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State of charge and heat impact on Li-ion batteries during calendar aging

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State of charge och värmepåverkan hos Litiumjon-batterier under kalenderåldring

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Populärvetenskaplig sammanfattning

Uppladdningsbara batterier som driver vår vardagselektronik går igenom sin livstid med otaliga laddnings-/urladdningscykler, efter några år kommer kapaciteten att minska märkbart. Men batterier som istället används i ett reservkraftssystem där anslutning till elnätet inte är möjligt kanske bara utför en handfull cykler, skulle det betyda att de håller för evigt?

På uppdrag av Getinge AB riktar sig denna kandidatuppsats till att utforska detta ämne som benämns kalenderåldring. Fokus har dels varit på om en ändring av den laddning som batterierna innehar under tiden, det vill säga State of charge, skulle påverka deras livslängd och dels på hur en ökad värme i miljön som batterierna var i skulle påskynda åldrandet. Studien är gjord genom omfattande litteraturforskning och ett experimentellt test. På så sätt kan testresultaten som framtagits under begränsad tid jämföras med andra studier inom detta ämnesområde.

Testet gick ut på att undersöka 12 stycken NMC Li-ion batterier laddade till 3 olika nivåer av State of charge, 90 %, 95 % och 100 %, där 2 batterier från varje State of charge-nivå var i en kontrollerad uppvärmd miljö och de andra 2 placerades i rumstemperatur. Testet pågick under 8 veckors tid och varannan vecka utfördes mätningar och dataloggning på batterierna, vid behov laddades även batterierna till ursprunglig spänningsnivå. All data dokumenterades i Excel för vidare analys.

Resultatet var inte tillräckligt för att dra några slutsatser. Däremot visade det tendenser som överensstämmer med litteratur som studerades under projektets gång. Testmetoden i detta projekt visade sig lämplig att fortsätta med för studie av batteriers kalenderåldring.

Framtida arbete rekommenderas att fortsätta för vidare styrka resultat. Även en uppgradering av testutrustningen kan vara värt att övervägas.

Abstract

Rechargeable batteries that are powering our everyday electronics go through their lifetime with countless charge/discharge cycles, after a few years the capacity has dropped noticeably. But how about batteries that are working as a back-up power system for when connection to the AC mains is not possible, they might only perform a handful of cycles but does this mean they last forever?

On behalf of Getinge AB, this bachelor thesis aims to explore the subject named as 'calendar aging'. Focus of the project has been mainly the impact of charging capacity, State of charge, on battery life for calendar aging and secondly the impact of heat on battery. Elevated environmental temperature during calendar aging test would imply acceleration in battery aging. The study is made with partly literature study and partly experimental testing on batteries during relatively limited time, though the results could be benchmarked with likely studies by others.

The test was to investigate 12 units of NMC Li-ion batteries charged to 3 different levels of State of charge, 90 %, 95 % and 100 %, where 2 from each State of charge level were in a controlled heated environment and the other 2 were at room temperature. The test was in progress for 8 weeks and every two weeks measurement and data logging were collected and, if required, the batteries were recharged to origin voltage level. All data was documented in and analyzed in Excel.

The results acquired were not significant enough to draw any conclusions but did show some tendency as would be expected from the literature studied during the time of the project. Future work is recommended to continue the test in this project to acquire more useful results. Further improvements in testing equipment should also be considered.

Acknowledgement

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Terminology

BMS - Battery management system

C-rate - The discharge and charge rate of the battery. A battery with capacity of 5 Ah should provide a current of 5 A for 60 minutes at the rate 1 C and a current of 10 A for 30 minutes at the rate 2 C and so on.

DMM - Digital multimeter

DoD - Depth of discharge

$\mathbf{R_{INT}}$ **-** Internal resistance, the internal resistance a battery experiences when delivering current

Li-ion - Lithium ion

NMC - Li-ion cells with Nickel Manganese Cobalt chemistry

PnP tool - Plug-n-Play, a computer software that is used to communicate with the BMS of the battery

RS232 - Is a ANSI-standard serial bus connection, in this case it is used to communicate between computer and devices

SEI - Solid Electrolyte Interface

SoC - State of charge

SoH - State of health

Contents

1 Introduction

1.1 Background

Getinge AB (mentioned as Getinge) is a medical technology concern with a subsidiary company, Maquet Critical Care AB (later mentioned as Maquet), that develops and manufactures ventilators. A ventilator is connected to AC mains via a power supply and 2 lithium ion (Li-ion) batteries as a back-up solution, for the time when the AC mains is not available. Therefore the batteries are not cycled as often as batteries in many other applications where the batteries are cycled frequently, a mobile phone as an example. When the batteries are not in use they will be charged at nearly 100 % capacity, the reason is to be able to deliver as much power as possible when needed. This gives a different aspect to the aging of the batteries since the major part of the aging process happens through charge/discharge when heat is generated during electron transportation inside the battery cell. This aging mechanism is defined as 'calendar aging' and has been a topic of many studies [1, 9, 16].

Serving as a back-up energy system, Getinge emphasizes the importance to precise the life expectancy in both environmental friendly aspects and customer satisfactions. The question of what the Li-ion life expectancy will be with constant standby charging for the majority of the run time is a reliability issue that needs to be taken care of.

This report is a study to approach the calendar aging topic on the behalf of Getinge, aiming at better understanding of such aging mechanisms and improving battery life expectancy for medical equipment.

1.2 Purpose and goals

The purpose of this study is to analyze health degradation and capacity losses on Li-ion batteries experiencing calendar aging, with an accelerated test through a heated environment. Another part of this study is to investigate how batteries with different State of charge (SoC) levels will be affected during calendar aging.

The goal of this project is to study capacity loss depending on heat and SoC, to explore publications in this subject, and to establish a test method that could be used for further investigations.

1.3 Limitations

There were some limitations for this study, the timeframe of the testing and the use of testing equipment. The timeframe of this thesis was only 10 weeks which is quite short for this type of investigation. The testing equipment used was a test station already accessible at Getinge, since the time was limited it was not prioritized to procure and create a testing station suitable for the project.

