safety tests without a thermal chain reaction occurring makes it the best choice if safety aspects are top priority e.g., in the automobile branch. Still, poor electrical and lithium conductivity limit the range of electric vehicles operated with such a battery configuration. Research has shown, though, that carbon coating can improve conductivity substantially (Mauger and Julien, 2017, 1936; Graf, 2018, 38).

Coming to the anode of a lithium-ion battery, Table 1 gives back the most commonly used anode material: Graphite. The reasons are the high electrical conductivity of graphite and the high ionic conductivity for Li^+ . The low potential of 0.15-0.25 V between C and lithiated graphite (LiC_6) furthermore allows a high operating voltage of the battery. However, with 69 % of natural graphite occurrence situated in China, the EU cites the mineral on its critical raw material list. Enhanced efforts in recycling are therefore called for the future (Mauger and Julien, 2017, 1940; European Commission, 2017, 6).

To combat resource scarcity and enhance safety, a lithium titanate oxide (LTO) anode presents an alternative to graphite. The advantage is, amongst others, an outstanding rate capability with

no danger of Li plating and its associated dangers, which are discussed in the pages to come. A smaller energy density poses as the only disadvantage compared to graphite (Mauger and Julien, 2017, 1940f.; Wurm et al., 2018, 54).

Table 1: Most popular Li-ion technologies developed so far (according to Mauger and Julien, 2017, 1935)

Acronym	Cathode	Anode
LCO	LiCoO_2	Graphite
NCA	$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$	Graphite
NMC	$\text{LiNi}_y\text{Mn}_y\text{Co}_{1-2y}\text{O}_2$	Graphite
LMO	LiMn_2O_4	Graphite
LFP/LTO	LiFePO_4	$\text{Li}_4\text{Ti}_5\text{O}_{12}$

2.3 Dangers arising from the use of lithium-ion batteries

2.3.1 Failure modalities

Today, products containing lithium-ion batteries are manifold. However, the technique's omnipresence in daily life has led to a spark in accidents involving such a battery. Be it through electric vehicles or cell phones catching fire, dangers arising from the use of lithium-ion batteries gain more and more public attention. This chapter sets out to describe said dangers followed by another chapter showing up safety designs meant to avoid them (FAA, 2018, 1ff.; Tomboy, 2018, 21).

The life cycle of a lithium-ion battery comprises its production, transport to and from a reseller, its use phase and finally recycling. In each phase, cells are exposed to a variety of unsuitable conditions, endangering their functionality (Mikolajczak et al., 2011, 71). In the worst, case a thermal runaway reaction ends the useful life completely. "Cell thermal runaway refers to rapid self-heating of a cell derived from the exothermic chemical reaction of the highly oxidizing positive electrode and the highly reducing negative electrode" (Mikolajczak et al., 2011, 46).

In detail, a thermal runaway reaction first causes an internal cell temperature rise to 600 °C. Drivers are the reaction of the electrodes with the electrolyte and a release of stored energy. Both separator and aluminium current collector melt. The aluminium may additionally alloy with the copper, which causes the negative current collector to take damage, too. In the further course, the decomposition and vaporizing of the electrolyte result in swelling of the cell. This is accompanied by a "pop" sound, signalling a breaching of the cell casing at defined points,

so-called vent ports. Through these, black vent gas is released containing methane (CH_4), carbon monoxide (CO), monophosphane (PH_3), hydrogen fluoride (HF), hydrogen (H_2), aldehydes and carcinogenic cathode oxide dust. Furthermore, the sudden pressure difference at the venting port and the rest of the cell may lead to cell components being ejected. With an environment rich enough on oxygen to sustain a hydrocarbon combustion and a hot enough cell case, the vent gas can ignite. Additionally, heat transfer mechanisms like case-to-case contact might spread the thermal runaway reaction to other cells (Mikolajczak et al., 2011, 47ff.; Fleischhammer and Doering, 2018, 264).

The seeds for such an unfavourable outcome are often laid as early as in the production phase. Manufacturing defects are, amongst others, made up of contamination being introduced during assembly, defects in the cell raw material, damaged components, defects in the electrode coating and damaging of the electrodes. Figure 3 shows introduced contaminations (a) and poor welds (b) as an example. A useful classification of manufacturing defects is one by impedance. So-called hard shorts lead to immediate discharge of the cell, whereas soft shorts cause a slow and steady discharge over time, comparable to a high self-discharge rate. Manufacturing defects are revealed very early in the battery life, usually during the first charging cycle. It initiates a volume growth of the components, leading contaminants to puncture the separator. Possible shorting points are also provided with energy, which may induce thermal runaway (Mikolajczak et al., 2011, 62ff.).

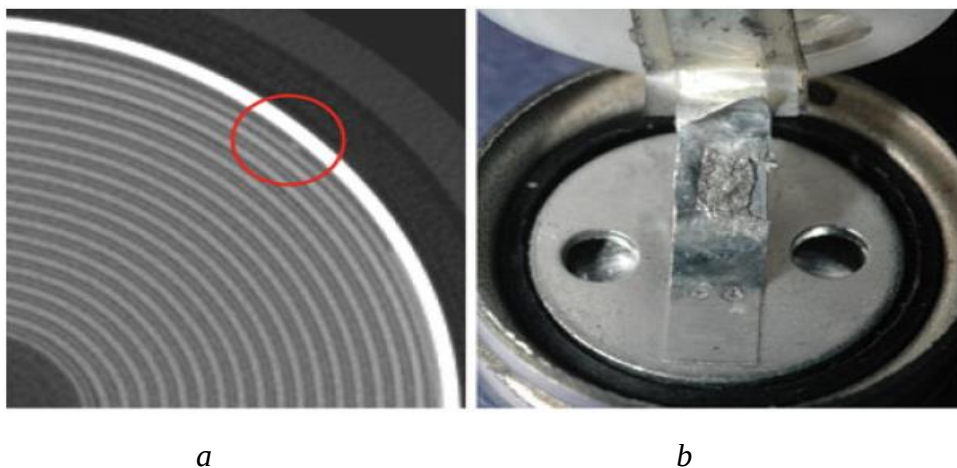


Figure 3: Manufacturing contamination (a) and poor weld (b) (Mikolajczak et al., 2011, 63)

Mechanical abuse acts as another critical failure modality. Damages can hereby occur in multiple ways. Cells can be subjected to shocks due to dropping, punctures or crushes. This can lead to shorting between cell electrodes, leading to localized cell heating and, ultimately, thermal runaway. Even if thermal runaway does not occur immediately, continued cycling may still trigger it. Points of mild mechanical damage can hereby become points of electrode or separator

degradation. To avoid mechanical damage, safe storage and handling with care is advised. Also, shipping at a state of charge (SOC) not higher than 50 % is recommended (Mikolajczak et al., 2011, 55ff.).

Following the life cycle of a battery, next comes the use phase. Here, electrical abuse may cause the cell harm. Overcharge, for instance, causes severe degradation of both cathode and anode. On the anode, this can lead to plating instead of intercalation of lithium-ions. Formed dendrites not only react with the electrolyte but can also puncture the separator causing internal shorting. Overcharge also leads to excessive removal of lithium from the cathode material, which in turn destabilises its crystalline structure, provoking exothermic reactions. The so generated heat may then lead to thermal runaway. It is therefore recommended to use only chargers specified by the manufacturer (Mikolajczak et al., 2011, 59; Thomas et al., 2012, 245).

External short-circuiting, as a second form of electrical abuse, could also cause cells to exceed thermal stability limits. At points of high impedance, like weld points, high rate (dis-)charging might lead to cell heating up to the point of thermal runaway. Hence, lithium batteries should not be placed near metal objects unless the electrodes are shielded (Mikolajczak et al., 2011, 60).

As a last form of electrical abuse acts over-discharge. Over-discharging is especially a matter of concern during storage over longer periods at a low voltage cut-off, which can force batteries in over-discharge, or with differently aged cells within a battery pack caused by manufacturing failures. During the over-discharging process, the copper foil may be oxidized to Cu^+ and Cu^{2+} and form copper dendrites after diffusing to the cathode. Furthermore, metallic lithium may deposit on the cathode surface due to excessive lithium-ion amounts being extracted from the anode, which also decomposes the SEI layer. The continuous growth of metallic dendrites finally penetrates the separator, causing an internal short circuit (Mikolajczak et al., 2011, 60f.; Ouyang et al., 2019, 3432).

Another form of mishandling during the use phase is thermal abuse. The optimal temperature range for the cycling of lithium-ion batteries lies between 20 and 40 °C. Lower temperatures cause a reduction of the electrode material activity resulting in drastic performance decline. Whereas a decline by 30 % at 0 °C can be expected, temperatures well below it can cause the electrolyte to freeze. On the other end of the temperature scale, capacity loss at temperatures up to 60 °C happens due to repeated film formation over the anode's surface, leading to increased lithium loss and an increase in negative electrode resistance while cycling. Storage and use at temperatures above the self-heating point of 70-90 °C are a matter of concern for densely

packed large format batteries with no possibility of heat removal. To avoid safety risks, batteries should not be handled in a heated (e.g., next to hot combustion products), or too cold environment and, if possible, be isolated from each other (Wiebelt and Zeyen, 2018, 156; An et al., 2017, 394; Thomas et al., 2012, 245; Mikolajczak et al., 2011, 54ff.).

Last but not least, ageing shall be mentioned here. If properly handled, cells with an NMC cathode lose 20 % of their original capacity after 300-6000 charging cycles depending on the depth of discharge due to thickening of the SEI. This naturally terminates their use e.g., in electric vehicles. To even get to this point, though, the aspects mentioned here should be followed. Longer periods of storage without use should be carried out at a SOC of 40 % and in a cold environment (e.g., refrigerator) (Dorn et al., 2018, 166; Thomas et al., 2012, 246).

2.3.2 Safety aspects

As has been seen, failure modes are various, but so are safety measures developed to avoid them. Figure 4 gives an overview of them. On a chemical level, used active materials and cell design play an important role. Since active materials of cathode and anode have already been presented, electrolyte additives shall be further discussed. Their tasks extend to a great level from creating a passivation layer on the cathode and anode. Shutdown additives, for example, are a good way to interrupt overcharging. Under regular operation conditions inert, they activate once the cell voltage reaches a critical value. One can hereby distinguish between gas releasing additives like pyrocarbonates, which activate a current interrupter device and polymerizing additives like biphenyl, which block the ion transfer that way (Balakrishnan et al., 2006, 408).

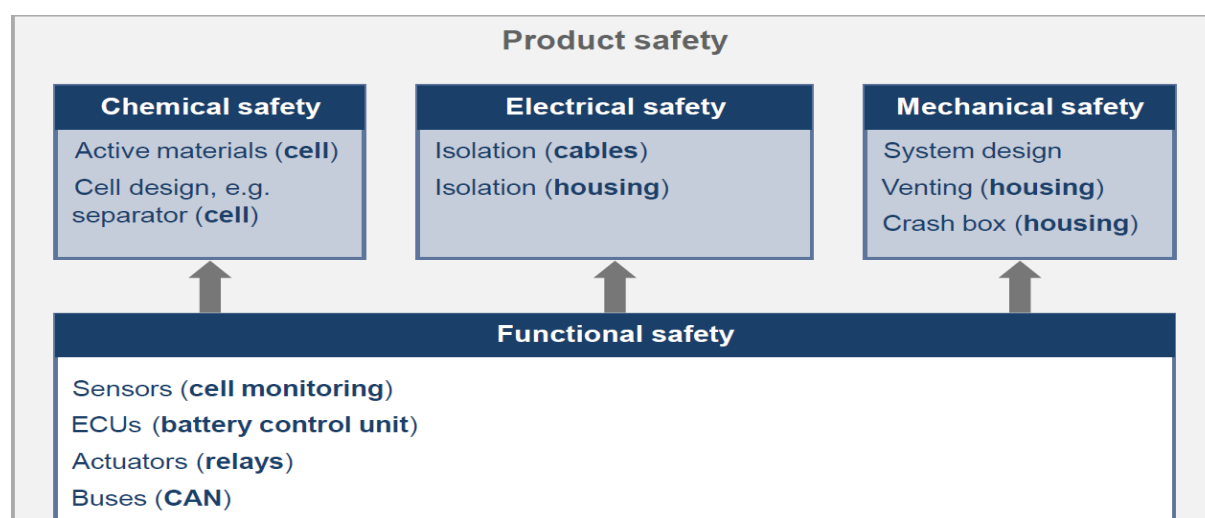


Figure 4: Product safety of lithium-ion batteries (Leuthner, 2018, 17)

A drawback of this class of materials is the termination of the useful life of a battery once they are activated (Balakrishnan et al., 2006, 408). So-called redox shuttles, on the other hand, do not lead to the end of the battery life. “The additive is oxidized at the positive electrode and migrates in the electrical field to the negative electrode, where it is reduced. It then diffuses to the positive electrode and the process starts over” (Hartnig and Schmidt, 2018, 71). A working redox couple is still in development, though. However, research in this field might be obsolete in the near future. A solid electrolyte made of glass might not only lower fire and short circuit risks. Batteries equipped with it, are also said to recharge within one minute and have triple the energy density of today’s batteries with no measurable loss of capacity (Balakrishnan et al., 2006, 407; Mörer-Funk, 2017, s.p.).

Cell design is the second column of chemical safety. Since shutdown additives are no sure-shot against electrical abuse, more and more manufactures opt for the integration of shutdown separators in their products. In addition to the separator’s tasks already described, PE and PP separators soften and close the micropores in the film during abnormal conditions like overcharge. This “shutdown” occurs at around 135 °C. Ion flow and thereby heat development is stopped. If the overstress situation is not dealt with, separator “meltdown” can occur. Separators made of PP melt down at temperatures above 135 °C, whereas a combination of PP and PE are mechanically intact till 165 °C. The meltdown leads to direct electrode contact and thermal runaway (Balakrishnan et al., 2006, 406).

Moving on to electrical safety, insulation of cables and housing is to be mentioned. This explicitly gains importance when individual cells are connected to obtain a high total voltage, needed with EVs and stationary applications. The subsequent danger to human health concerns especially service personnel, maintaining and disassembling the batteries. To avoid dangerous situations, insulation of cables between cells and of the battery housing is mandatory. Fixed insulation and clearance and creepage distances between the batteries to prevent live current flow and fire spreading are hereby the way to go. These rules should also be enforced during storage. Insulation of the electrodes and separation of the cells can prevent short circuits and thereby caused damages (Sattler, 2018, 280).

Venting, as part of mechanical safety, occurs at severe overstress situations like overcharge or mechanical damage. The chemical reactions and heat development within the cell lead to the formation of gas. Build-up pressure in the cell then causes a plastic membrane to be punctured by a spike, which is incorporated in the safety valve, as seen in Figure 5, that way releasing the gas. Excessively high temperatures of the cell, which lead to thermal runaway can be averted;

on the other hand, this safety device terminates the useful life of the battery (Balakrishnan et al., 2006, 403f.).

There are several system designs to be found on the lithium-ion battery market. High-rate capability prismatic cells are produced by stacking alternating layers of electrodes, for example. Coiling up long strips of alternating electrodes divided by the separator is typical for cylindrical cells, on the other hand. Those “jelly-rolls” are then inserted into afterwards sealed cases, as seen in Figure 5. To increase capacity, lithium-ion cells are then connected in parallel or in series to increase current or voltage (Mikolajczak et al., 2011, 3ff.).

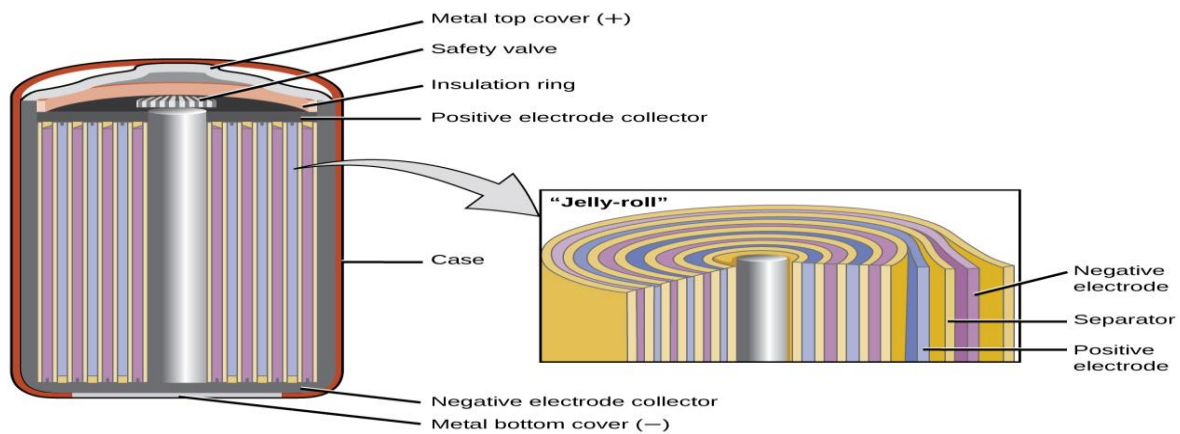


Figure 5: "Jelly-roll" design of cylindrical cell (BCcampus, 2020, s.p.)