1.4 Responsibilities defined

The study has been divided into two key subjects, how heat will affect the aging of Li-ion batteries and how different SoC will affect the aging of Li-ion batteries. Martin has looked at how the SoC on a battery will affect the aging and is the main author of sections 2.2, 2.4.1 and 5.1. Tobias was in charge of how heat is affecting batteries and is the main author of sections 2.4.2, 2.4.3, 2.4.4 and 5.2. Study results and joint sections have been discussed and written by both together.

2 Theory

Presented in this chapter are some basic concepts and more detailed information about Li-ion batteries and the aging mechanisms incident to State of charge and stress occurring from heat, for an insight to the method on section 3.

2.1 Li-ion battery

A Li-ion battery cell is constructed with four main components: anode, cathode, separator and electrolyte. The anode and cathode can be described as having two metal strips rolled around each other. Between the two metal strips there is an electrolyte coating and a separator. The electrolyte is a gel or liquid that is electrically conductive and the separator is a non conductive material that lets only the Li-ions pass from the anode to the cathode [2].

When a battery cell is charging or discharging there are two types of reactions, an internal reaction and an external reaction. The internal reaction is the move of Li-ions between anode and cathode. During charging the Li-ions are passing through the separator from the cathode side to the anode side, and for the discharge the Li-ions instead goes from the anode side to the cathode side. The external reaction is that the electrons are moving the opposite direction from the Li-ions between the anode and cathode through a load connected to the cell, this creates a current in the circuit. Figure 1 is a simplified illustration of a battery cell that does not include any external load but where the anode, cathode, separator and electrolyte are shown [2].
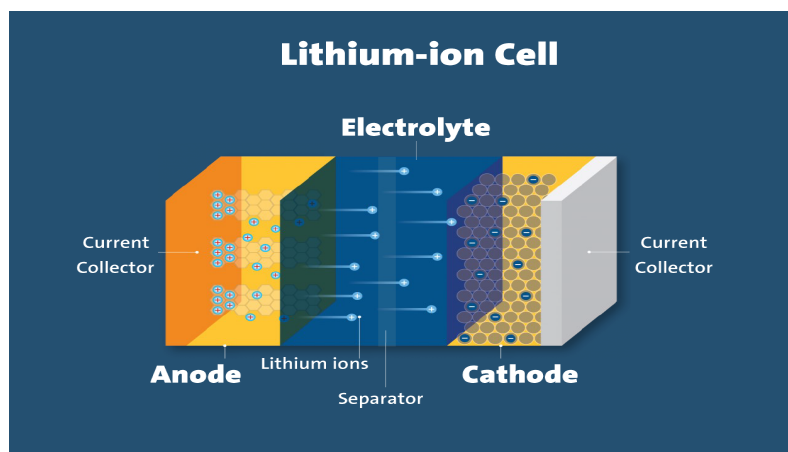

Figure 1. Battery cell model [2].

2.2 SoC - State of charge

SoC is a way to describe the actual energy level of a battery in relation to its measured maximum capacity. As an example shown in Figure 2, SoC is what describes how much energy is left in a phone in percentage. SoC usually is determined by the battery

management system (BMS) which is integrated in a battery pack, see further details in section 2.4. An important aspect is that 0 % SoC is not related to 0 V since the minimum voltage within Li-ion battery cells is generally between 2-3 V [3]. Given this the whole scale for SoC is then depending on the difference from lowest voltage possible to highest voltage possible.

Figure 2. Illustration of SoC on a mobile phone [4].

2.3 BMS - Battery management system

BMS is the control unit of a battery pack and there are many different stages of complexity available. Most advanced BMS have been designed for sampling individual cell voltages, and current, predicting SoC and measuring temperature. Some BMS have capabilities such as balancing the voltage between different cells to make sure none of the cells are overcharged or over discharged. Another important function of a BMS is to reduce risk of failures such as turning off the power output when the cell temperatures are too high or when the current drawn is too high for one cell capacity. Noteworthy is that it can not eliminate all risks of failures so there is no guarantee for safety [5].

2.4 Battery aging

Battery aging is related to the remaining capacity a battery cell can store and the performance of a cell. The rate a battery cell ages could be affected by many factors such as calendar storage, depth of discharge (DoD), SoC, number of cycles, and environmental as well as cell temperatures. Battery cells that experience cycle aging are considered to have mechanical strain on the lithium plating while cells that experience calendar aging may mostly be affected by formation of solid electrolyte interface (SEI) and electrolyte oxidation.

On the anode side there is a small gap towards the electrolyte. In that gap a thin SEI-layer can form due to the move of ions. The growth of SEI-layers will affect the movement of

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ions during charging and discharging, some ions will stick to the already existing layer and not be able to pass through. This will result in loss of cycling ions and thus capacity fading, less C-rate capabilities, and self-discharge [6].

Similar to the SEI-formation, electrolyte oxidation instead occurs on the cathode side. During electrolyte oxidation a layer is created that will consume cyclable Lithium ions which cause capacity losses and some self-discharge. This occurs mostly on high cell voltages [6].

2.4.1   State of charge impact

A Li-ion battery cell could have 100 % SoC at 4.2 V level in general. This is dependent on the chemical mix of a cell at its cathode and anode and also for each individual cell due to electrode balancing during manufacturing [8]. According to a site called "Battery University", Li-ion battery cells being charged to 4.2 V can deliver about 300-500 full discharge cycles through their lifetime [7]. By reducing the charging voltage to 4.1 V, the same battery cells could double the estimated number of full discharge cycles deliverable. This indicates that the stress on the cells, due to high voltage storage, is harmful for the lifetime of the cells. However it is not really the high SoC that is the main reason for this.

The level of SoC within a Li-ion battery cell during calendar storage has been proved to only play a minor role on the capacity loss, at least for accelerated tests where the temperature was elevated as test conditions. Referring to the report written by Peter Keil et al. [6], a large study has been done on a wide range of SoC levels for three different Li-ion battery types. It could be observed that capacity degradation does not follow proportionally with the SoC, but instead plateau regions covering SoC intervals of more than 20-30 % of the cell capacity the capacity fades are similar. Looking into Figure 3a-3c, these plateaus are showing nearby SoC levels have somewhat the same capacity fade after 10 month storage in the same environment, at low SoC the degradation rate is more linear. It was also concluded that no simple approximation could be made for the relationship between storage SoC and capacity loss without considerable deviation of the SoC. Interesting is, shown in Figure 3a-3c, that around 60-70 % SoC level there is a noticeable bigger degradation in capacity fade between two plateaus for all types of cells during their 10 month storage test.