Last but not least, functional safety is guaranteed by the battery management system (BMS) composed of the parts seen in Figure 4. The first function of this system is checking the balance of the battery. For this, the BMS constantly monitors the voltage of each cell, stopping the current if they differ more than a few percent. By doing so, a chain reaction between the cells can be avoided. As a second function, it estimates the state of health (SOH) of the battery. The SOH describes the current state of health compared to that of a new battery. A BMS cannot prevent thermal runaway, but it avoids explosions and is an efficient way to determine the SOH (Mauger and Julien, 2017, 1943; Dorn et al., 2018, 166).

2.4 Hazard analysis techniques

“HP expands laptop battery recall due to fire and burn hazards - 78,500 laptop batteries are to be recalled after eight new reports of battery packs overheating, melting, or charring” (Kwan, 2019, s.p.).

“Microsoft to extend Xbox 360 warranty, take \$1 billion hit - Software maker says it's seeing unacceptable number of repairs; investigation finds several factors could lead to hardware failures” (Fried, 2007, s.p.).

To avoid negative headlines like these, which, on top of hurting customers, can very well put them out of business, companies invest large amounts of time and money into so-called hazard analyses (Carlson, 2012, 26).

“Hazard analyses are performed to identify hazards, hazard effects, and hazard causal factors. Hazard analyses are used to determine system risk and thereby ascertain the significance of hazards so that safety design measures can be established to eliminate or mitigate the hazard” (Popović and Vasić, 2008, 182f.). A hazard itself is defined as “any real or potential condition that can cause injury, illness, or death to personnel; damage to or loss of a system, equipment or property; or damage to the environment” (Ericson, 2005, 14). It is comprised of the following three elements:

- Hazardous element (HE): Resource creating the impulse for the hazard
- Initiating mechanism (IM): Trigger causing the hazard to occur
- Target and threat (T/T): Object or person being exposed to the hazard

Together they form the so-called hazard triangle, which is necessary for a hazard to exist. Since the outcome of a hazard is mostly unchangeable, hazard analyses help to prevent or at least reduce its effects (Popović and Vasić, 2008, 181f.).

A hazard causal factor model, as shown in Figure 6, helps with this task by illustrating specific items causing hazards in a system. Level one is made up of the three hazard triangle components, which cause the hazard and a following mishap. A mishap is an unplanned event, leading to damage or loss of property, injury or death. Its occurrence depends on the risk involved. Level two further splits down HE, IM into hazard causal factor categories like hardware or software and specifies T/T. On the third level, these categories are broken down accordingly to their detailed cause (Ericson, 2005, 22).

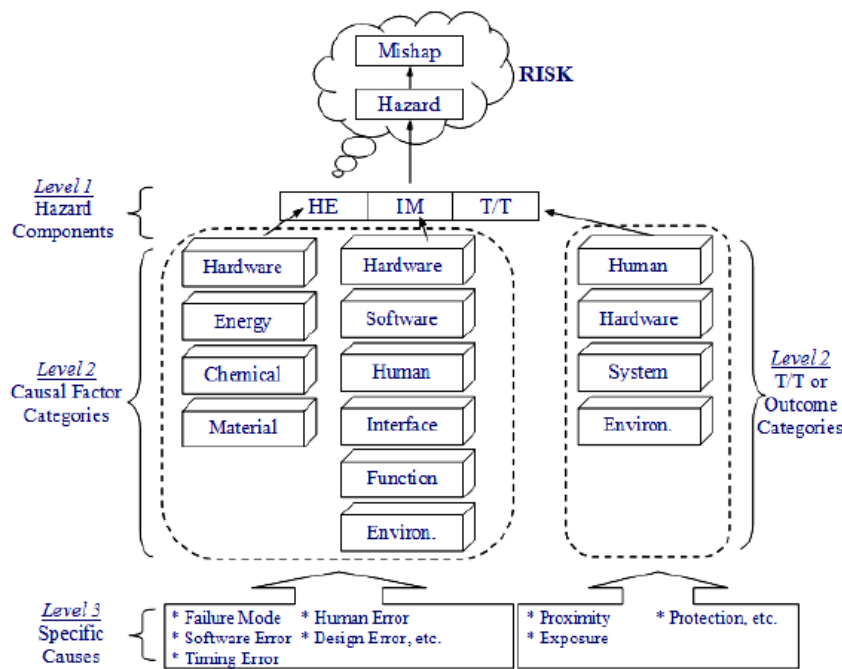


Figure 6: Hazard causal factor model (Popović and Vasić, 2008, 182)

In order to identify a specific cause like a design error most efficiently, hazard analyses are grouped into two categories: Techniques and types. Depth of detail, analysing time and system coverage are laid out in the type, whereas specific results are gained by a unique analysing methodology set by the technique. The main differences between type and technique are presented in Table 2 (Ericson, 2005, 31).

Table 2: Hazard analysis type vs. technique (Popović and Vasić, 2008, 183)

Type	Technique
Establishes what, where and when to analyse	Establishes how to perform the analysis
Establishes a specific analysis task at a specific time in the program life cycle	Sets a specific, unique analysis methodology
Establishes the desired outcome	Provides the information to satisfy the intent of the analysis type
Provides a specific design focus	

Basically, there are seven analysis types. Each type identifies hazards for a specific design phase in the development cycle of the system in question. Once more information is available in later development stages, the depth of detail for the analysis type increases. However, the goals to be reached by an analysis type can be achieved by various analysis techniques. A proper selection of the techniques is, therefore, of paramount importance. Also, one analysis type alone

might not be enough to identify all hazards found in a system. Listed below are the seven analysis types:

1. Conceptual design hazard analysis type
2. Preliminary design hazard analysis type
3. Detailed design hazard analysis type
4. System design hazard analysis type
5. Operations design hazard analysis type
6. Health design hazard analysis type
7. Requirements design hazard analysis type

After performing all seven analyses, all hazards in a system should be identified (Popović and Vasić, 2008, 183).

As stated before, an analysis technique defines a unique analysis methodology. Following specific rules, the technique comes up with specific results. There are over 100 different techniques to date, but often, they vary only slightly. One criterion to distinguish them by is whether they follow a deductive or inductive approach. This refers to the form of logic being used. A deductive logic draws a conclusion based on a set of premises and contains no more information than given by the premises. For example, all cats are animals; this is a cat, therefore, it is an animal. The quality of the conclusion depends on the quality of the premises.

An example for a deductive approach is the FTA, which determines root causes and probability of occurrence of a specific undesired event by modelling the unique combinations of fault events that lead to the undesired event. Deductively, it transverses from a general problem to a specific cause (Ericson, 2005, 48).

Inductive approaches draw a conclusion that contains more information than the observations it is based on. Only future experiences can verify the truth of the conclusion and only if all possible instances have been considered. For example, all elephants ever known were grey, therefore all elephants are grey. Even if it is highly unlikely for an elephant to have another colour than grey, it is possible. An inductive conclusion may imply more than guaranteed by the premises based on the data available. A method extensively discussed in the pages to come is the FMEA (Ericson, 2005, 48f.).

An FMEA can also be classified as bottom-up analysis, meaning it starts at a low system level and moves upwards till the top level is reached. In contrast to that, a top-down analysis works its way down from a high level into deeper levels of detail until the problem causing level is

reached. As a rule of thumb, one can say that deductive analyses are based on a top-down approach, whereas inductive ones are based on the bottom-up approach (Popović and Vasić, 2008, 186).

Last but not least, techniques are either qualitative or quantitative. A qualitative method uses categories to separate different parameters. Qualitative definitions establish hereby the ranges for each category. It is a subjective approach, which allows more generalization and is, therefore, less restricting. For example, mishaps can be categorised according to the likelihood of occurrence. Events that occur frequently are assigned to an index level A, less frequent events level C. This index value is used further on in qualitative risk calculations. It is a very effective approach if time, money and available data are meagre (Ericson, 2005, 51f.).

Quantitative analysis relies on measured quantitative data. It is more objective and often more accurate. Since the input data might not be fully valid and accurate, the result can be biased, however. Quantitative results should therefore always be considered within a range and not as an exact number. Generally speaking, it makes sense first to evaluate all identified hazards qualitatively and only conduct quantitative analysis for high-risk hazards (Ericson, 2005, 51f.).

For the purpose of this work, a qualitative FMEA was selected. It is to be carried out as part of the detailed design hazard analysis type, whose task it is to identify components whose performance loss or functional failure could lead to hazards. Especially single-point failures, which cause a breakdown of the whole system, are of particular concern (Ericson, 2005, 37).

An FMEA, therefore, treats each failure mode separately. It is designed to identify and fully understand failure modes and their causes and the effects of failure on the end-user or system for a certain process or product. Furthermore, it assesses the risk interlinked with identified failure modes and ranks as well as carries out issues for corrective action. These corrective measures should be performed before the product finds its end consumer (IEC, 2006, 7; Carlson, 2012, 21f.).

There are several types of FMEAs, this work is based on an FMECA, though. Theory and definitions are the same as with an FMEA. That said, an FMECA uses a different standard, a different set of scales and it adds a calculation or assessment of criticality to the analysis. A benefit and reason for being applied here is the more detailed risk-ranking information obtained from the criticality analysis (Carlson, 2012, 285f.).

2.5 Data processing

2.5.1 Background and classification of the FMECA

The FME(C)A standard goes back to military procedure MIL-P-1629 titled “procedures for performing a failure mode, effects and criticality analysis”, which was published on November 9., 1949 (Carlson, 2012, 8). Used as a reliability evaluation technique, it determined the effect of system and equipment failure. Classification of failures followed according to their impact on equipment safety and mission success. In the 1960s, the use of FMEAs was encouraged by NASA and played a critical role in getting a man on the moon. In light of the Pinto affair (several incidents of exploding Pinto automobile gas tanks), FMEAs were reintroduced by the Ford Motor Company in the late 1970s. Driven by the success in the automobile branch, the Automotive Industry Action Group (AIAG) and the American Society for Quality Control (ASQC) copyrighted industrywide FMEA standards in 1993. Today FMEAs are used in a variety of industries like foodservice, plastics, automotive and healthcare (Ericson, 2005, 237).

An FMECA analyses two distinct elements of a system: Its hardware and its function. This is referred to as either a structural approach or a functional approach. The functional approach examines functionality, whereas the structural approach focuses on potential hardware failure modes. Both can be carried out on any system level. As a third approach is the hybrid approach to be mentioned, a combination of the two previous ones, this work uses the structural approach, though (Ericson, 2005, 239f.).

As a further classification, depending on its application, an FMECA serves either as product or process FMECA. Figure 7 shows, that process FMECAs analyse processes in production, maintenance and use of a product and how they affect the operation of the product or system in question. Product, or system/design FMECA on the other hand, are subdivided in hardware, software and function screenings and how potential failure here affects the product’s functionality. In summary, a product FMECA with a focus on hardware, using a structural approach, is described and carried out in the following (Ericson, 2005, 242; Carlson, 2012, 10).

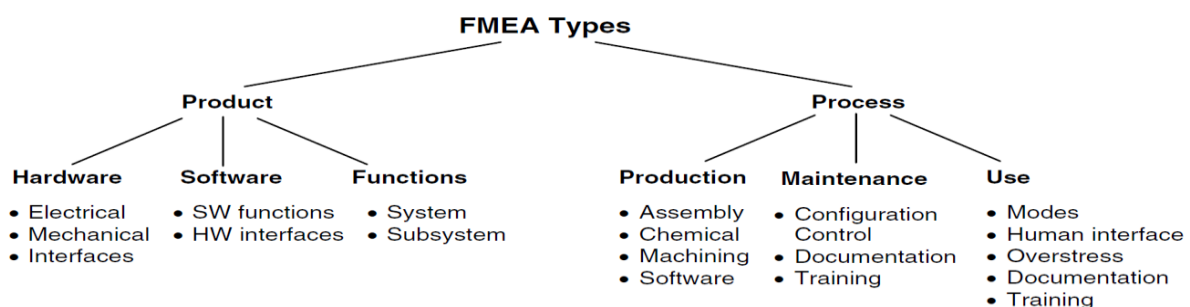


Figure 7: FMEA types (Ericson, 2005, 242)

2.5.2 Steps of the FMECA

An FMECA is composed of the following four main steps:

1. Establishment of FMECA ground rules including planning and scheduling
2. Execution of FMECA with the help of suitable worksheets and logic diagrams
3. Composing a report of the analysis including conclusion and recommendations
4. Updating FMECA according to advance in development

Step one is carried out in this chapter. For this, a program plan is written, containing a detailed description of the FMECA method. Definitions of goals and expected results, set boundaries of the analysis, documentation and other basic rules are put down in writing. The FMECA is executed in “results”, which also contains the final report. The fourth step, on the other hand, is the task of future works (IEC, 2006, 9).

The individual tasks of previously mentioned step one is visualised under “preparation” in Figure 8, whereas steps listed under “conducting the meetings” refer to the results and presented recommendations can be seen as “follow-up”. The “preparation” tasks have to be done for every new FMECA carried out for the system under focus. There are preparations, though, which only need to be executed once per system. In the case of this work, most of them are integrated into the “preparation” step or do not apply. Under not applicable falls software selection for the FMECA, because of the low complexity of the system. Roles and responsibilities are set beforehand and do not have to be identified. Since the members of the team are either already trained or see this FMECA as training, prior training is not needed. Meeting logistics are discussed for every team meeting separately and are not restricted to a certain place. The selection of scales and columns, the definition of a system hierarchy and access to failure information are all part of the steps to come (Carlson, 2012, 67).

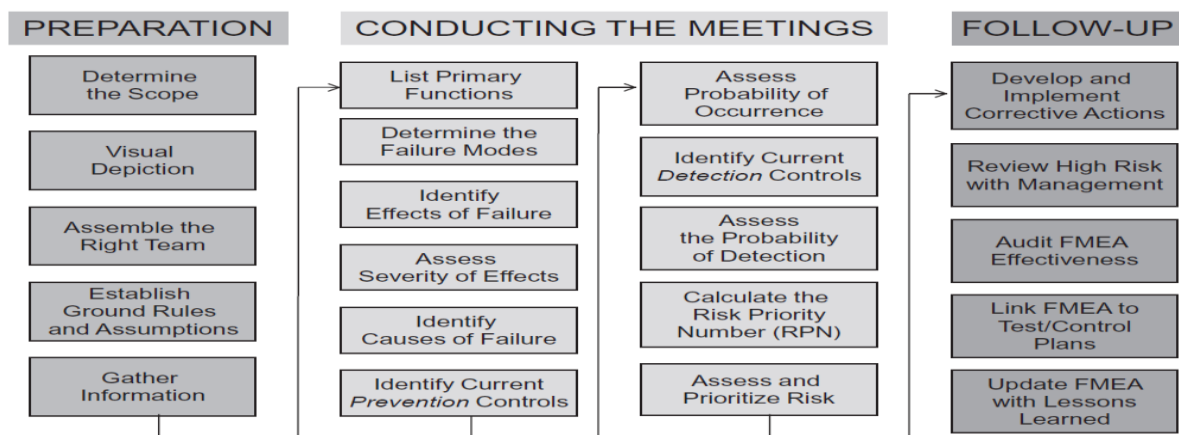


Figure 8: Roadmap of FMECA (Carlson, 2012, 79)

Coming back to Figure 8, as a first step, the scope of the analysis must be determined. This is critical for the whole analysis, because without set boundaries, those might expand from team meeting to team meeting. Clearly defined boundaries establish not only the issues to be considered but also the used approach. FMECAs focus either on the whole system or on specific aspects of it. Product FMECAs are carried out with the intention of improving the design and ensuring the safe operation of the system in question. In the case of the work at hand, the system is a single lithium-ion battery cell as shown in Figure 5. The boundaries are hereby clear since the cell is not part of a bigger system while being tested (Carlson, 2012, 79ff.; IEC, 2006, 10).

Next, this system is to be visualised. The visualisation should clearly demonstrate the boundaries of the system, to clarify what is included in the FMECA and what is not. Through this step, physical and logical linkages between system components are shown. Connections and dependencies between components, in this case material and energy exchange, as well as inputs and outputs are identified. For the visualisation, the reader's attention is once again drawn to Figure 1, which serves this purpose well. Single components of the system like cathode, anode, or separator are as clearly shown, as their relationship to each other. A system hierarchy does not come into play since all components are at the same level (Carlson, 2012, 82).

Assembling the right team is another task of great importance. Since there is a variety of things to be considered during an FMECA, a well-chosen team can eliminate "blind spots" a single team member might have. This can be enhanced by selecting persons from different backgrounds. The interdisciplinarity guarantees consideration of all necessary aspects (Carlson, 2012, 93). For the purpose of this FMECA, the author, a student of an interdisciplinary master program, is supported by his supervisor, who's background of machinery and plant engineering, a branch familiar with hazard analyses, is of high value to the successful execution of the FMECA. The team is completed by a technician who ensures the correct experimental set-ups and helps with needed constructions (Ericson, 2005, 248).

Before beginning the analysis, specific ground rules and assumptions must be established. Part of this step is clearly defining goals to be reached by the analysis. The goal of the FMECA at hand is to expose the in silicone oil submerged battery cells to a number of overstress conditions, namely overcharging, nail penetration and over-discharging, and test the theory of liquid silicone as a pacifier. Its great electric insulating properties, its heat stability up to 150 °C and non-flammability, as well as its relatively high specific heat capacity makes silicone oil a promising candidate. Part of the FMECA is the calculation of inner cell energy transformed into calorific energy, which is taken up by the oil. The stress tests were chosen since they are most

likely to happen if a failure occurs during future tests (over-(dis)charge) or represent a worst-case scenario (nail penetration) (Silikonfabrik.de, 2020, s.p.).

The results are of paramount importance for future battery tests, done by the university subsequent to this hazard analysis. In order to obtain reference values, the test series are conducted once with the cells placed in liquid silicone and once with them being exposed to the atmosphere. Whereas the test set-ups follow the UL 1642 battery testing standard, conducting the tests with and without silicone oil is innovative and has not been done anywhere else. A second outcome of these reference values are recommendations for safe storage of lithium-ion cells not currently used. Therefore, Chapter 3.4 offers a set of rules for the safe storage of the cells on University grounds, created by combining findings of the stress test and in relevant scientific literature.

In the next chapter, a detailed description of the test conditions can be found. Since single experiments will run all night long without personnel being around, possible worst-case scenarios must be known to prevent damage to equipment or threaten human health. Because work is taken up as soon as the FMECA is completed, a finishing date not later than April 2020 is targeted.

Next, a worksheet is created to provide analysis structure, consistency and documentation. In order to create this worksheet, a number of terms have to be defined (Ericson, 2005, 247).

- *“Item:* The focus of the FMECA project. For a Design FMEA, this is the subsystem or component under analysis” (Carlson, 2012, 49). In the case of this FMECA, the components are anode, cathode, separator, electrolyte and casing.
- *“Failure:* Departure of an item from its required or intended operation, function, or behaviour; problems that users encounter. The inability of a system, subsystem, or component to perform its required function. The inability of an item to perform within previously prescribed limits” (Ericson, 2005, 237).
- *“Failure mode:* The manner in which the item or operation fails to meet or deliver the intended function and its requirements. Depending on the definition of failure established by the analysis team. Failure modes may include failure to perform a function within defined limits, inadequate or poor performance of the function, intermittent performance of a function, and/or performing an unintended or undesired function. There may be many failure modes for each function” (Carlson, 2012, 49).
- *“Failure mechanisms:* Failure mechanisms are the physical, chemical, thermodynamic or other processes that result in failure. Failure mechanisms are categorized as overstress

mechanisms. Overstress failure arises as a result of a single load (stress) condition, which exceeds a fundamental strength property.” (Carlson, 2012, 132).

- *“Effect:* The consequence of the failure on the system or end-user. There can be more than one effect for each failure mode. However, in most applications, the FMEA team will use the most serious of the end effects for the analysis.
- *Cause:* The specific reason for the failure, preferably found by asking “why” until the root cause is determined. For Design FMEAs, the cause is the design deficiency that results in the failure mode. In most applications, particularly at the component level, the cause is taken to the level of failure mechanism. By definition, if a cause occurs, the corresponding failure mode occurs. There can be many causes for each failure mode.
- *Occurrence:* A ranking number associated with the likelihood that the failure mode and its associated cause will be present in the item being analysed. For System and Design FMEAs, the occurrence ranking considers the likelihood of occurrence during the design life of the product. It is based on the criteria from the corresponding occurrence scale. The occurrence ranking has a relative meaning rather than an absolute value and is determined without regard to the severity or likelihood of detection.
- *Severity:* A ranking number associated with the most serious effect for a given failure mode, based on the criteria from a severity scale. It is a relative ranking within the scope of the specific FMEA and is determined without regard to the likelihood of occurrence or detection.
- *Detection:* The detection ranking considers the likelihood of detection of the failure mode/cause, according to defined criteria. Detection is a relative ranking within the scope of the specific FMEA and is determined without regard to the severity or likelihood of occurrence.
- *RPN:* RPN is an acronym that stands for “Risk Priority Number”. It is a numerical ranking of the risk of each potential failure mode/cause, made up of the arithmetic product of the three elements: severity of the effect, likelihood of occurrence of the cause, and likelihood of detection of the cause” (Carlson, 2012, 49f.).

These terms are then used to create the worksheet used for the FMECA. For each test scenario (nail penetration, overcharge, over-discharge) one exemplar is filled out. In order to be able to fill it out correctly, a detection (Table 3), severity (Table 4) and occurrence scale (Table 5) must be created and the failure modes ranked accordingly. A higher-ranking number means hereby a greater hazard. It has to be noted that since this FMECA is a qualitative analysis, the produced results are subjective (Ericson, 2005, 477).

Table 3: Detection scale

Ease of detection	Method of detection	Rank
Low	Failure mode causes no visible effects and cannot, or not right away, be detected through connected equipment	3
Moderate	Failure mode causes little to no visible effects, can be detected through connected equipment, though	2
High	Failure mode is easily detected through visible signs (smoke, explosion) and/or via connected equipment	1

Table 4: Severity scale

Effect	Severity of effect on system	Rank
Failure to meet safety and/or regulatory requirements	Potential failure mode terminates system function and poses a threat to operators and the surroundings	3
Loss or degradation of function without immediate safety concerns	Potential failure mode terminates system function but poses no immediate threat to operators and the surroundings	2
Loss or degradation of function with little to no safety concerns	Potential failure mode terminates system function but poses little threat to operators and the surroundings	1

Table 5: Occurrence scale

Likelihood of occurrence	Occurrence of failure	Rank
High	Strict safety regulations obedience is needed to avoid failure occurrence	3
Moderate	The occurrence of a failure through mishandling is possible but unlikely	2
Low	The occurrence of a failure through mishandling is very little to not existing	1

Once the worksheet is filled out to this point, the RPN can be calculated using the following computation:

$$Severity + Occurrence + Detection$$

The RPNs of all items affected are then added up and written in the RPN result row. This process is repeated for each test scenario.

Finally, the resulting RPNs with their corresponding severity numbers are projected on a severity – RPN matrix, as seen in Figure 9. Low-risk failure modes are projected into the bottom left corner, high-risk ones into the upper right corner.

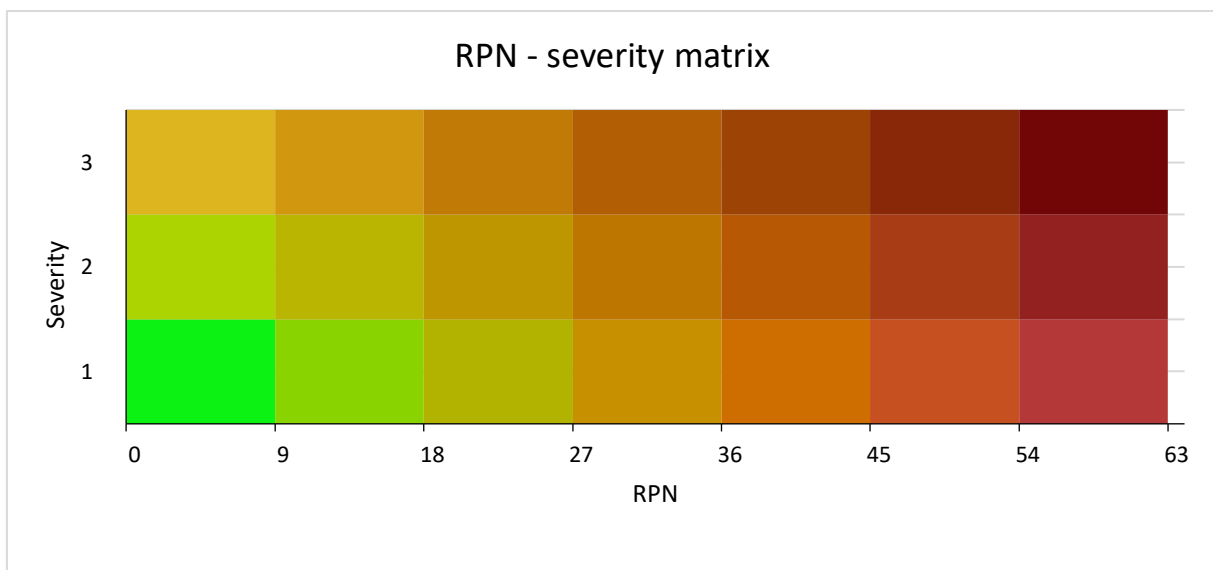


Figure 9: Severity – RPN matrix

As written before, the results shall also include a breakdown of potentially released energy of a cell into calorific energy in case of an overstress situation. This environmental heat is absorbed by the liquid silicone and is set as ΔQ . It can be calculated with the following formula:

$$\Delta Q = c_p * m * \Delta T$$

c_p is the specific heat capacity of silicone, m is the mass of the silicone and ΔT is the heat difference before and after a hazardous event (Lumitos AG, 2020b, s.p.).

The results gained from the FMECA then lead to recommendations on how to avoid the tested failure modes, or at least lessen their outcomes. Since wrong storage can also lead to hazardous events, they further advocate safe storage possibilities. To ensure that the recommended risk reduction measures are noticed and followed, the final results are presented by the author to the

other team members and the deputy of the Institute for Chemical and Energy Engineering at the University of Life Sciences Vienna by whom the FMECA was commissioned.

As a final preparation step, access to needed information, e.g., about the University's battery testing system (BaSytTec), must be secured. Special information like that is provided by the author's supervisor, whereas more general information about the FMECA procedure, for example, is gained via literature research. With this step completed, the next chapter provides a detailed description of the FMECA battery testing set-up, before the FMECA itself can be conducted.

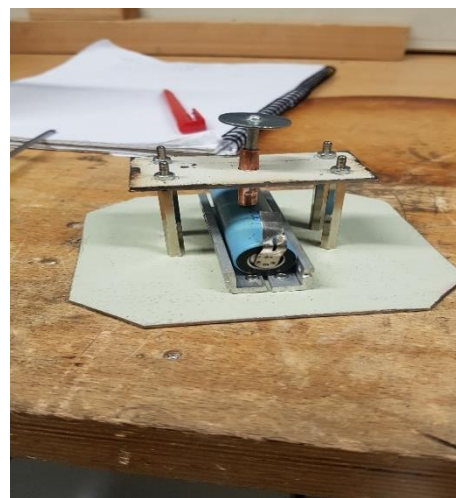
2.6 Experimental

2.6.1 Nail penetration test

For the tests conducted for this FMECA, three different test set-ups were used. For the nail penetration test, the set-up can be seen in Figure 10 a. For the test, two devices were constructed. The first one was made up of a wooden plank, in which a hole was cut close to one of its ends, whose diameter lets a 1 m metal pipe be firmly screwed into it until the pipe stood on its own. Close to the upper end of this pipe, two holes at the same height were drilled into it. Through both, a metal pin was introduced. This acted as a barrier for a falling weight in form of a 1.05 kg metal rod placed on top of metal pipe and thereby on top of the barrier pin. Furthermore, a plastic string was tied to one end of the pin, so the pin could be pulled out, which released the falling weight. The whole construction was placed on an elevation from its surroundings with enough weight placed on the one end of the plank so that the wrought part floated freely in the air.



a



b

Figure 10: Test set-up nail penetration test (a) nail penetration construction (b)

The second construction for this test was placed right underneath the metal pipe in a pot, which, depending on the test series, was filled with silicone oil (SF -V50, sold by silikonfabrik.de), or not. It is displayed in Figure 10 b. Four metal pins screwed onto a metal plate held a smaller plate. This smaller plate contained a hole in its middle, holding a copper pipe in place. The pipe acted as a guide for a nail, whose sharp end sat on top of a battery cell and whose head was hit by the falling weight. The cell, placed directly underneath the nail, was secured by two metal brackets, as well as braided wire. Finally, a temperature sensor (TSIC 306) attached to the cell with duct tape, measured the heat produced by the cell, once the nail penetrated it. The test procedure was also filmed from several angles.

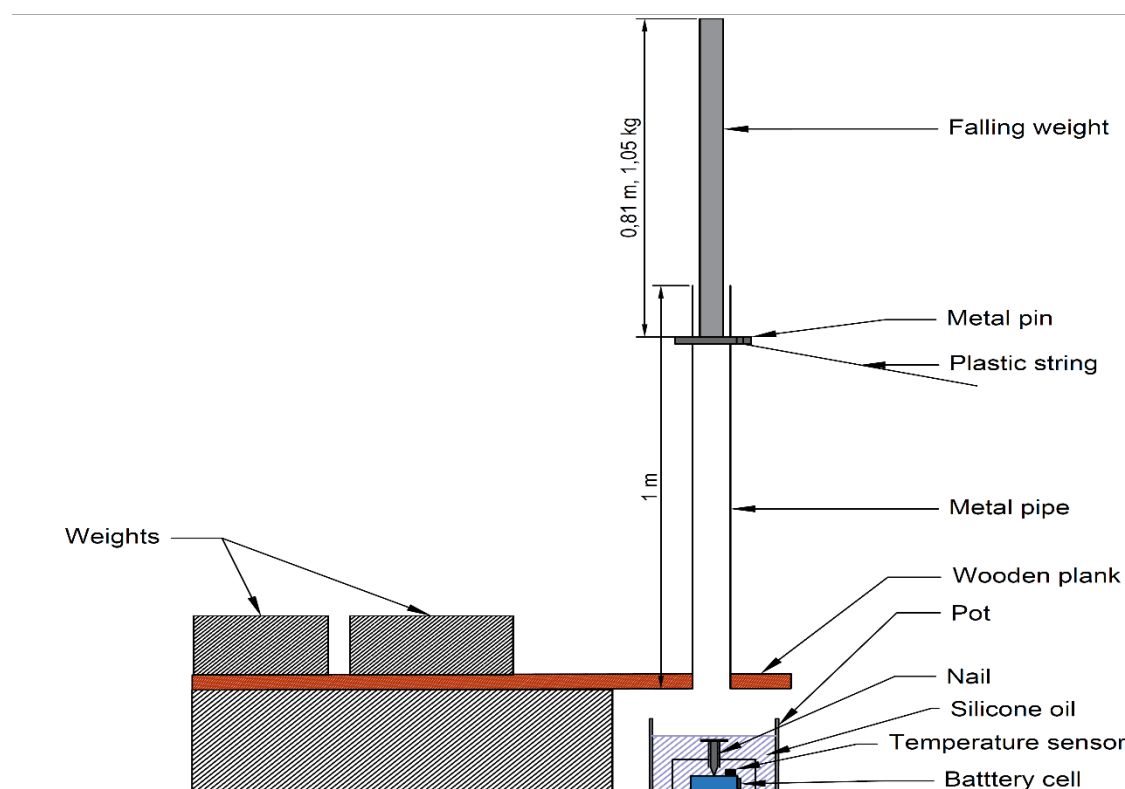


Figure 11: Drawing of nail penetration test set-up

Figure 11 shows the set-up as a simplified drawing. To initiate the test, the plastic string was pulled, removing the metal pin from the pipe and thereby releasing the falling weight. The weight then fell on top of the nail, forcing it into the battery cell.

The battery cells used for the tests were equipped with an NMC cathode, as described in Chapter 2.2. More specifically, the single cell was a 3.63 V LG Lithium-ion INR18650 M36T 12.50Wh cell with a diameter of 18.51 mm and a height of 65.60 mm. It was chosen due to its widespread cell chemistry. A detailed listing of the cell's parameters is found in Table 6.

Table 6: Battery specifications (Kim and Roh, 2017, 4)

LG INR18650 M36T 12.50Wh	
Producer	LG Chem Ltd.
Cell chemistry	$\text{LiNi}_y\text{Mn}_y\text{Co}_{1-2y}\text{O}_2$ – “NMC”
Energy	12.5 Wh
Nominal voltage	3.63 V
End-of-charge voltage	4.2 V
Cut-off voltage	2.5 V
End current (cut-off)	50 mA
Max. charge current	0 ~ 24 °C: 0.3 C (1000 mA) 24 ~ 50 °C: 0.7 C (2330 mA)
Max. discharge current	-30 ~ -20 °C: 0.2 C (670 mA) -20 ~ 5 °C: 0.3 C (1000 mA) 5 ~ 60 °C: 1.5 C (5000 mA)
Weight	48.2 g
Dimensions	$\leq 18.51 \text{ mm} * \leq 65.60 \text{ mm}$
Cycle life (80 % of remaining useable capacity)	1000 cycles

2.6.2 Overcharge test

Coming to the test scenario of overcharging, Figure 12, Figure 13 and Figure 14 illustrate the test set-up.