Comparing capacity fade to the internal resistance it showed no direct correlation (see Figure 3a and Figure 3d), medium SoC level shows a constant internal resistance where the capacity has two different plateaus. Low anode voltage potential on the other hand, is connected in a more obvious way. Shown in Figure 4a-4f, it is visual that when the capacity fade hits a new plateau the anode potential does the same. More specific comparison for Figure 4b and 4e, at ~60 % SoC it is noticeable this occurs. When the potential in the anode reduces, the loss of cyclable lithium ions accelerates, electrolyte reduction aggravates and SEI growth promotes.
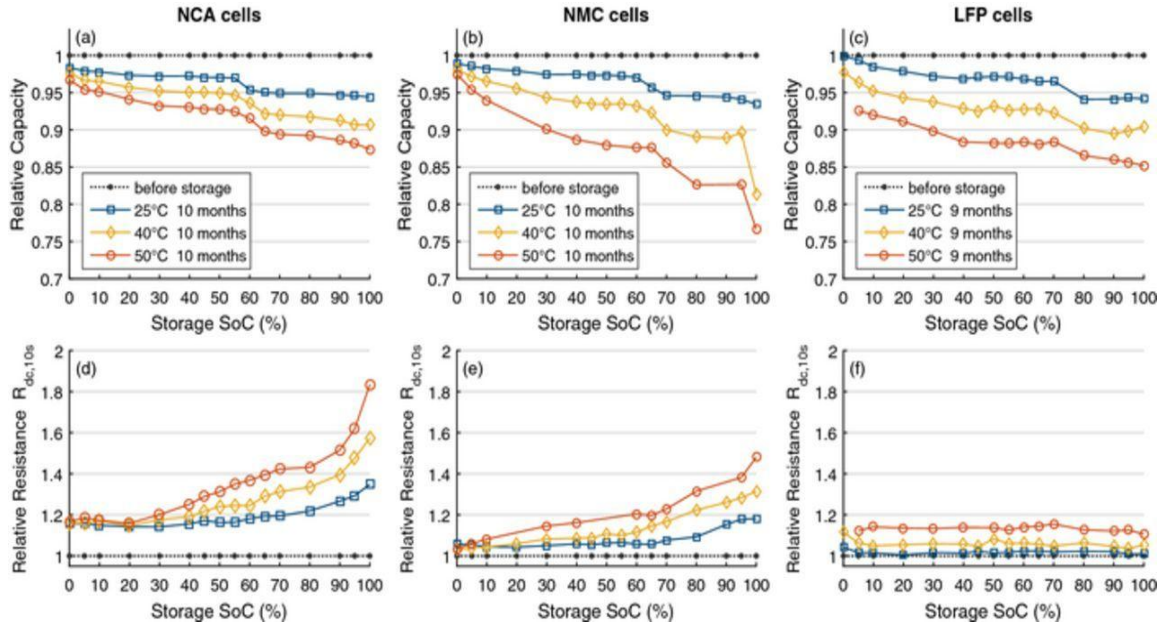
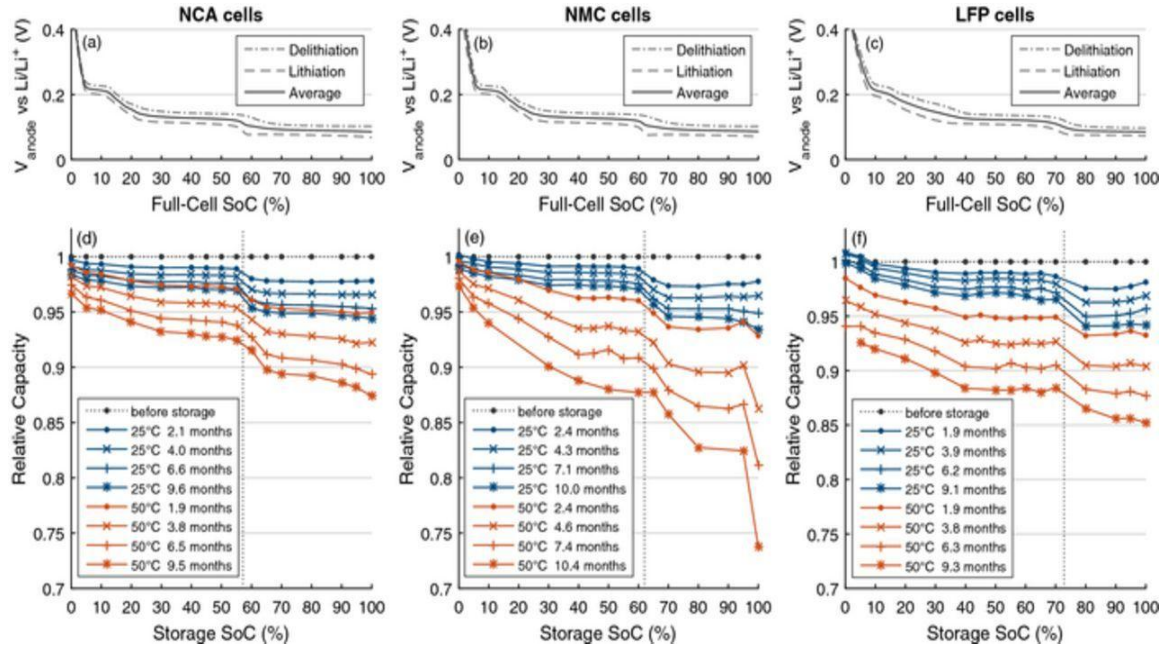*Figure 3. Capacity fade and internal resistance vs SoC [6].*

Figure 4. Anode potential and capacity fade vs SoC [6].

Looking into electrolyte oxidation, which is a cathodic side reaction, there are some split opinions on its impact to capacity loss. Professor Jeff Dahn and his team at Dalhousie University in Halifax emphasized that a voltage level above 4.10 V/cell , which is roughly around 90 % SoC for a Li-ion cell with 4.2 V maximum voltage, at elevated temperature can be more harmful than cycling a cell. The longer the battery cell stays in a high voltage, the faster the capacity degradation occurs [7, 9]. Björn Rumberg and his colleagues on the other hand found that electrolyte oxidation is compensating some of the capacity loss that comes from SEI-layers as it is adding Li-ions to the cathode side, this would reduce cathode potential [10]. According to the report, the biggest capacity fade occurs at around 70 % SoC due to the maximum loss of mobile Li-ions, which also causes the anode potential to drop to its lowest plateau as mentioned earlier in this section.