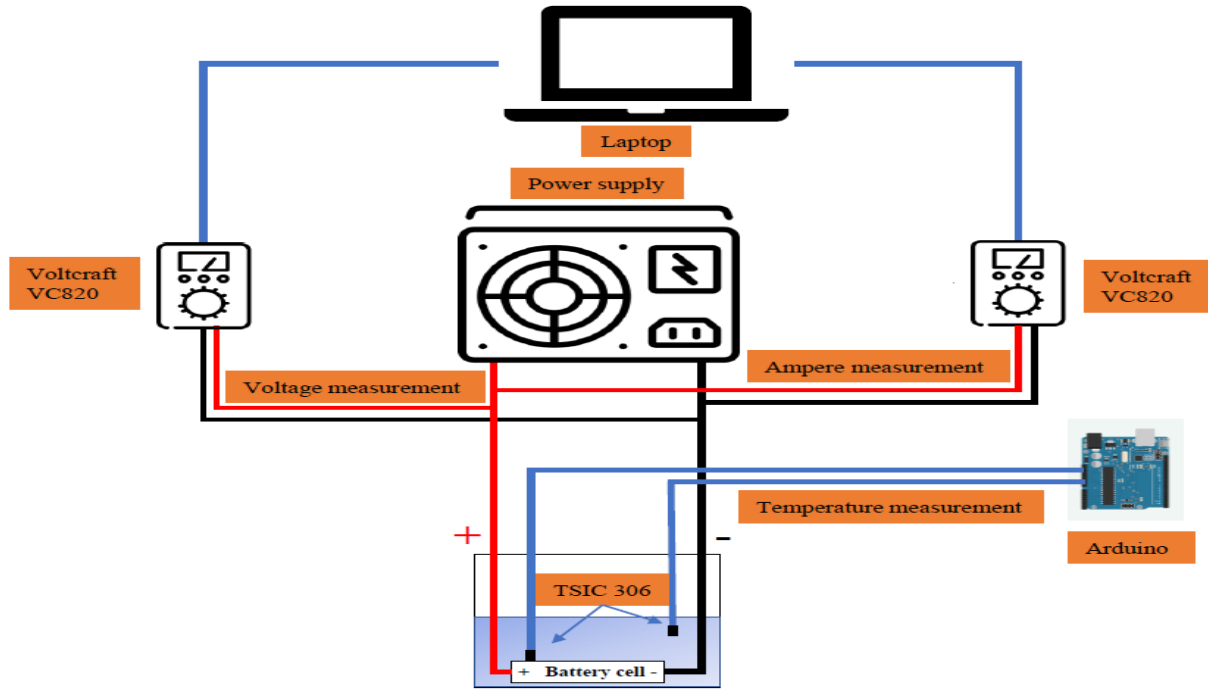


Figure 12: Schematic illustration of overcharging set-up

Figure 13 a shows the battery cell covered in silicone oil, which was connected to the power supply unit seen on the left in Figure 14 with a live cable at the positive and negative electrode (Figure 13 b). The cell was pinned down by a magnet attached to the bottom of the pot. Also, there was a TSIC 306 temperature sensor directly attached to the cell with duct tape, measuring its heat development, as well as one sensor clamped to the pot's wall, which was measuring the rise in temperature of the liquid silicone. Before starting, the pot containing the cell was placed on a hot plate, heating the silicone up to a temperature of 40 °C. Doing this replicated the working environment of the University's battery test unit, where future research will take place.



a



b

Figure 13: Pot with cell, temperature sensors and silicone oil (a) and wiring of battery cell (b)

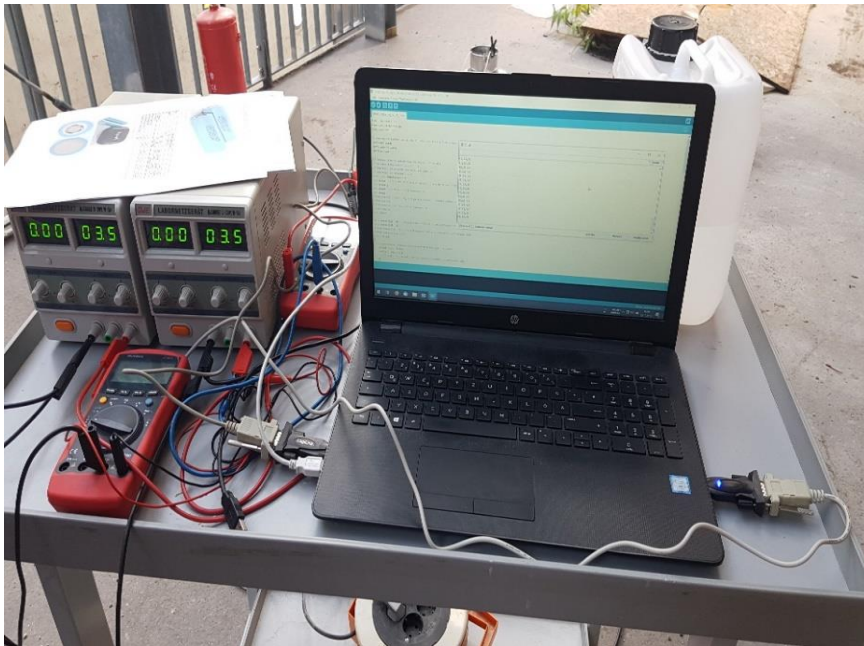


Figure 14: Measuring devices and power supply for overcharging

As seen in Figure 14, two digital ammeters (Voltcraft VC820) measured voltage and ampere values of the cell during the test. Both were also connected to a laptop, where a corresponding software was installed to, every second, log these values for the duration of the overcharging test. The temperature, on the other hand, was recorded by an Arduino Leonardo equipped with a micro SD-card. This set-up was modified after the first test, though. The consistent amperage was no longer recorded and only one temperature sensor, attached to the cell and connected to

the laptop via one of the ammeters, was used. Its values were recorded by the ammeter's software. A schematic illustration of the set-up can be found in Figure 12.

After making sure that all needed values were being recorded, the cell was overcharged with a constant current of 10.44 or 20.00 A, respectively. These conditions were kept, until measured values and visible signs indicated a cell breakdown.

2.6.3 Over-discharge test

The over-discharge test is schematically illustrated in Figure 15. As one can see, four batteries were connected in series, with one battery fully discharged and the other three fully charged.

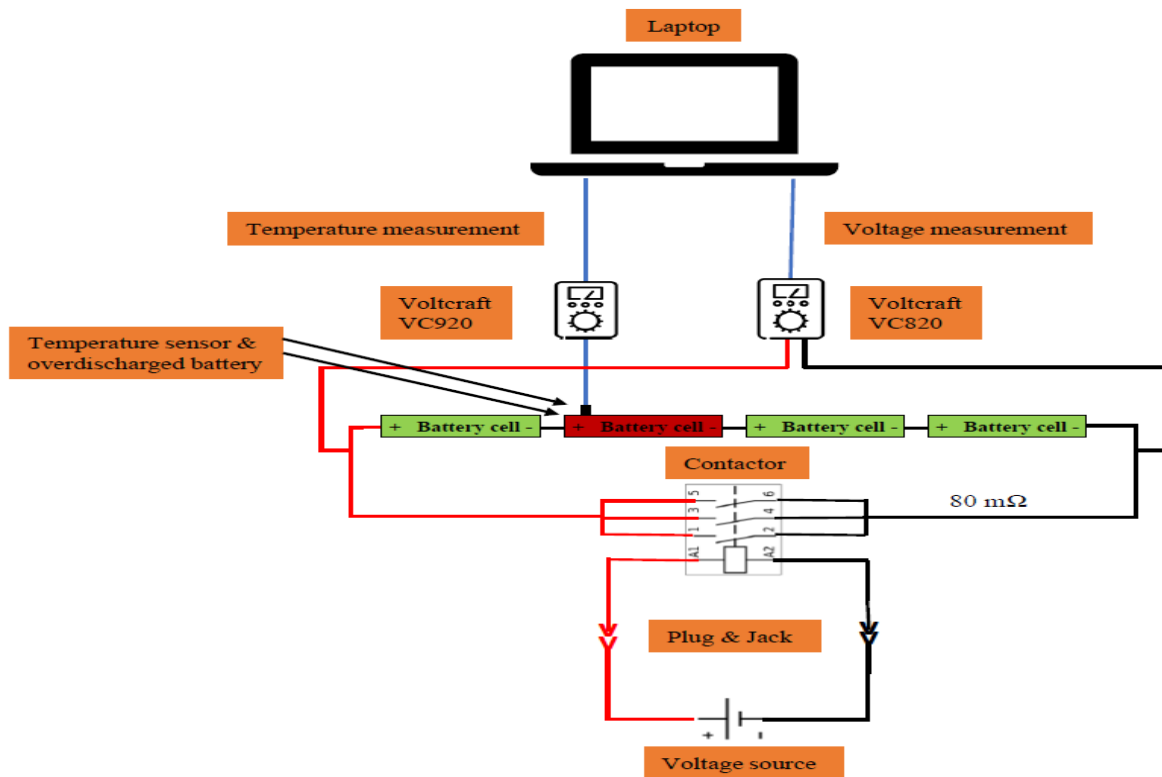


Figure 15: Schematic illustration of over-discharging set-up

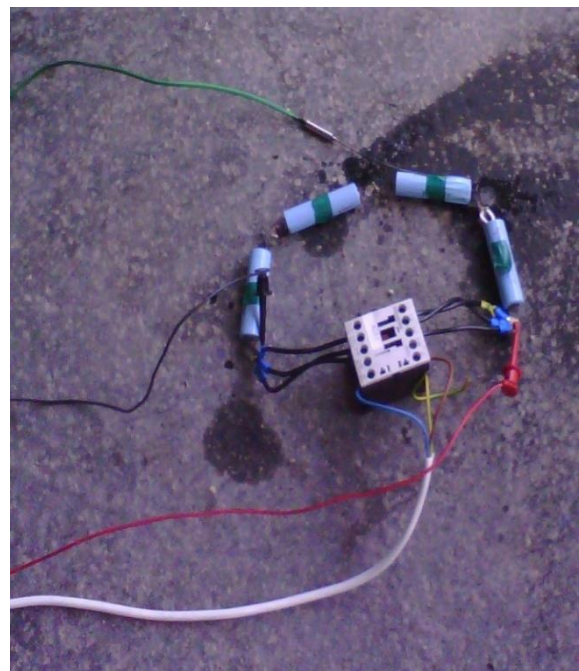
The positive and negative pole of the series connection then were wired to a contactor, using three ports each to split the resistance into thirds. This guaranteed an 80 mΩ resistance, as required by official safety standards. Auxiliary port one and two were connected to a voltage source, on the other hand. By manually closing the circuit, the conductor's electromagnet switched its ports to "active", thereby established a short circuit with high current flow due to the low resistance. The current flow path during an external short circuit is comparable to a normal discharge, which forces the already discharged cell into over-discharge. The conditions

were kept, until measured values and visible signs indicated a cell breakdown (UL, 2012, 16; Abaza, 2017, 51ff.).

During testing, two digital ammeters every second logged both the heat development of the discharged cell via a temperature sensor attached to the cell and the short circuit voltage. These values were then sent to and saved on a computer. Finally, Figure 16 a shows the complete set-up and Figure 16 b the series connection with interconnected contactor and the temperature sensor.



a



b

Figure 16: Set-up of over-discharge test (a) and battery series connection with contactor (b)

Since the batteries used for the test were shipped at a state of charge of 30 %, they had to be conditioned beforehand, though. As Figure 15 shows, three cells had to be fully charged, whereas one cell had to be fully discharged before the test could start. This was done with the University's own BaSyTec XCTS battery testing system. For this, the cells were placed in a Huber CC-K25 cooling bath filled with the same silicone oil as used for the stress tests. Then a (dis-)charging profile adapted to the used LG cells was created with the corresponding software and ran on the batteries. Figure 17 shows the charging profile of one of the cells.

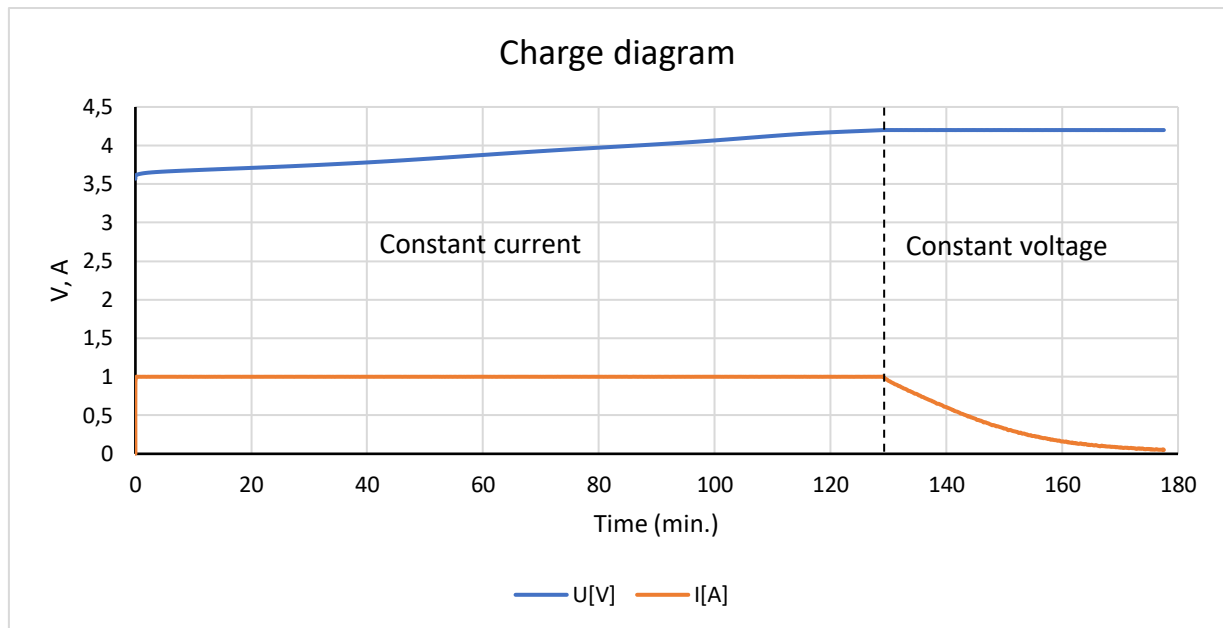


Figure 17: Charge profile of LG INR18650 M36T 12.50Wh battery

The charging of a lithium battery can be split into two phases. In the first one, a constant current of 0.3 C (1000 mA) was applied as predefined by the manufacturer. During this phase, electrical energy was quickly restored back to the battery. After 130 minutes the continuously risen voltage plateaued at a pre-set level of 4.2 V and the charging process entered an approximately 50 minutes long constant voltage stage in which the battery was going through final adjustments to maximize capacity. Within it, the current slowly dropped to a cut-off current of 50 mA, which terminated the charging process (Kim and Roh, 2017, 4; Richtek, 2019, s.p.).

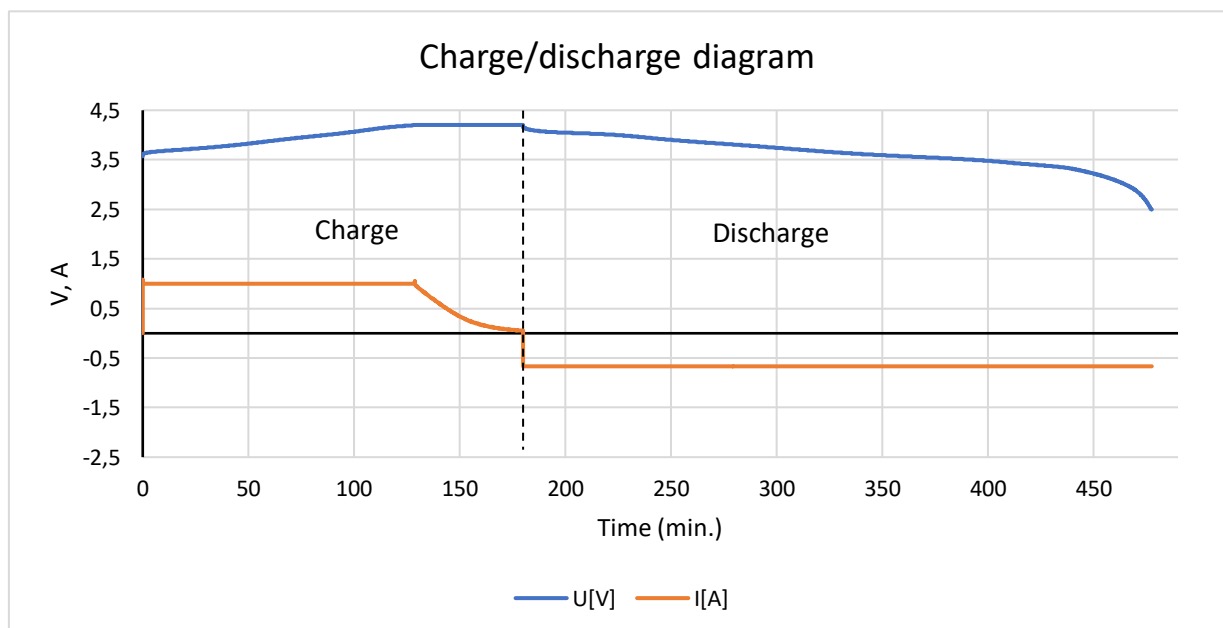


Figure 18: (Dis-)charge profile of LG INR18650 M36T 12.50Wh battery

To guarantee the health of the discharged battery, it underwent a full charging cycle, as seen in Figure 18. After the charge period as described above, the battery was discharged with a constant current of 0.2 C (670 mA) to a SOC of 0 %. During the around 300 minutes lasting discharge, the voltage slowly decreased to a cut-off voltage of 2.5 V. At this point, roughly 95 % of the stored energy was spent and the cell would have gone into over-discharge if discharge would have continued (Buchmann, 2020, s.p.).

With the FMECA and test set-ups described and the batteries prepared for testing, the following chapter presents the results and discussion of this work.

3. Results and discussion

3.1 Nail penetration test

As described in the previous chapter, releasing the falling weight of the built construction forced a nail into the battery cell. With the following formula, the speed of fall can be calculated to 4.4 m/s. The height (h) is hereby approximately 1 m and the force of gravity (g) is 9.81 m/s².

$$v(h) = \sqrt{2gh}$$

With a diameter of 18.51 mm, this means the nail punctured the cell within 4.18 milliseconds. By connecting the cell electrodes via a low resistance path, the nail body then caused an internal short circuit. The following discharge process is illustrated in Figure 19, representing the puncturing of only one electrode layer, though, not several as illustrated in Figure 5 and as it happened during the test (Abaza, 2017, 28).

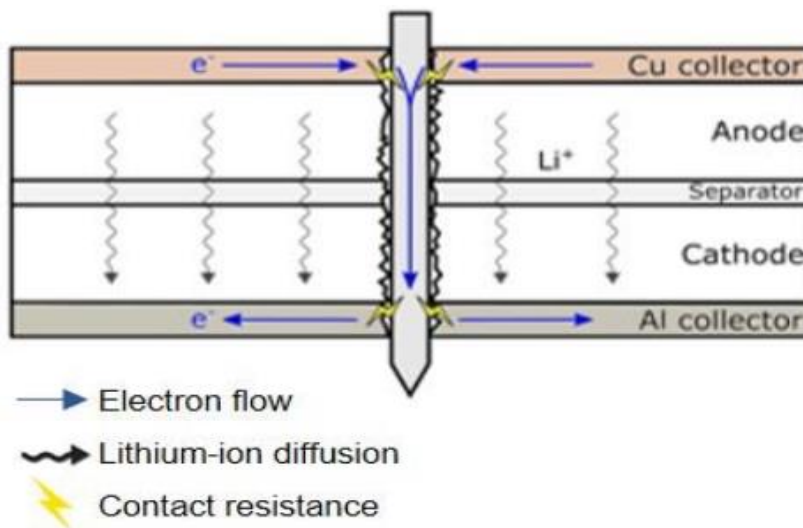


Figure 19: Schematic drawing of nail penetration induced short circuit (Abaza, 2017, 31)

Delithiation reactions at the anode active material produce lithium-ions and electrons. The lithium-ions are then transported from the anode to the cathode through the electrolyte and separator. The electrons on the other hand, travel to the anode copper collector, further on converging towards the short circuit contact spot induced by the nail. Here, they conduct along the nail to the Al current collector. Once the electrons and lithium-ions meet at the cathode active material, the lithiation reaction occurs. The large current flow creates Ohmic heat, which leads to local hotspots around the shorted area. These can provoke further exothermic reactions. Ohmic, or Joule heating, is defined as:

$$P = I^2 * R$$

with P being the power converted from electrical to thermal energy, I being the current traveling through the nail and R being its resistance. A large I causes large heat for that reason. A rapid increase of current and, therefore, temperature is followed by a limitation of shorting current and Ohmic heating as soon as the lithium-ions are depleted (Meier, 2006, 67; Abaza, 2017, 31).

The initial heating rate determines if Ohmic heating is followed by exothermic reactions, which lead to thermal runaway. A key factor in this is the nail penetration displacement. A long puncture distance causes a sharp temperature increase due to the shorting of several cell layers. Since in the conducted test, all electrode layers were punctured, these claims are undermined by Figure 20. It shows the cell casing temperature during the penetration test. The pot containing the cell was hereby either empty, half, or completely filled with silicone oil (Abaza, 2017, 31; Liu et al., 2016, 288).

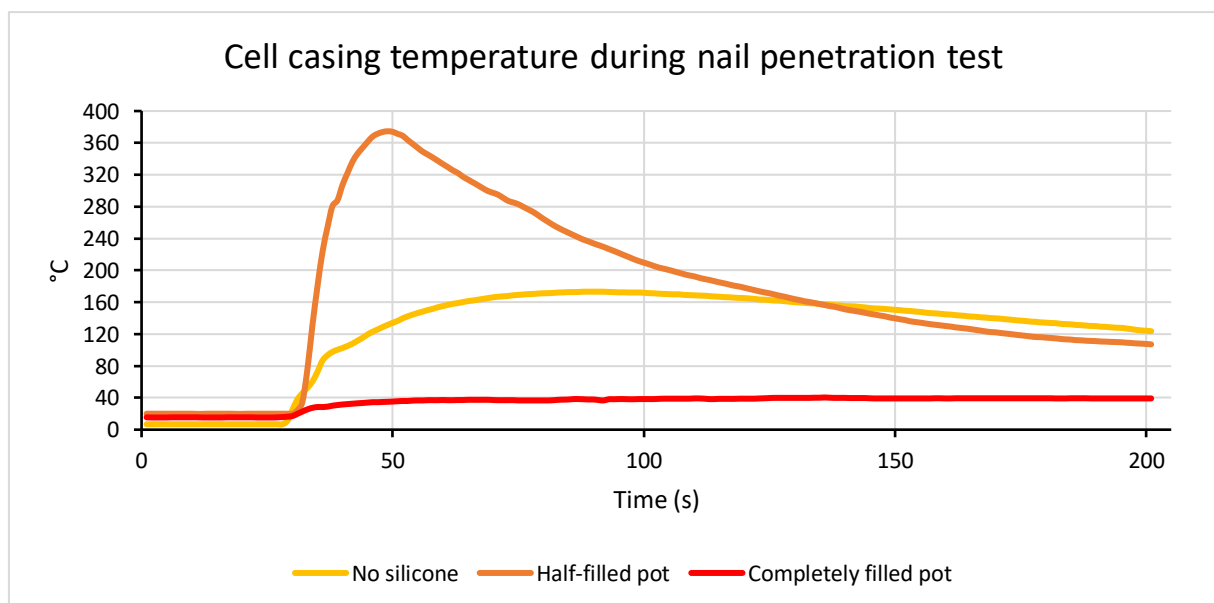


Figure 20: Cell casing temperatures during nail penetration

In all three scenarios, the puncturing led to thermal runaway. Ohmic heating was followed by severe exothermic reactions, as described in Chapter 2.3.1. Inner cell temperatures led to electrolyte decomposition and vaporizing, which in turn caused cell swelling due to build-up gases up to the point of venting. As Figure 21 a and b show, without being submerged in silicone oil, these gases ignited as a result of an oxygen-rich enough environment and a hot enough cell casing. Figure 21 c shows the destroyed cell after the thermal runaway event, more specifically the venting point situated at the positive pole of the cell (Mikolajczak et al., 2011, 47ff.).

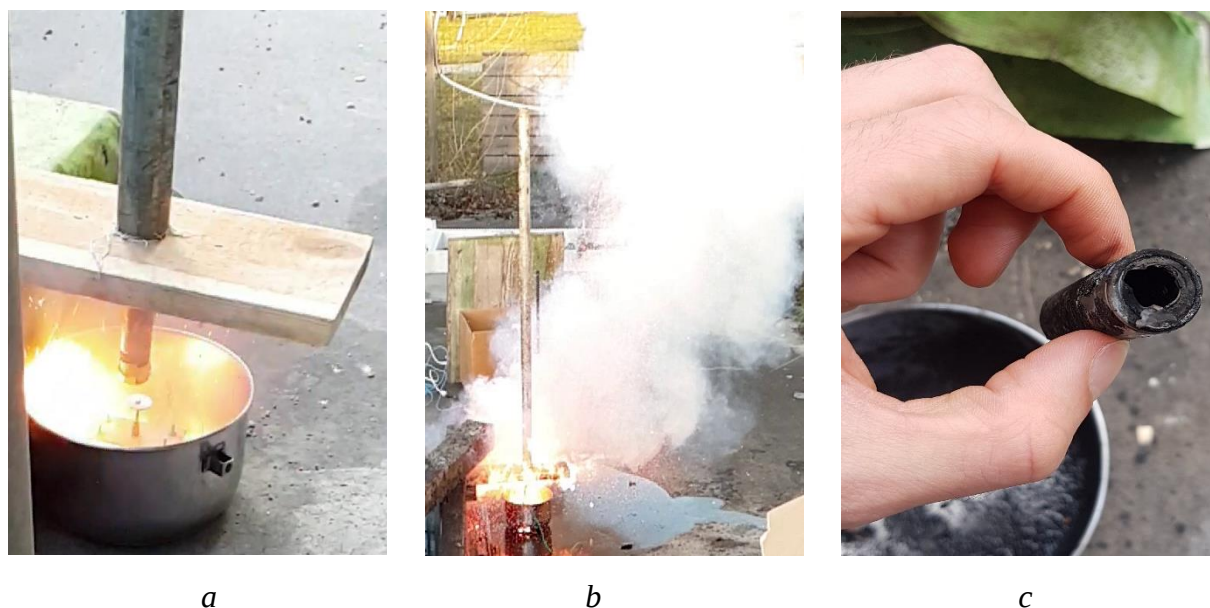


Figure 21: Exothermic reaction of cell in empty pot (a, b); destroyed cell after TR (c)

Coming back to Figure 20, the cell casing experienced a rise of temperature by $156.7\text{ }^{\circ}\text{C}$ within 60 seconds to a maximum of $173.2\text{ }^{\circ}\text{C}$, which calculates to $2.61\text{ }^{\circ}\text{C/s}$. 110 seconds after the temperature maximum, the cell has cooled down to $124.1\text{ }^{\circ}\text{C}$, which means $0.45\text{ }^{\circ}\text{C/s}$.

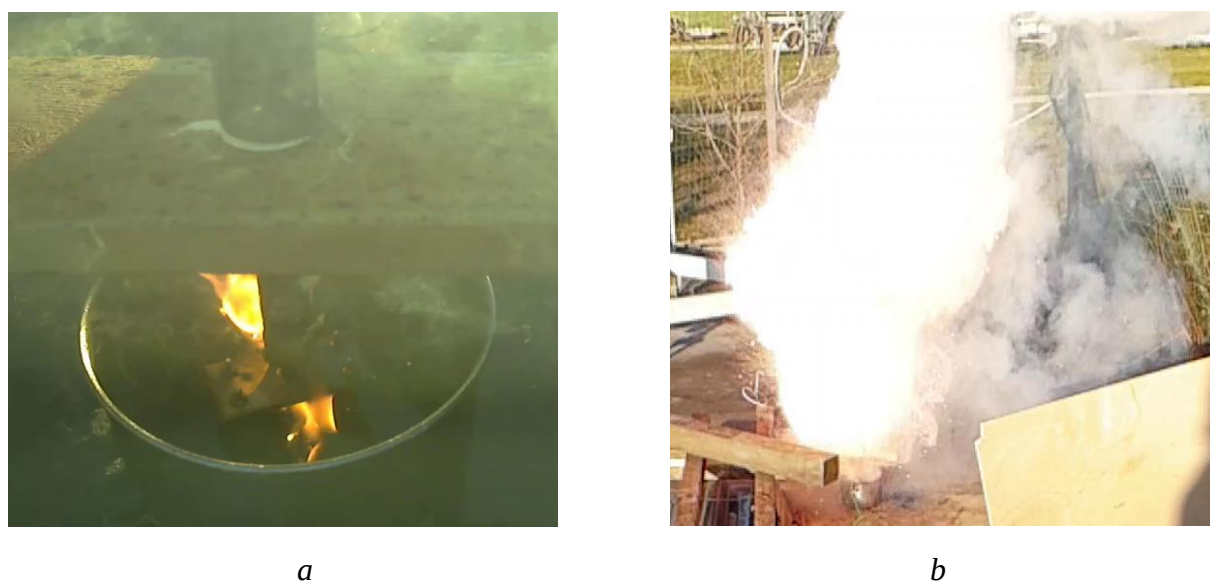


Figure 22: Exothermic reactions of cell submerged in with silicone half-filled pot (a, b)

Next, a test cell was placed in a pot half-filled with silicone oil. Figure 22 a and b illustrate the result. Here too, the released gases ignited. Figure 20 shows a much steeper temperature rise, though. Since the surrounding silicone not only took up some of the energy in form of heat, but also prohibited a too fast heat dissipation to the surrounding atmosphere, the temperature sensor had more time to register the temperature rise. This results in the displayed sharper increase compared to the test without silicone. The temperature rose hereby by 354.6 °C within 20 seconds, which computes to 17.73 °C/s.

The force with which the nail was driven into the cell by the weight led to silicone oil splashing from the pot, exposing the cell to the atmosphere. This way, oxygen reacted with the released gases and ignited them. Due to the ignition, the oil experienced temperatures above its flash point of more than 200 °C, which explains the strong formation of smoke seen in Figure 22 b (Lumitos AG, 2020a, s.p.).

Furthermore, Figure 20 shows not only a steeper temperature rise, but also decrease after thermal runaway. Within 151 seconds, the temperature decreased to 107.6 °C, amounting to 1.77 °C/s. When recording stopped, the cell had cooled down by 16.5 °C more than the one not being surrounded by silicone, which once again speaks for the excellent heat dissipation features of the used liquid silicone.

Finally, one cell was placed in a pot completely filled with liquid silicone. Figure 23 a and b demonstrate the visible reaction, once the nail penetrates the cell.



a



b

Figure 23: Exothermic reaction of cell submerged in with silicone filled pot (a, b)

Due to the absence of oxygen, the gases had no opportunity to ignite. Once again, smoke was formed, which means the oil was locally brought to its flashpoint, but to a far lesser extent than

when oxygen was involved, as a comparison between Figure 22 b and Figure 23 b illustrates. By looking at Figure 20, also a far lesser heat development becomes evident. The oil was heated up by 24.8 °C to a maximum of 40.1 °C within 108 seconds. The sharpest increase is visible within the first 10 seconds, though from 15.8 to 30.1 °C. Since the temperature sensor was not directly placed at a venting port, but still the silicone partly vaporized, one can assume, that at these points, the oil heated up to its flash point caused by the temperature of the released gases. These localized heating points did not lead to the vaporizing of greater amounts of oil, though, but rapidly increased the overall temperature of it by 14.3 °C.

Responsible for the increase in temperature of the silicone oil was the calorific energy produced by the cell during nail penetration. As written in the previous chapter, it can be calculated using following formula:

$$\Delta Q = c_p \cdot m \cdot \Delta T$$

With c_p being 1,45 kJ/kgK, the mass of the silicone oil 1,18 kg and the change of temperature 24.8 °C, ΔQ results in 42.43 kJ, which transforms to 11.79 Wh. According to the calculation, 94 % of the stored energy was transformed into calorific energy due to exothermic reactions caused by the short circuit. Nonetheless, findings by Yayathi et al. indicate, that during a thermal runaway event, the total energy release is even greater than the electrochemical energy stored in a battery due to internal reactions such as the decomposition of the cathode (2016, 204). The discrepancy in findings can be explained by the cell's release of great amounts of energy in the form of smoke during the tests done for this work. Its temperature was only partly captured by the installed temperature sensor.

After thermal runaway, no noteworthy cooldown of the oil could be noticed. This can be explained by the high heat capacity of the liquid silicone, which prohibits its fast cooldown.

What conclusion can be drawn from all this? The nail penetration test led to severe exothermic reactions, which posed great danger to its surroundings, especially if the cell was exposed to oxygen. The severity of the reaction hereby depends on several factors. The number of electrode layers punctured plays the most important role, as written before. Another key factor is the shape of the object puncturing the cell. Cone-shaped objects like the used nail cause an early force drop and thereby an elevated stress concentration, whereas the blunt head of a spherical form delays the failure of the separator and can, therefore, be considered less dangerous (Liu et al., 2016, 285).