2.4.2   Temperature degradation

A major factor in battery degradation is heat, especially when batteries experience a stressful temperature which is considered anything above 30 ℃ [11]. Batteries that are stored in higher temperature will experience an increased thermal decomposition on the electrolyte, anode and cathode. This will result in a loss of capacity and performance. If the temperature is too high the separating layer between anode and cathode will fail and the battery will have an internal short circuit. This is also called thermal runaway which is something no one wants to experience [11].

2.4.3   Batteries in lower temperatures

Batteries that are experiencing lower temperature for example -18 ℃ will only be able to deliver 50 % of their capacity compared to the same batteries when used at 27 ℃ [11]. An even more extreme scenario is that batteries that are used in -40 ℃ will lose 98.75 % of its output power and 95 % of its capacity compared to using it at 25 ℃. The reason why this is happening is that the chemistry changes a lot when being at -40 ℃ [11]. The electrolyte gets more viscosity and the ions conductivity drops, so the internal resistance (R_{INT}) increases. When R_{INT} increases the battery will have higher internal losses that can be described with ohm's law in equation 1 [17].

$$I^2 * R = P \tag{1}$$

Using batteries in the cold will not contribute to any permanent capacity loss as long as the current drawn is low [13].
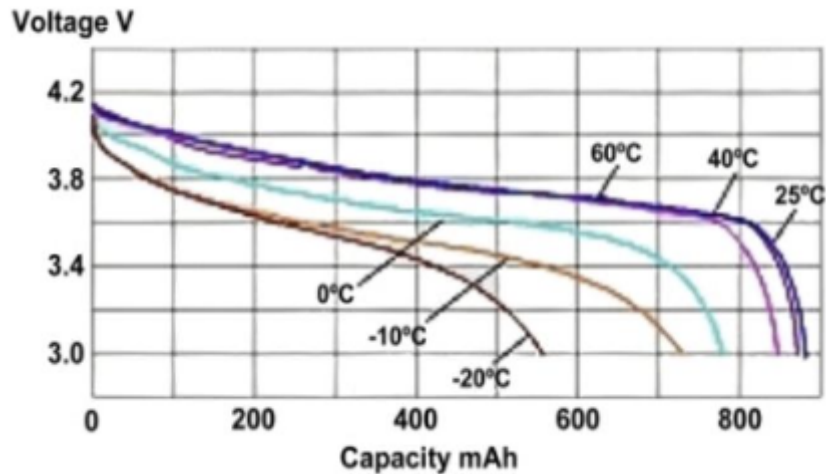
Figure 5. Voltage vs capacity in different temperatures [13].

2.4.4   Batteries in higher temperatures

Batteries used or stored in higher temperatures will experience permanent losses in both capacity and power output. For example, batteries that are stored at temperatures such as 60 ℃ will have a higher degradation factor compared to batteries stored at temperatures at 20 ℃. This effect is mostly seen as a thermal decomposition on the electrolyte, anode and cathode [14].

In Table 1 a prediction is made that batteries will only retain 85 % of the capacity after a year stored at 40% SOC and 40 ℃. If the temperature in that environment would be further increased 20 ℃, the capacity losses would be another 10 %.

Table 1. Battery aging, how different temperature and SoC affect the SoH [13].

Temperature	40% charge	100% charge
0 ℃	98% (after 1 year)	94% (after 1 year)
25 ℃	96% (after 1 year)	80% (after 1 year)
40 ℃	85% (after 1 year)	65% (after 1 year)
60 ℃	75% (after 1 year)	60% (after 3 months)

The effect of thermal decomposition on the electrolyte layer will result in a growth of the SEI-layer. The SEI-layer is a side effect that comes from the gas that is created during aging and accelerated by thermal decomposition. The resistance created in the SEI-layer is described as R_{SEI}. Batteries that are completely new will have some SEI resistance seen in Table 2, but for batteries that have been aged and have 90 % SoH there is an increase

of 60 % of R_{SEI}. The Growth on the SEI-layer will lead to self-discharge, lower performance and eventually malfunction due to the SEI resistance being too high [14].

Table 2. Table of how the internal resistance changes with different SoH [15].

SOH (%)	R_{SEI} (mΩ)
100	17.1
95	19.2
90	27.5

Looking at the anode and cathode under a microscope the degradation can be clearly visible. In Figure 6 (A) and (B) shows the anode, (C) and (D) shows the cathode. Image (A) and (C) show a fresh new battery, (B) and (D) show a degraded battery that has changed both color and finish. On image (B) the anode looks to be uneven and has a rough surface causing increased R_{INT} and capacity losses. Image (D) has a major color change and has a more diffuse finish.

Figure 6. Pictures of Anode and Cathode under microscope [14].

3 Method

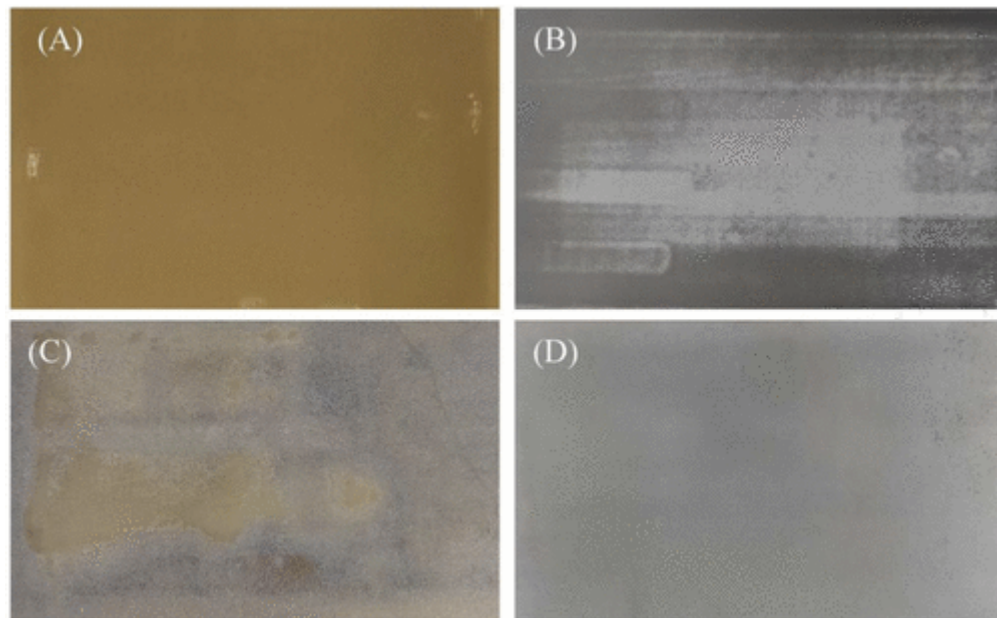This chapter describes the experimental test on battery aging that was performed.