The size of the nail determines the short-circuited area, with a larger nail causing a larger short circuit area and, thus, a larger reaction force. With R^{nl} being the nail radius size, the failure displacement of the separator d can be calculated as:

$$d = 3.3 * R^{nl} \text{ (Liu et al., 2016, 286).}$$

The state of charge of the battery is also a point of consideration. Here, a linear relationship between SOC (1 = 100 %) and failure displacement can be assumed:

$$d = 3.12 - 0.7 * SOC$$

The larger d , the more the separator is damaged, which leads to heavier reactions. Continuing, a high enough SOC keeps a stable current long enough up, to cause thermal runaway. Since the used cells were not conditioned beforehand, a shipping SOC of 30 % is assumed. As the tests showed, this was enough for thermal runaway to occur. The speed of inducing the short circuit determines if thermal runaway initiates at the inner (high speed) or outermost cell (low speed) (Liu et al., 2016, 287; Kim and Roh, 2017, 4).

As Abaza states, a final factor is the material used for penetration. His findings indicate copper as the material most likely to cause a full discharge, followed by steel due to its lower electrical conductivity. Non-conducting material like plastic, cause almost no shorting, on the other hand (2017, 37).

Coming to the evaluation of the test as part of the FMECA, nail penetration can definitely be seen as a worst-case scenario. Even though authors like Ruiz et al. criticize the test's usefulness due to its unlikeliness to occur in a real situation, accidents like the so-called LAX-incident of 1999, where a fork-lift operator punctured two cargo pallets loaded with 120,000 primary lithium cells, causing their thermal runaway at the Los Angeles cargo facility, prove the scenario's possibility of occurrence (2018, 1434; Farrington, 2001, 263).

As Table 7 shows, nail penetration means extreme conditions for all cell components. Whereas the aluminium current collector melted, the temperatures reached are not high enough to melt the copper, though. The mentioned limited thermal stability of electrolyte components like $LiPF_6$ led to the formation of toxic gases. Temperatures also reached the previously written boiling point of EC. The highly exothermic breakdown of the cathode active material along with the carbonate $LiPF_6$ electrolyte ultimately allowed the cell to catch fire. The force of the reaction was strong, yet the high unlikeliness of the event transforms to ranking digit 1 on the occurrence scale (Warner, 2019, 67).

The reaction obtained in the different test settings not only terminated the useful life of the battery but also posed a danger to its surroundings. The nail size radius (3 mm) and form (cone-shaped), its material (steel) and the SOC (30 %) formed a dangerous situation. By denying the cell oxygen (O₂), the silicone oil played a vital role in lessening the outcome, though. The formation of flames could be prevented. Still, toxic, hot gases were produced, which justify the highest severity ranking of 3.

The force of reaction was fierce, which makes it easy to detect. Therefore, the lowest ranking of 1 is assigned for the ease of detection.

After adding up all separate RPNs, the result is 35. Displaying it in the RPN-severity matrix below clearly illustrates the combination of high severity with high unlikelyness of occurrence and easiness of detection. Even though the silicone prevented a catastrophic outcome, the tests clarify, that the batteries should always be handled with care, since dropping them on sharp objects, for example, might lead to the same outcome. Also, the surroundings of the cooling bath should bear no possibility for foreign objects to fall into the silicone bath (UL, 2012, 17).

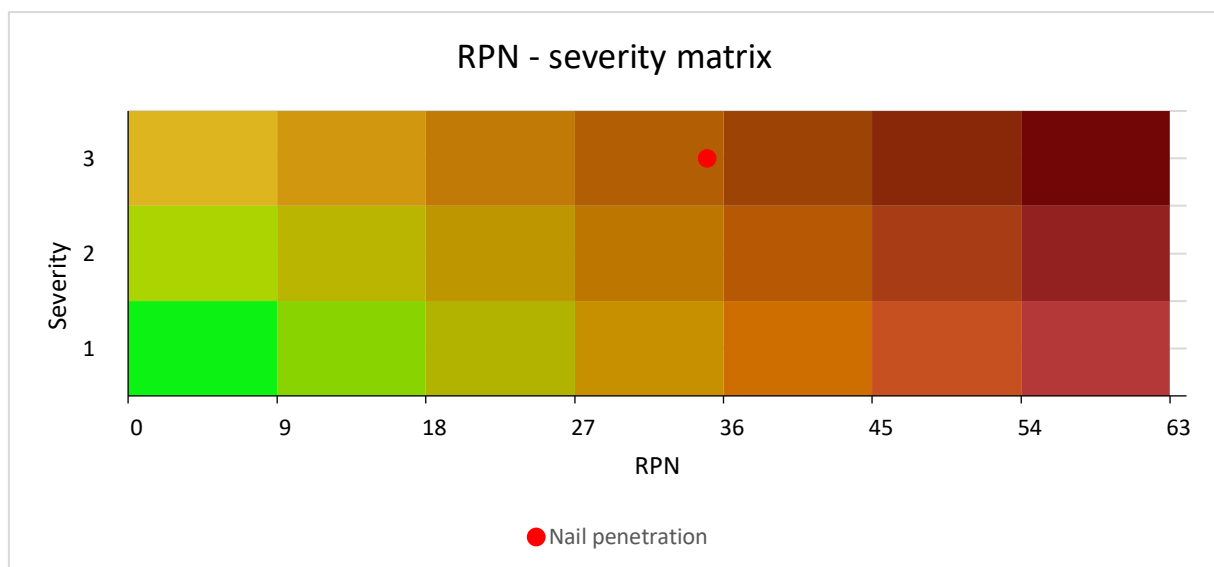


Figure 24: Nail penetration test RPN-severity matrix

Table 7: FMECA worksheet nail penetration test

Battery component (Items)	Potential failure mode(s)	Observed effect	Potential failure cause	Likelihood of occurrence	Severity of occurrence	Ease of detection	RPN
Anode (Active material)	Graphite particle fracture; SEI decomposition ¹	Evolution of H ₂ , C ₂ H ₄ , C ₂ H ₆ and CO ₂ ² ; pressure increase and venting ¹	Thermally/electrochemically driven reactions ²	1	3	1	5
Anode (Current collector)	Al/Cu alloy damages Cu current collector ³	Loss of function, becoming friable ³	High internal temperature ³	1	3	1	5
Cathode (Active material)	Decomposition; particle fracture ⁴	Evolution of CO ₂ , carbon monoxide (CO) and O ₂ ² ; pressure increase and venting ¹	Thermally/electrochemically driven reactions ²	1	3	1	5
Cathode (Current collector)	Melting of Al current collector ³	Melted Al alloys with Cu ³	High internal temperature ³	1	3	1	5
Separator	Hole in separator ¹	Internal short circuit ¹	Nail puncturing ¹	1	3	1	5
Electrolyte	Chemical decomposition ⁴	Leakage, boiling; evolution of HF, LiF, PF ₅ ⁴	Thermally/electrochemically driven reactions ²	1	3	1	5
Casing	Casing break ¹	Meltdown of wrapping; opening of vent ports ¹	Nail penetration; built-up pressure ¹	1	3	1	5
RPN result							35

¹ Bubbico et al., 2018, 77ff. ² Golubkov et al., 2014, 3639f. ³ Mikolajczak et al., 2011, 47 ⁴ Hendricks et al., 2015, 115.

3.2 Overcharge test

Lithium-ion batteries are very specific when it comes to the amount of charge they can absorb. If the manufacturer's limits are not followed, be it via a wrong charger, or due to wrongly set limits at the University's BaSyTec system, a battery is easily overcharged. Therefore, an overcharge test is included in this FMECA. Its findings are presented and discussed in the following (Thomas et al., 2012, 245).

The overcharge test is divided into three stages. In the first, the battery is charged to a SOC of 100 %. Throughout this phase, normal charging processes occur. Lithium-ions are extracted from the cathode crystal and transferred to the graphite anode via the electrolyte (Ouyang et al., 2018, 33416).

Next, the cell goes into overcharge. With the cathode potential increasing, the metal on the cathode oxidizes from its metallic form to metallic ions and the oxidation of the electrolyte begins. Some of these ions wander to the anode, propelled by the concentration difference between anode and cathode. Furthermore, the SEI layer thickens due to metallic lithium depositing on the anode's surface after being fully packed with intercalated lithium. The steady increase in cathode potential accelerates the electrolyte oxidation and build-up of heat and gas. This leads to the melting of the separator, which, combined with the SEI layer thickening, causes an increase of internal resistance and limits further current flow.

Built-up gases up to this point are vented. With the continued apply of current, the separator gives in due to its loss of integrity, which causes a decrease of internal resistance. Further overcharging could finally lead to a separator breakdown and a short circuit induced thermal runaway. Figure 25 illustrates the overcharge process as it occurred in this work's tests (Ouyang et al., 2018, 33416; Roth et al., 2007, 581f.).

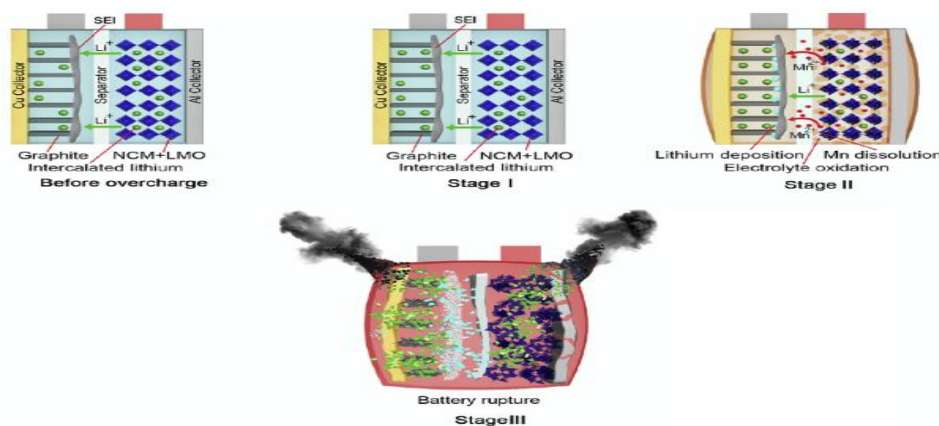


Figure 25: Scheme of overcharge process (Ren et al., 2017, 332)

Figure 26 to Figure 28 represent the voltage, ampere and temperature evolution during the conducted tests. Figure 26 hereby gives back the results of the test conducted without any liquid silicone. As during normal charging, the voltage increased first, approaching a constant voltage phase of approximately 7.2 V shortly after the start of charging. Accompanied was this increase in voltage with a steady rise in temperature from 17 to 93.3 °C through Ohmic heating.

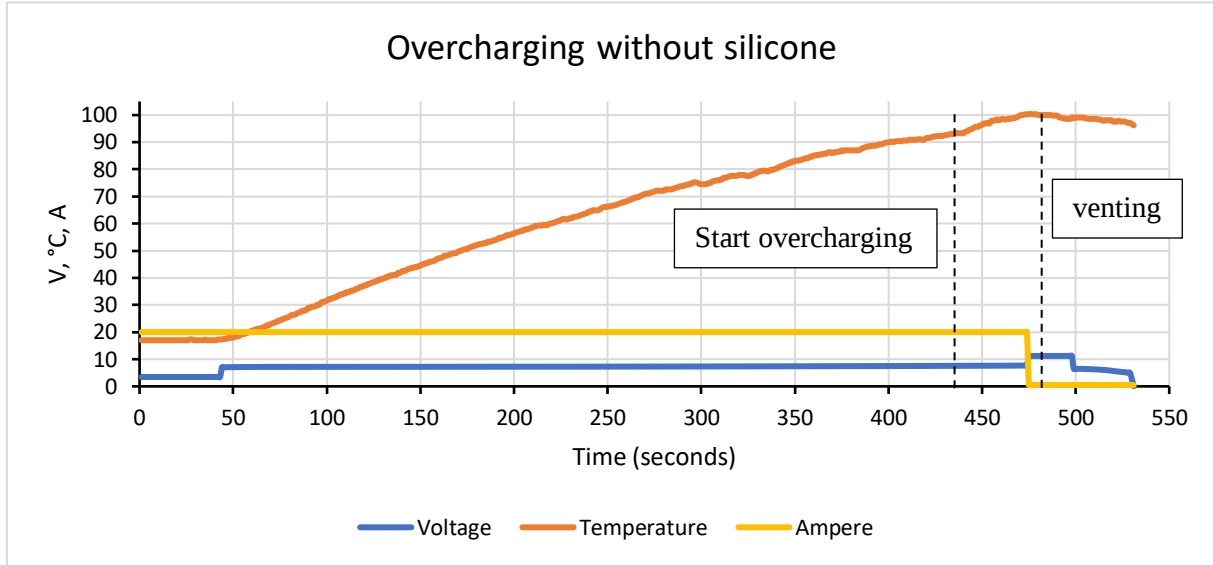


Figure 26: Overcharge test without silicone oil

As described above, the first 433 seconds can be seen as stage one, where the cell was charged to a SOC of 100 %. Between 433 and 477 seconds, an increased rise in temperature could be noticed. This is the overcharging phase. After 477 seconds, voltage increased sharply to almost the full supply voltage of the power supply unit, and current flow dropped to almost 0. Reason was the previously described separator shutdown starting at a cell case temperature of 100,3 °C. An inner cell temperature of at least 135 °C is to be assumed. This limited the current flow and increased internal resistance. The shutdown occurred at a SOC of 107 %, calculated with the following formula:

$$SOC(t) = SOC(t-1) + \int_0^t \frac{I}{C} dt$$

SOC (t) is the battery SOC at time t (in %), SOC (t-1) is the initial SOC (30 %), I is the charge current (20 A), t the time in hours (0.1325 h) and C the battery capacity (3.44 Ah). The relatively low state of overcharge can be explained by the fast increase in temperature due to the high current flow and, therefore, fast shutdown of the separator, which prohibited further charging. The cell case temperature reached a maximum of 100.5 °C before built-up gases vented shortly after. In contrast to the nail penetration test, the vented gases did not ignite, though (Hanifi, 2016, s.p.; Roth et al., 2007, 582).

The melted separator kept its integrity for 23 seconds, after which intermediately formed pin-holes formed a large enough hole, which caused a loss of its resistance, as illustrated by the voltage drop. With the hole size increasing, the voltage further decreased to around 2.3 V. Since a sharp drop to 0 V could not be noticed, an internal short was not occurring. As Roth and colleagues write, thermal runaway cannot be ruled out, though, if overcharging continuous to the point of complete separator meltdown (2007, 581).

In comparison, Figure 27 shows the same test conditions with a cell submerged in silicone oil. Several things strike the eye. The initial phase up to a SOC of 100 % after 433 seconds was characterized by an initial temperature increase due to an increase in voltage to a steady-state (the values between second 126 and 175 can be seen as measuring inaccuracy). Through heat dissipation, a plateau level of 55 °C could be obtained for 58 seconds. Thereon after, the surrounding silicone was heated up itself, leading to a steady, but not sharp temperature increase from 55 °C to 70.9 °C for the next 385 seconds. Even though the cell was overcharged to a SOC of 126 % until the separator melted, no sharp increase in temperature could be observed during this phase, speaking for the silicone oil as a proper heat dissipator.

After a total of 595 seconds, 118 seconds longer than without silicone, the separator shut down, leading to a steep temperature increase to a maximum of 79.8 °C, an amperage drop to around zero and a voltage increase from 8.2 to 13.5 V. The temperature rise was triggered by an increase in internal resistance. The maximum temperature reached was notable well below the maximum without silicone. Reason for the voltage increase at a lower temperature was not only the melted separator but also the higher SOC, which implies more side reactions like the thickening of the SEI layer. As described above, this too leads to an increase in internal resistance. Shortly after, the cell vented, which only caused the formation of some bubbles in the oil (Abaza, 2017, 144).

After 23 seconds, the separator lost its integrity and voltage dropped. Testing was terminated once again before a complete meltdown induced a short circuit. It can be said that the liquid silicone cools down the cell, allowing it to withstand a longer range of overcharge. Still, the oil has no influence on the reactions happening within the cell. Venting and cell breakdown can, therefore, only be delayed, not prevented.