3.1 Test specification (description)

The purpose of the test is to study calendar aging of Li-ion batteries with different SoC levels and at different temperatures. Twelve NMC units of Li-ion batteries have been charged with three different SoC levels and stored in two different environments. The batteries contain 4 cells each with a maximum voltage at 4.15 V, the cells are limited to 4.15 V/cell instead of 4.2 V/cell as requested by Getinge. The three SoC levels are 90 %, 95 % and 100 % and were determined from information provided by Getinge's supplier Accutronics (Appendix A3). These SoC levels were considered by Getinge as the levels most interesting, in respect for high capacity for the ventilator applications. The voltage for each SoC level was given tolerance intervals for the limitation thus the charging and discharging process were controlled manually. 16.35-16.40 V for 90 % SoC, 16.45-16.50 V for 95 % SoC and 16.55-16.60 V for 100 % SoC. Two batteries from each SoC level were placed at room temperature in the testing area and two in a heated chamber and left untouched for the duration of the storage, except when data was collected (see section 3.5). To simulate as if the batteries were plugged into a ventilator and connected to the AC main, the batteries were charged up to correct voltage intervals if the SoC had dropped 5 % just as the BMS is programmed to operate. The criteria of charging voltage was also determined from the same information by Accutronics, i.e 16.28 V for batteries at 90 % SoC, 16.39 V for 95 % SoC and 16.46 V for 100 % SoC.

3.2 Test station

All the tests were performed in a dedicated laboratory at the Getinge office in Stockholm. There are four test stations with the capacity to cycle four batteries each. There are also four computers to monitor and log data from the batteries during cycling. The test stations are designed to use a similar battery charger and load of a ventilator developed by Getinge. A view of the test stations can be found in appendix A4.

3.3 Test environment

During this study the batteries were placed in two different environments, half of the batteries were placed in room temperature around 23 ℃ and the other half in a heat chamber set to a constant of 50 ℃. The chamber temperature was set to 50 ℃ due to that being the maximum value available at the time. Figure 7a and 7b demonstrates how the batteries were placed in each environment in the lab.
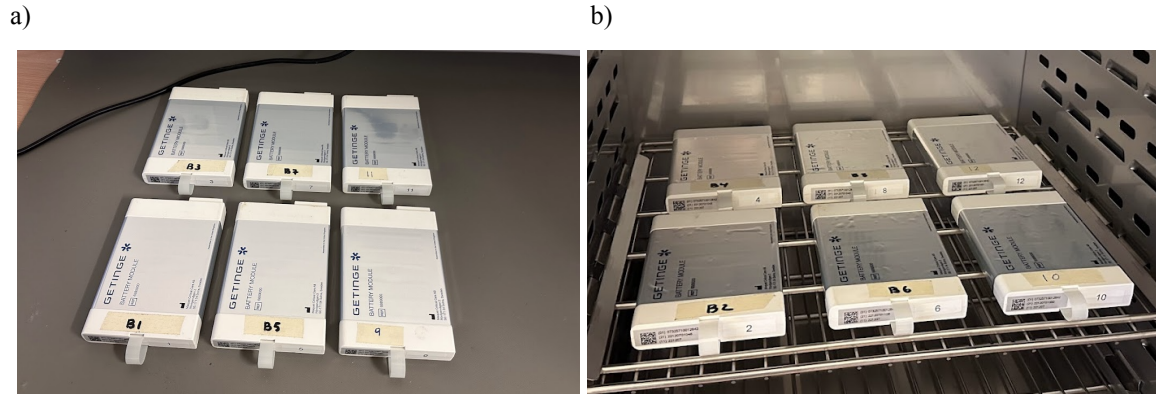
Figure 7. a) Batteries placed in room temperature vs b) batteries placed in heat chamber at 50 ℃.

3.4   Hardware equipment

For this study the hardware used includes a heat chamber, digital multimeter (DMM) and thermocouple. The heat chamber was set to 50 ℃ as storage temperature and had enough volume to contain all batteries. Two Fluke 289 DMM calibrated at different dates was used to measure and verify that the values were correct. The thermocouple accessory was used with the help of the DMM to get a reading of the temperature in the room.

To charge and discharge the batteries, a station Getinge had developed inhouse with custom parts was used. A self-written handbook is available on site that specifies how the station works.

More about the equipment and their specifications can be found in the appendix A1.

3.5   Data collecting

Two methods were used to collect data, "Analog Logging" by using a calibrated DMM and "Digital Logging" by using a computer and communicating with the BMS of the batteries. The test first started with a full cycling of all batteries to get initial values on the capacity. Every two weeks, the batteries were removed from the heated chamber and placed under a fan to cool down. After around 30 minutes all batteries got logged both via the DMM and PnP tool. After all data was collected, the batteries were put back in their respective testing/storage environment. As a final checkup to end the test for this thesis work, all batteries were fully cycled once more to update the BMS of the batteries and to find out if there has been any capacity loss.

3.5.1   Analog Logging

The DMM used for the analog logging is a Fluke 289 DMM that has been certified calibrated. To measure the voltage of the battery, two small probes are used that will fit in the connector pin position 1 and 6 which are the positive output and negative output of the battery, respectively.

3.5.2 Digital Logging

The PnP tool used for digital logging communicates with the BMS in the battery via USB to RS232 cable. The PnP is capable of reading almost all parameters from the BMS such as SoC, cell voltage, capacity etc. When a battery was connected in a charging port of one of the test stations, the logging parameters were to default in the PnP tool program and the log interval to 1 s. A new log file was created for each of the batteries every logging and the logging lasted for about 10 s. The logging contains a small data dump in CSV format.

3.6 Usage of the data

The data gathered from the logging is documented in Excel. In Excel the data was divided into separate spreadsheets for different types of logging being used. One of the spreadsheets was named DMM measurement and belongs to the data from the analog logging. Other spreadsheets include, Logging by PnP (after recharge) and Logging by PnP (real value) from digital logging. Through the PnP tool a large amount of battery data can be gathered, though the chosen data that matters the most were Voltage, Current, Relative SoC, Remaining capacity, Absolute SoC, Full charge capacity, Max error, Cycle count and Temperature.

4 Results

Results from our data collection and compilation are presented via graphs and Tables and further discussed in chapter 5, including data mostly relevant to capacity degradation. A complete presentation of all data logged is available in the appendix A2.

Table 3. Full charge capacity from the BMS at start (2023-03-31) and end (2023-05-22) of test and change of the capacity for each cell.