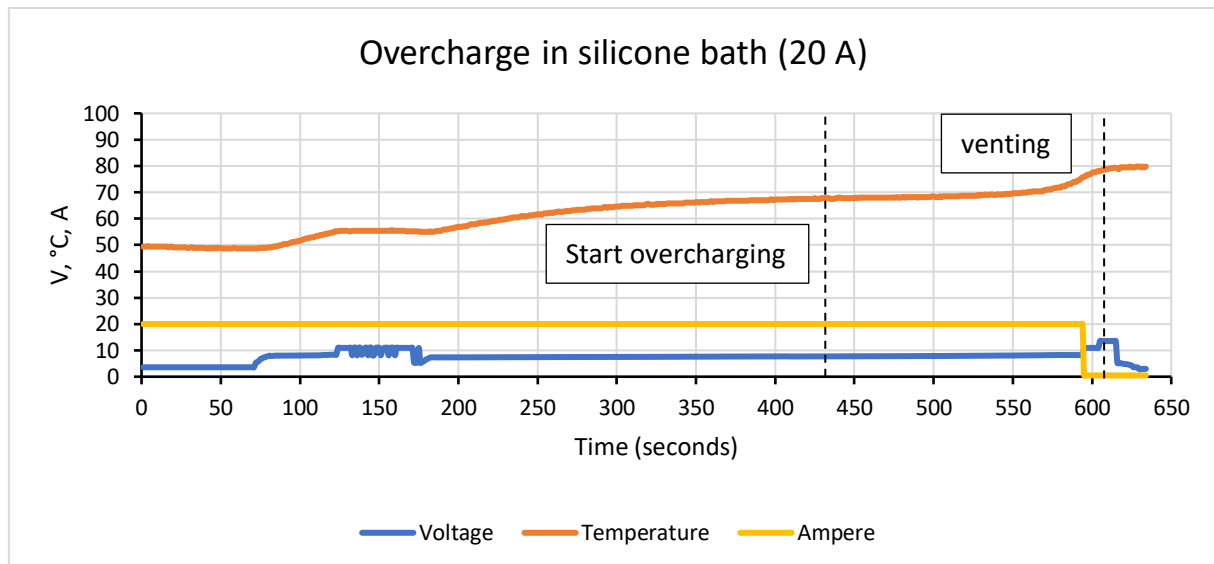


Figure 27: Overcharge test in silicone bath (20 A)

Finally, ΔQ is calculated to 14.45 Wh. At first sight, this can be seen as an unexpected result, since the stored energy amounts only to 12.5 Wh. As written in Chapter 3.1, a breakdown of the cell releases a total of energy, larger than the electrochemical energy available during normal cell cycling, though. Since no greater amount of heat was released in the form of smoke but was gradually transferred to the oil via the cell casing, the oil heated up more, leading to a bigger ΔQ .

For a third and last test setting, Figure 28 shows the results of overcharging a cell within liquid silicone, but at a lower amperage of 10.44 A. The decrease of ampere has a great influence on the outcome, as one can see. The shutdown of the separator occurred only after 791 seconds, 196 seconds later than with double the amperage and 314 seconds later than without silicone. These findings are in line with Ouyang et al., who also come to the conclusion that a higher charging rate leads sooner to battery failure (2018, 33419).

When the shutdown occurred, the SOC was 93 % according to the calculation. Since overcharge was not reached, one must assume a higher initial SOC than 30 % due to previous unknown tests. For the following, a SOC of more than 100 % is presumed. This level of charge was reached after longer time, reason being the reduced charging current. Once a SOC above 100 % was obtained, the temperature rose to 60 °C and the separator melted.

The reduced separator melting temperature compared to the tests done before needs further explanation. Both cell casing and silicone temperature measured at the pot's wall indicated no temperature increase, rather a decrease, before separator melting. Reason is the refilling of the pot with ambient tempered silicone oil during overcharge to bring its temperature closer to the

required 40 °C. Therefore, it can be assumed that the cell temperature was higher than 60 °C. The cooling effect gained by the added silicone, disguised the real temperature, though. Another finding is the only slight increase of the silicone oil close to the pot's wall from 35 to 38 °C during venting. It shows that only the oil close to the cell got heated up. Continuous stirring of the oil might, therefore, lead to better heat dissipation and allows the cell to withstand longer periods of overstress situations.

After separator melting, the voltage level rose to the full supply voltage, in this case 30 V. The separator kept its integrity 73 seconds longer than in the test before due to the reduced ampere level and, therefore, temperature. 791 seconds after testing started, the separator finally gave in and venting occurred. The prolonged time till venting after separator shutdown was caused by the slower gas built-up until the point of vent breaching. Due to the adding of silicone during overcharge testing, ΔQ is not calculable.

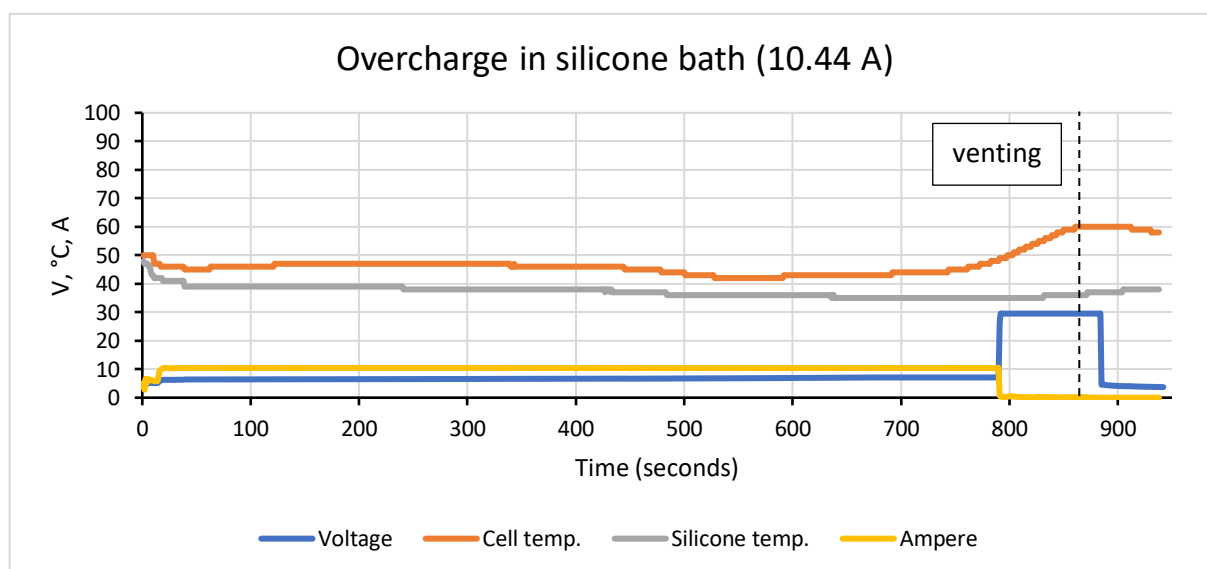


Figure 28: Overcharge test in silicone bath (10.44 A)

What are the conclusions of this test series? In all three test cases, overcharging led to cell venting and breakdown. Compared to the nail penetration test, the vented gases did not ignite, though. It could be shown, that the built-in shutdown separator prohibited overcharging to the point of thermal runaway.

Its breakdown should be seen as a matter of concern, though, since scientists like Roth et al. showed that a complete failure of the separator could lead to a delayed thermal runaway if overcharging continues (2007, 582).

Compared to overcharging without silicone oil, findings show that cells submerged in silicone can withstand longer periods of overcharge. An important role plays the applied current. The

lower it is, the longer it takes the cell to break down since it takes longer to reach a state of overcharge and less heat is produced. Once the separator shuts down, a lower amperage lets it also keep its integrity for a longer period of time due to the lower internal temperature caused by Ohmic heating. The second temperature sensor at the pot's wall furthermore revealed a sharp temperature increase only for the oil directly surrounding the heated cell. Stirring the oil might, therefore, increase the time a cell can withstand overcharge conditions.

On a cell component level and illustrated in Table 8, the graphite on the anode led to lithium plating, an event that, as stated in Chapter 2.2, would be preventable if LTO was used instead. LiPF_6 also could not prevent Al corrosion anymore due to the high charging potential. Furthermore, the described lower thermal stability of the NMC cathode resulted in increased side reactions with the electrolyte, causing the formation of gas.

Coming to an FMECA verdict, using the wrong charger or setting wrong charging limits in the BaSyTec systems are sources of failure with a moderate, but still existing possibility of occurrence, especially if tests are conducted by students as part of a lecture exercise. To decrease the possibility of occurrence, a proper introduction to the BaSyTec system and dangers of lithium batteries for students is advised (2).

As for the severity of occurrence, the tests showed that overcharging led to cell failure and venting, but not the occurrence of flames. Overcharging did not pose an immediate threat to the surroundings, especially if the cell was submerged in silicone oil and overcharging was terminated before separator breakdown. This results in ranking digit 2.

Last but not least, even though the venting event itself is easy to detect if one is standing by closely, its occurrence might not be visible right away, if it happens unmonitored. In comparison to nail penetration, no silicone oil was spilled or vaporized. A submerged vented cell might, therefore, not be detected immediately. Also, neither the ampere nor the voltage curve hinted an imminent overcharge situation up to the point of separator melting. Only the temperature curve showed irregularities before. For future testing, the cooling bath should be equipped with a temperature sensor for that reason. If heat development during a normal charging cycle is known, the sensor could trigger an alarm, or even prompt a charging stop, if a set temperature limit is crossed. By following the recommendations of this work, overcharging can be detected before separator melting happens. Therefore, a ranking of 2 is appropriate. In summation, the RPN amounts to 36.

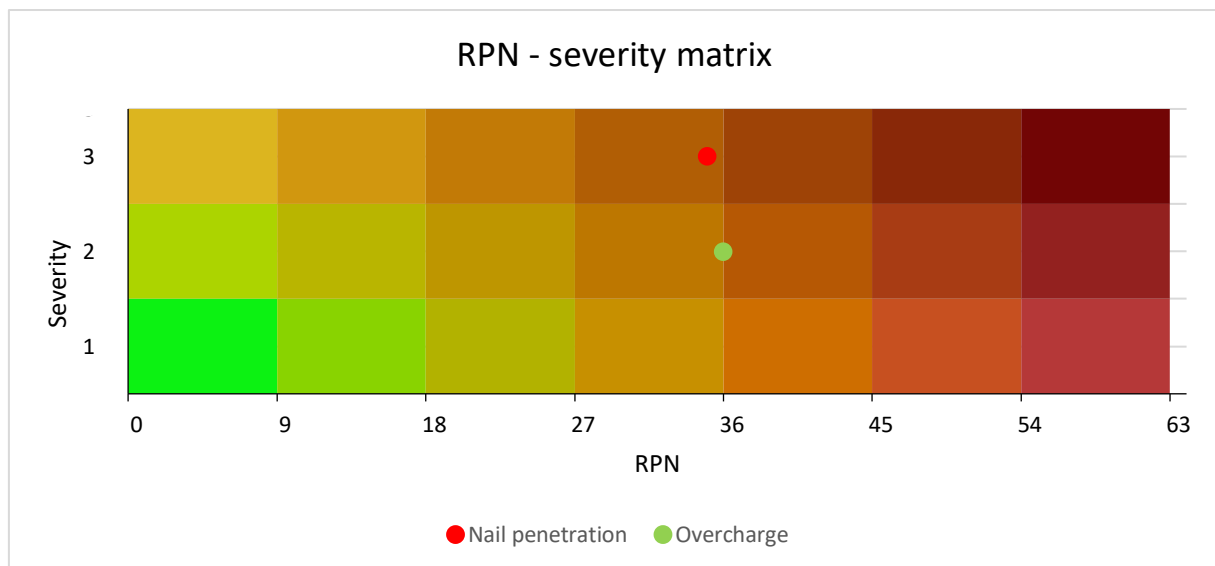


Figure 29: Overcharge test RPN-severity matrix

Table 8: FMECA worksheet overcharge test

Battery component (Items)	Potential failure mode(s)	Observed effect	Potential failure cause	Likelihood of occurrence	Severity of occurrence	Ease of detection	RPN
Anode (Active material)	Thickening of SEI due to lithium plating ²	Increased internal impedance ²	High current rate charging ²	2	2	2	6
Anode (Current collector)	No failure	No effects	/	/	/	/	/
Cathode (Active material)	Excessive removal of lithium causes instable crystalline structure ¹	Gas generation and cell bloating ³	Thermally/electrochemically driven reactions ³	2	2	2	6
Cathode (Current collector)	Pitting corrosion of Al ²	Solid products of corrosion increase the electrical resistance ²	High voltage ⁴	2	2	2	6
Separator	Melting, later breakdown of separator ³	Resistance increase; current drop; short circuit ³	High internal temperature ³	2	2	2	6
Electrolyte	Decomposition of solvent ³	Increased resistance; evolution of gases ³	Thermally/electrochemically driven reactions ³	2	2	2	6
Casing	Bloating of cell ⁵	Opening of vent ports ⁵	Gas built-up ⁵	2	2	2	6
RPN result							36

¹ Mikolajczak et al., 2011, 47 ² Bubbico et al., 2018, 77ff. ³ Hendricks et al., 2015, 59 ⁴Zhang and Jow, 2002, 460 ⁵Ouyang et al., 2018, 33417.

3.3 Over-discharge test

As described in Chapter 2.3.1, over-discharge can occur during long periods of storage at a too low voltage cut-off. On the other hand, different ageing behaviours of single cells can lead to over-discharge if they are connected in a battery pack. Since it is difficult to maintain the exact same SOC for all cells in a battery pack, it is inevitable that single cells experience over-discharge to a certain degree. This makes an investigation of over-discharge effects an important part of this FMECA (Mikolajczak et al., 2011, 60f.; Ouyang et al., 2018, 33414).

Just as the overcharge process, the over-discharge process can be divided into three stages. During the first stage, the applied voltage forces the lithium-ions to be extracted from the anode and transferred to the cathode via the electrolyte, where they are intercalated into the cathode crystal (Ouyang et al., 2018, 33418).

Severe over-discharge causes an increase of the anode potential and an oxidation of the anode copper current collector to Cu^+ and further to Cu^{2+} . The concentration difference between cathode and anode lets some Cu^{2+} ions diffuse to the cathode side. An excessive loss of lithium-ions in the anode also leads to SEI layer decomposition. The lithium lost at the anode side is then deposited in its metallic form onto the cathode surface (Ouyang et al., 2018, 33418).

During the last stage, continuous deposition of lithium onto the cathode's surface leads to lithium plating. Cu^{2+} , which transferred to the cathode as already described, reduces to Cu^+ ions and Cu metal, forming metallic dendrites. With their continuous growth and without a shutdown separator, eventually, the separator is punctured, causing an internal short circuit and cell venting/breakdown due to built-up gases. The process is illustrated in Figure 30 (Ouyang et al., 2018, 33418).

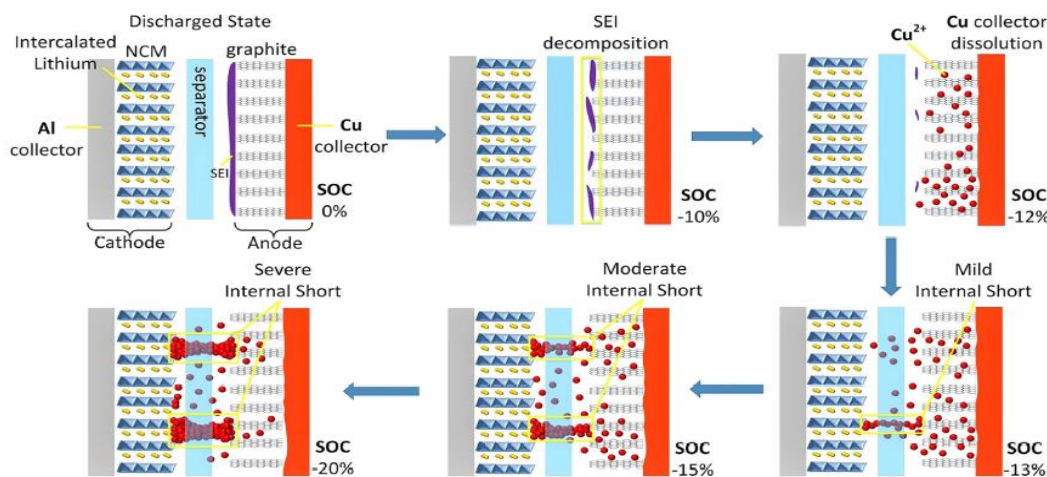


Figure 30: Internal cell reactions during over-discharge (Guo et al., 2016, 3)

Since the overcharge tests have shown that, if soon enough stopped, there is no severer reaction to be expected, the over-discharge tests were conducted without the use of silicone oil. Figure 31 gives back the result of the first over-discharged cell. During the first 10 seconds, the cells were not yet shorted. Therefore, no temperature increase could be measured, and the voltage curve represented the open-circuit voltage of the series connection. With second 11, the circuit was closed, which caused an instant voltage drop due to the low resistance connection. Accompanied was this with an immediate rise in temperature since the battery started to discharge at a SOC of 0 % and hence went right away into over-discharge. The shorting resistance is hereby responsible for the temperature rising rate, with a lower resistance allowing a bigger current flow and so more heating (Abaza, 2017, 62).

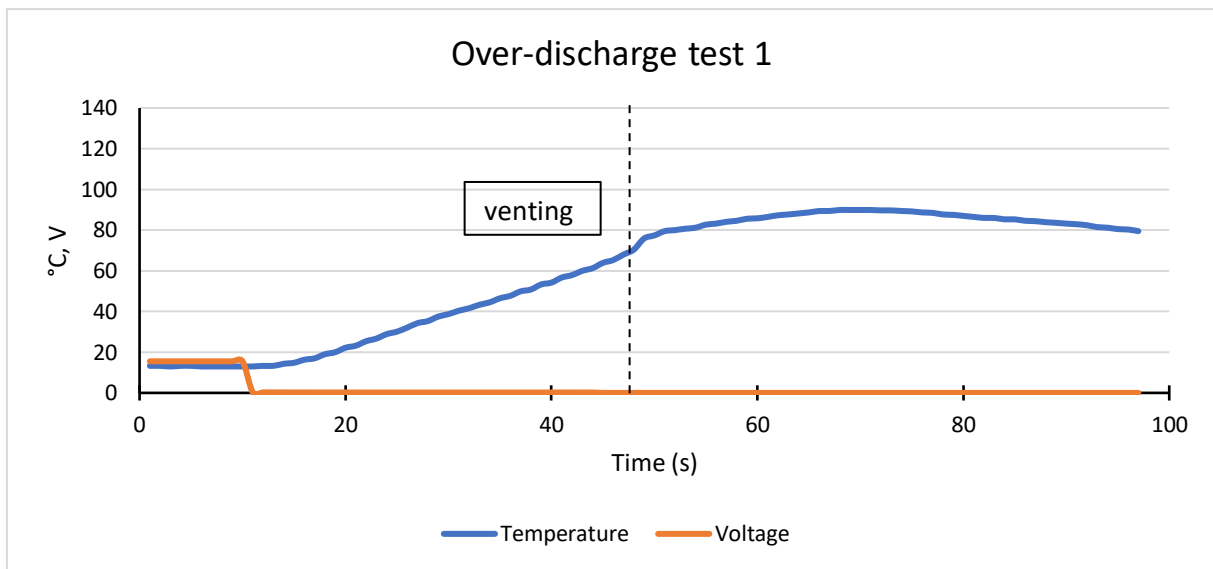


Figure 31: Over-discharge test 1

An open-circuit voltage of 15.52 V and a total resistance of 224 m Ω (80 m Ω circuit resistance and 36 m Ω inner cell resistance) calculates to a 69.29 A short circuit current. The high current caused a rapid discharge to a SOC of -21 % and temperature rise, until, after 37 seconds, the separator melted. It prevented further dendrite growth, and an internal short circuit, as illustrated in Figure 30, could be averted. However, a voltage increase due to the separator shutdown, as it was during overcharging, could not be measured, since no external voltage was supplied. Shortly after the shutdown, the cell vented due to the inertia of internal reactions. This and the release of hot gases close to the sensor was also the reason for the further rise in temperature, leading to an 89.9 °C maximum before it started to fall again. It has to be noted that compared to the overcharge test, cell breakdown occurred a lot faster due to the higher current flow (Abaza, 2017, 60; Bubbico et al., 2018, 77).

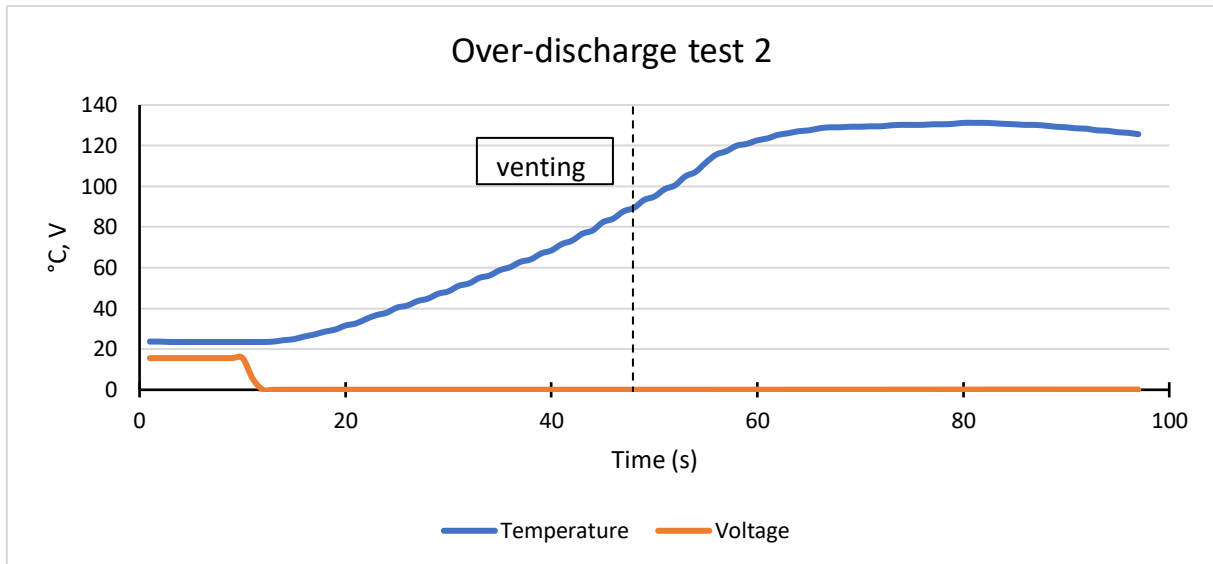


Figure 32: Over-discharge test 2

Figure 32 illustrates the results of the second over-discharge test. Since in contrast to the first one, it was not filmed, the exact venting moment cannot be determined anymore. For the purpose of illustration, the same amount of time as during the first over-discharge situation is assumed, which is reasonable. The peak temperature of 131.2 °C, 41.3 °C more than the first test's temperature maximum, is explainable by the position of the temperature sensor as Ouyang et al. write. For the second test, it was attached closer to the venting port's side, which allowed a registration of the gases' genuine venting temperature (2018, 33421).

Furthermore, the thermal image shown in Figure 33 demonstrates that, up to this point, shorting the series connection only had a notable impact on the over-discharged cell. The inertia of internal reactions explains the continued temperature rise after venting.

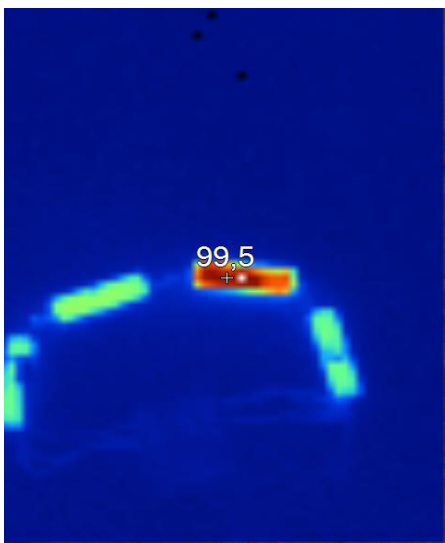


Figure 33: Thermal image of shorted series connection

Coming to the FMECA verdict, over-discharge can be seen as the scenario most likely to occur. Not only that single cells will experience moments of over-discharge when connected with others due to slight differences in their state of charge at some point in their life. Especially longer periods of storage, or storage without shielded electrodes close to metal objects are a matter of concern due to shorting. Rank 3 for the likeliness of occurrence is therefore reasonable (Thomas et al., 2012, 246).

The severity of occurrence, on the other hand, is rated with rank 1. The cell broke down and vented with little amounts of electrolyte being ejected. Compared to overcharging the cell, even with the occurrence of an internal short circuit, thermal runaway is unlikely to happen since the caused discharge would have little cyclable lithium left to provoke it.

Since the cell did not break down immediately once over-discharge started, signs of overstress were not immediately visible. This is especially true if a series connection is following a normal discharge circle and is not short-circuited. Just like during overcharge, the temperature development was the only reliable indicator of over-discharge. Once again, the importance of equipping the thermal bath with a temperature sensor is stressed. All in all, the ease of detection is ranked 2.

In conclusion and seen in Table 9, the RPN is again calculated to 36, but as a result of a different composition. Furthermore, the lower severity due to the low SOC, positions over-discharge below overcharge, as seen in Figure 34.

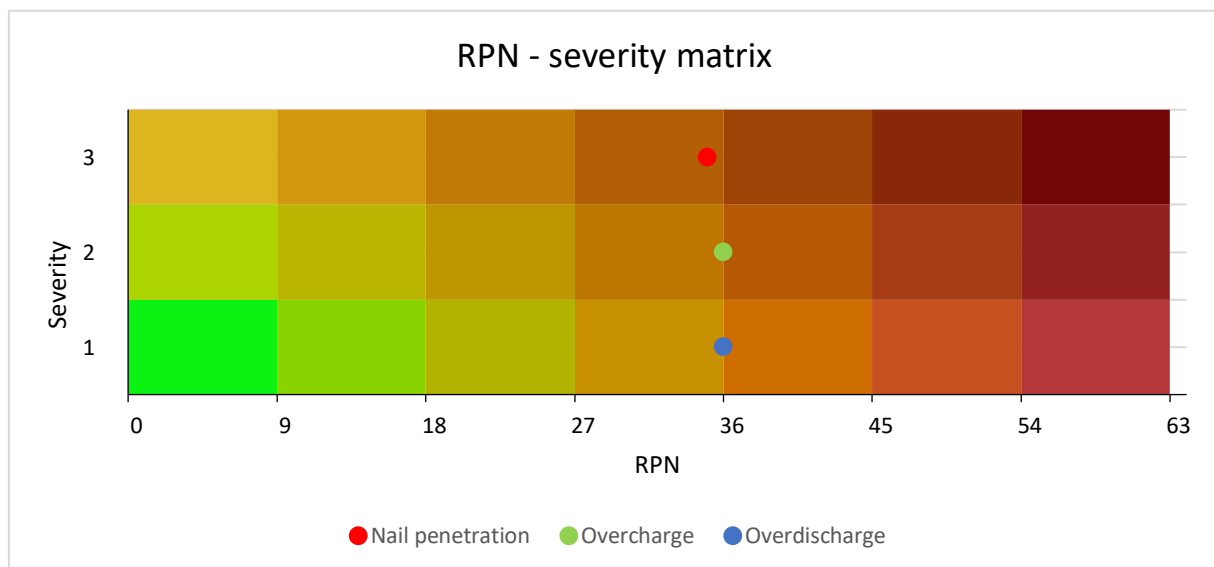


Figure 34: Over-discharge test RPN-severity matrix

Table 9: FMECA worksheet over-discharge test

Battery component (Items)	Potential failure mode(s)	Observed effect	Potential failure cause	Likelihood of occurrence	Severity of occurrence	Ease of detection	RPN
Anode (Active material)	Decomposition of SEI ³	Gas generation; heat development ³	Severe delithiation ¹	3	1	2	6
Anode (Current collector)	Dissolution of copper; oxidation ³	Reduction of current density; increased resistance; short circuit ³	Increased anode potential ¹	3	1	2	6
Cathode (Active material)	Copper plating; lithium plating; dendrite growth ¹	Without shutdown separator, dendrites lead to separator puncturing ¹	Prolonged lithium intercalation; copper plating ²	3	1	2	6
Cathode (Current collector)	No failure	No effect	/	/	/	/	/
Separator	Shutdown of separator ²	Current drop ⁵	High internal temperature ⁵	3	1	2	6
Electrolyte	Copper dissolution into solvent; reaction with SEI ⁴	Dendrite growth; gas generation ²	Increased anode potential ¹	3	1	2	6
Casing	Bloating of cell ⁵	Opening of vent ports ⁵	Gas built-up ⁵	3	1	2	6
RPN result							36

¹ Ouyang et al., 2018, 33418 ² Guo et al., 2016, 3 ³ Bubbico et al., 2018, 77ff. ⁴ Abaza, 2017, 68 ⁵ Hendricks et al., 2015, 115ff.

3.4 Safe storage

With the FMECA concluded, this chapter provides guidelines for safe storage of lithium batteries. As the nail penetration test has shown, fierce chemical reactions are to be expected, if a cell is severely mechanically damaged. Even though the likeliness of occurrence of this test scenario is low, crush tests like dropping a cell onto a sharp object, have also shown severe heating rates and the occurrence of hard shorts and are more likely to occur. To avoid this outcome, scientists propagate storage at a SOC of 40 %. This reduces the stiffness of a cell due to fewer lithium-ions inserted in the anode. Its failure susceptibility and the outcome of a thermal runaway event are hence lessened (Buchmann, 2018, s.p.; Wang et al., 2020, 8).

Storage at a reduced SOC not only limits negative reactions in the case of failure but also reduces the effects of cell ageing. Even if not used, cells age due to internal chemical processes. This so-called calendric ageing causes internal impedance growth through SEI layer thickening and reduces the cyclability of the cell. A higher SOC means a lower anode potential. This leads to anode oxidation, on the one hand, and an ongoing electrolyte reduction, on the other, thickening the SEI layer and consuming cyclable lithium thereby. However, elevated temperature causes SEI layer degradation, which again consumes otherwise cyclable lithium through its reconstruction (Keil et al., 2016, 1872).

For that reason and displayed in Table 10, storage at 25 °C or below is advised. This way, cells can stay in an acceptable voltage range with minimal impedance growth for several years. Nevertheless, storage at a too low SOC is also to be avoided. As discussed before, this can lead to the corrosion of the copper current collector, which leads to dendrite growth and finally shorting upon recharging (Mikolajczak et al., 2011, 73).

Table 10: Permanent capacity loss after storage at different temperatures and SOC's (Buchmann, 2018, s.p.)

Temperature	40 % SOC	100 % SOC
0 °C	2 % (after 1 year)	6 % (after 1 year)
25 °C	4 % (after 1 year)	20 % (after 1 year)
40 °C	15 % (after 1 year)	35 % (after 1 year)
60 °C	25 % (after 1 year)	40 % (after 3 months)

Crush damage might not only happen as a result of dropping but also, and more likely, through objects being dropped onto a cell. Consequently, to eliminate the possibility of damage, the cells should be stored in a solid container. A nonconductive container also prohibits shorting of

the cell. Moreover, if several cells are stored in one container, shielding of the electrodes, as discussed in Chapter 2.3.2, is recommended, since their free movement within the container might connect them in series and lead to shorting.

Last but not least, padding the storage case with sand, or another chemically inert cushioning material prohibits heat transfer between single cells, which is especially a matter of concern if broken cells are stored with new ones. Delayed reactions of these cells might otherwise transmit their heat to healthy ones causing them to take damage (Thomas et al., 2012, 245f.; Hamel, 2020, s.p.).

With this chapter concluded, the results of this work are presented and shall be summarized once more in the following. By conducting an FMECA, several things could be shown. The nail penetration test demonstrated the force of reaction one has to face in a worst-case scenario. Overcharging and over-discharging findings on the other hand, speak for the reliability of built-in safety mechanisms. During both test settings, venting was the only severer cell reaction the team had to encounter. In any case and as written before, longer periods of, especially overcharge, can still lead to more severe reactions, which is why they should be prevented.

Moreover, conducting this FMECA revealed the good pacifying features of silicone oil. Through heat dissipation, cells were not only able to withstand longer periods of overstress situations but the shielding from oxygen also greatly diminished the fierceness of caused exothermic reactions. Answering the research question stated in the beginning, the hazard potential of lithium batteries can be reduced drastically by submerging them in liquid silicone.

In order to be able to detect and neutralize a dangerous situation before it even fully develops, the thermal bath should be equipped with a temperature sensor. This sensor can act as a backup indicator of cell overstress situations, since the voltage level of each cell is monitored during University testing, which can be seen as the more reliable indicator. In addition, a continuous stirring of the silicone helps to prolong the time a cell can endure such a situation, should it still evolve. After use, cells must be stored with their electrodes shielded, at a SOC of 40 % and a temperature of 25 °C or below. The container used for storage must be nonconductive and filled with sand, or comparable material to avoid heat transmission between cells. Following all recommendations proposed in this work creates not only a safer work environment but also ensures long usability of the tested cells.

4. Conclusion

The work at hand gives a comprehensive insight into the working principle and possible dangers of lithium-ion batteries, as well as their countermeasures. The conducted FMECA not only presented a detailed description of failure modalities during common overstress situations like overcharge and over-discharge but also during a worst-case scenario, namely nail penetration. With the submergence of the cells in liquid silicone, a new and proper way to prolong the time till cell breakdown and reduce the partly severe outcomes of it was demonstrated. The good heat dissipation properties of the oil and the absence of oxygen are hereby identified as relevant.

The findings can help scientists doing research on lithium-ion batteries worldwide to create a safer work environment and prevent battery caused fires. Still, the most crucial factor in avoiding accidents is solid knowledge about the dangers of lithium-ion batteries and the compliance to existing safety rules. With the expertise gained here about the basic working principle of this technology, as well as sources of danger, the work provides a good foundation, which can also help to prevent accidents at home.

A task of future works could be cell stress tests with stirred silicone oil, the extending of the over(dis-)charge period after separator breakdown, and stress testing batteries with different cell chemistry.

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