| Full charge capacity [mWh]					
Battery	Environment	SoC [%]	Start	End	Change
1	Room	90	90350	91670	1320
2	Chamber	90	89360	90690	1330
3	Room	90	87680	89460	1780
4	Chamber	90	86340	88810	2470
5	Room	95	91850	91960	110
6	Chamber	95	92000	93000	1000
7	Room	95	92530	91900	-630
8	Chamber	95	90360	90720	360
9	Room	100	90130	90290	160
10	Chamber	100	91200	90670	-530
11	Room	100	90870	90400	-470
12	Chamber	100	90060	88910	-1150
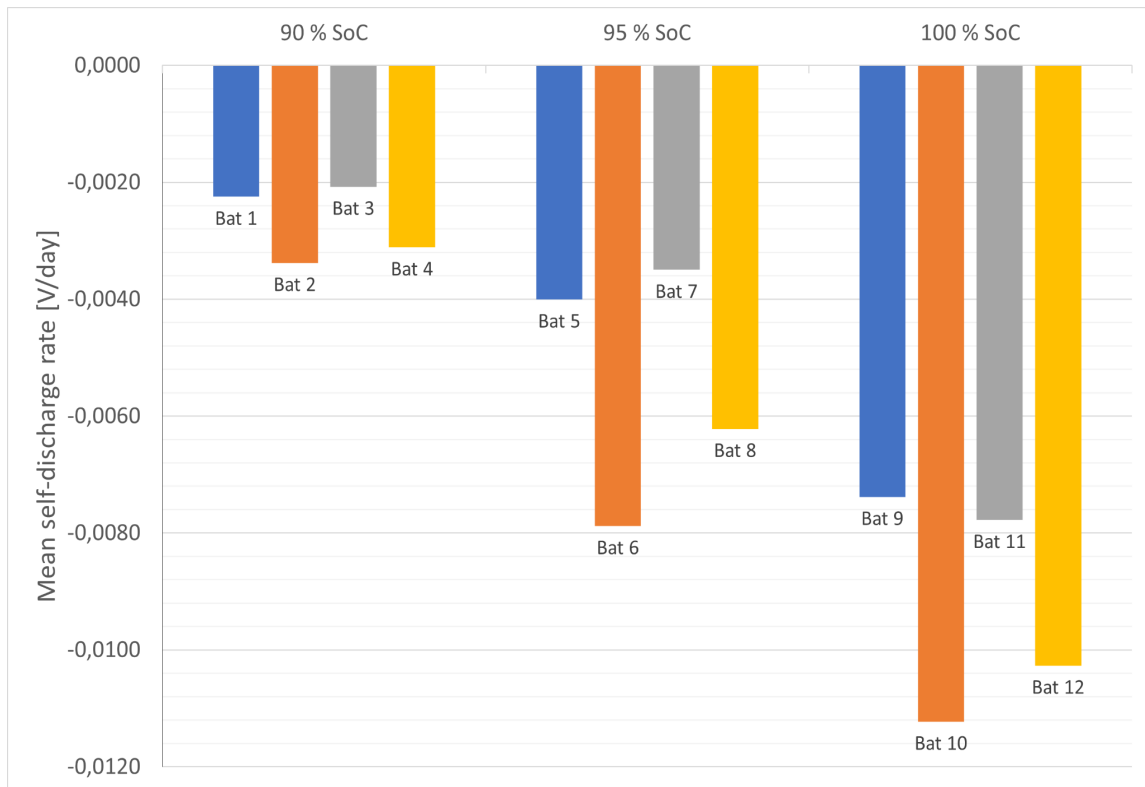
Figure 8. Mean self-discharge rate for all batteries during the test, even numbers are batteries in the heat chamber.
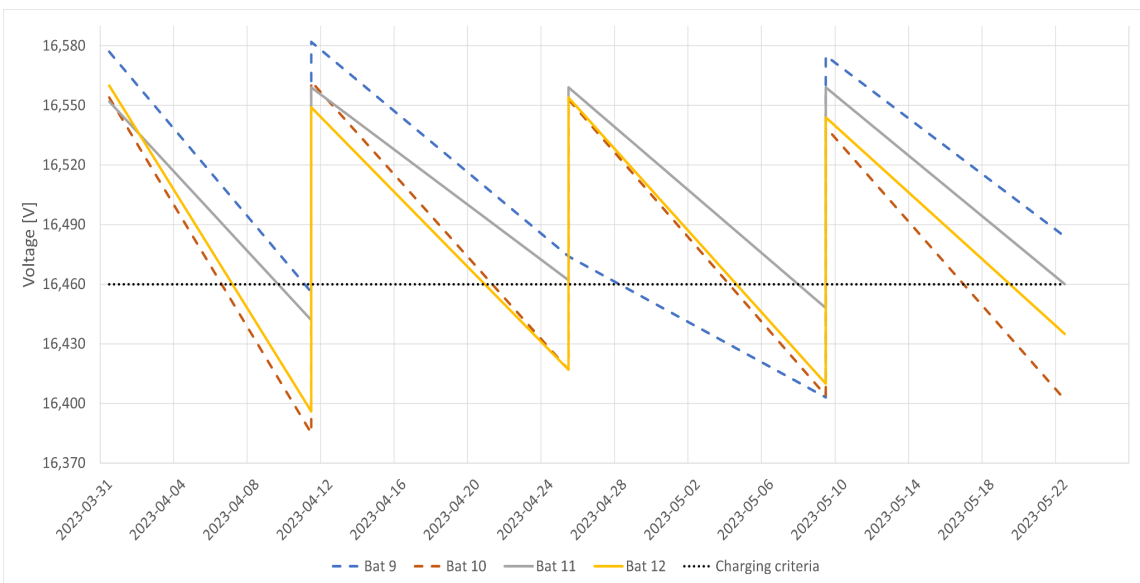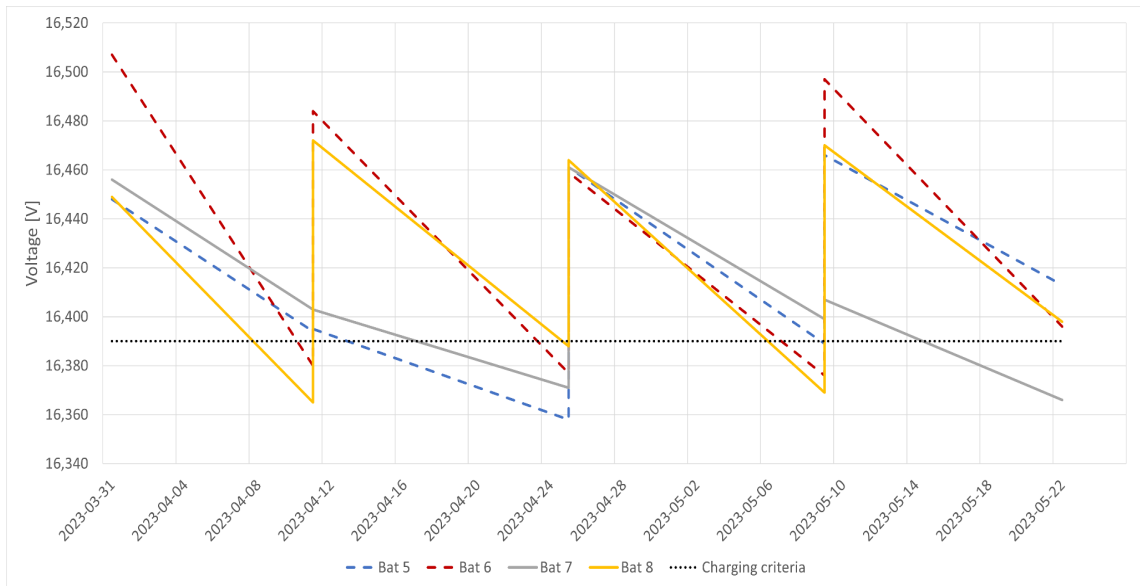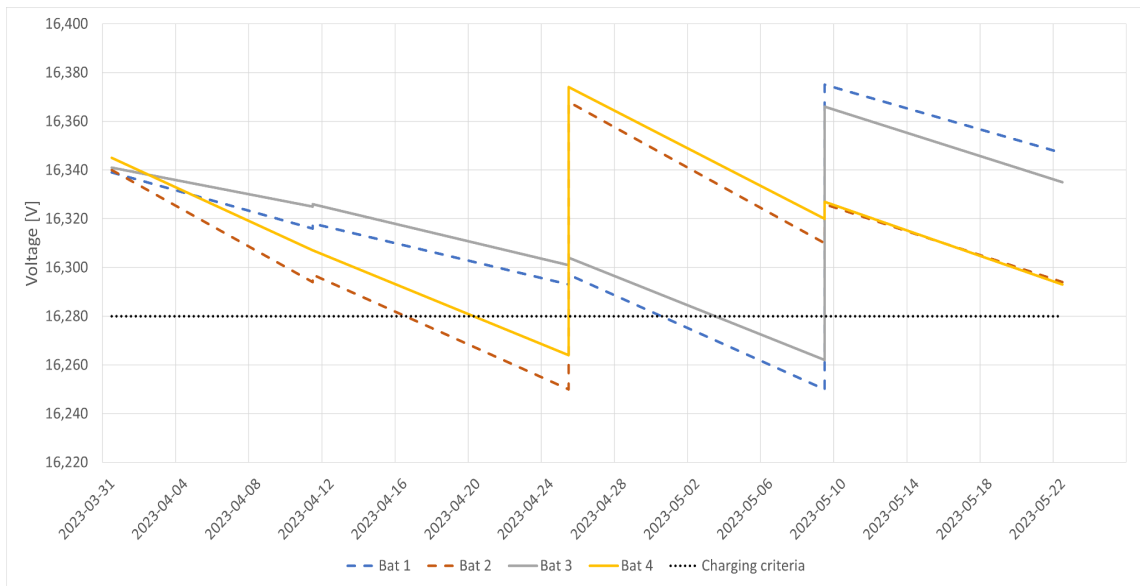
Figure 9, 10, 11. Behavior of the voltage for all batteries at each SoC level, even numbers are batteries in the heat chamber.

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5 Discussion

5.1 Battery capacity

Reviewing the full charge capacity data in Table 3 reveals that the data may not be fully reliable. Only 4 of 12 batteries showed a decrease in capacity as expected, while the others showed slight increase instead. Since the full charge capacity is predicted by BMS, it could be assumed that there has not been sufficient number of cycles for BMS to calculate a correct value at the start. When a battery is new from the factory the batteries have never subjected to any cycles, which was the condition for all battery units under test in this project. Another reason could be that the BMS correctly cannot make predictions due to historical data of SoC in a battery it had been stored at before delivery. It is known that the correctness of SoC-prediction by BMS will improve with increased number of charging/discharging cycles of a battery which may explain part of the uncertainty of capacity data observed in this study.

5.2 State of charge

Shown in Figure 8, the self-discharge is increasing for higher SoC and even more so for the batteries having been inside the heat chamber. This points towards the increase of internal resistance the NMC batteries gain especially at 100 % SoC and indicates that the SEI formation rate may be higher at this point during the storage test. Although all three SoC levels for the batteries are at the high end and should expectably follow each other in degradation, the need for recharging at 100 % SoC is more intense than at 90 % SoC (see Figure 9 and 11). Since the capacity fade is not significant during the test, no sufficient data could be used to support any conclusions about this. The result has tendencies that are pointing to larger and longer studies about calendar aging, so continuing this study over a longer time period would preferably provide more reliable evidence.

5.3 Heat degradation

One thing that can be observed from the data in DMM measurement is the different amount of self-discharge. For example, comparing batteries No. 11 and 12 in Figure 11, the gradients of their discharge curve are quite different. Battery No. 12 has a steeper angle of discharge curves compared with that of battery No. 11. The steeper angle of the discharge curve indicates higher losses inside the battery package. The losses are the result of batteries experiencing heat degradation that will result in higher self-discharge, and thus agrees with the discussions in section 2.4.4.

With the help of the measurement data an average voltage drop per day can be calculated, batteries that were placed in the heated chamber lost an average of 7 mV per day and batteries placed in room temperature lost an average of 4 mV per day. This resulted in batteries inside the heated chamber having a 56 % higher self-discharge than batteries placed in room temperature. Theory connected to this was presented in section 2.4.2.

5.4 Future work

To gain further usable data on the capacity fade for this application, it is naturally recommended to extend the test for a longer period of time than what is allowed in the current project. Even though this study has not been long enough to draw any definitive conclusion, the tendency already points in a positive direction and makes further study for more data over time to be encouraged.

There were also plans to make some improvements to the testing equipment and test stations, for example the need of a capacity tester. Depending on the level of development the solution could consist of using a raspberry pi, voltage and current sensor or use an existing solution from Arbin or similar [21]. A setup like this would improve the capabilities on how to charge/discharge the batteries and log the data. The data and control of the charging/discharging cycle could for example be hosted on a web server on which anyone with the right access could configure and use.

The information about electrolyte oxidation studied and presented in this report might be contradictory, there was no way to conclude if the reaction was accelerating or decreasing the capacity degradation. Since the experimental test in this project investigated high end SoC levels, those levels that should activate the electrolyte oxidation, more studies are needed to pinpoint the effects of this reaction and give the results underlying facts.

6 Conclusions

In this thesis a study has been done on calendar aging of Li-ion batteries with focus on SoC and heat impact in standby life on the behalf of Getinge AB. The subject calendar aging has been investigated in many studies before. Studying the publications on this subject has helped in necessary understanding on the tests performed in this project.

A test has been performed for 8 weeks, which is a relatively short time for this type of investigation. Meanwhile a heated environment was used to accelerate the aging process. With a heated chamber it could be seen that batteries experience higher stress compared to the batteries stored at room temperature, which was expected from the research.

Even though the result was not sufficiently significant to support any conclusion due to the short time, it did show some clear tendency that agrees with the literature studies in the same subject. Therefore it is considered to be meaningful to continue this study further.

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Appendix

A1. Hardware equipment

Type	DMM
Name	Fluke 289 true rms
Brand	Fluke
Usage	Digital multimeter
Serial number	99170011
Calibrated until	jan.-24
Calibration ID	EV364968
Specification	
Resolution	1 mV
Tolerance	2.5% + 2 counts

Source: https://pdf1.alldatasheet.com/datasheet-pdf/view/1354332/FLUKE/FLUKE-289.html

Type	DMM
Name	Fluke 289 true rms
Brand	Fluke
Usage	Digital multimeter
Serial number	99170004
Calibrated until	dec.-23
Calibration ID	EV364976
Specification	
Resolution	1 mV
Tolerance	2.5% + 2 counts

Source: https://pdf1.alldatasheet.com/datasheet-pdf/view/1354332/FLUKE/FLUKE-289.html

Type	Heat chamber
Name	SLW 115 IG SMART
Brand	Smart4lab
Usage	Temperature

	regulation
Serial number	SW11220089
Specification	
Temperature range	20 - 300 °C
Fan option	Yes
Resolution	0.1 °C

Source: https://smart4lab.eu/smart-en/

Type	Thermocoupler
Name	Fluke 80BK-A
Brand	Fluke
Usage	Temperature measurement for the environment
Serial number	NaN
Specification	
Resolution	+/- 2.2 °C or 2%
Tolerance	-40 to 260 °C

Source: https://www.fluke.com/en-us/product/accessories/probes/fluke-80bk-a

Type	Charging station
Name	No name
Brand	Own made by Getinge AB
Usage	Charge and discharge the batteries
Serial number	
Specification	
Max charge current	3000 mA
Max discharge current	2500-3000 mA

A2. Acquired data

- **Analog measurements**

Acceptable voltage zone [V]		(16.350-16.400)	(16.350-16.400)	(16.350-16.400)	(16.350-16.400)
Voltage level for recharge [V]		16.280	16.280	16.280	16.280
		Room	Heat chamber	Room	Heat chamber
Date	**Time**	Battery 1	Battery 2	Battery 3	Battery 4
3/31/2023	kl 13.30	16,339	16,340	16,341	16,345
4/11/2023	kl 10.10	16,316	16,294	16,325	16,307
4/11/2023	Kl 10.20	16,320	16,295	16,324	16,306
4/11/2023	kl 12.20	16,318	16,297	16,326	16,307
4/25/2023	kl 09.20	16,293	16,250	16,301	16,264
4/25/2023	kl 13	16,297	16,368	16,304	16,374
5/9/2023	kl 10	16,250	16,310	16,262	16,320
5/9/2023	kl 14	16,375	16,326	16,366	16,327
5/22/2023	kl 09.30	16,347	16,294	16,335	16,293

Acceptable voltage zone [V]		(16.450-16.500)	(16.450-16.500)	(16.450-16.500)	(16.450-16.500)
Voltage level for recharge [V]		16.390	16.390	16.390	16.390
		Room	Heat chamber	Room	Heat chamber
Date	**Time**	Battery 5	Battery 6	Battery 7	Battery 8
3/31/2023	kl 13.30	16,448	16,507	16,456	16,449
4/11/2023	kl 10.10	16,394	16,380	16,403	16,365
4/11/2023	Kl 10.20	16,394	16,381	16,402	16,354
4/11/2023	kl 12.20	16,395	16,484	16,403	16,472
4/25/2023	kl 09.20	16,358	16,377	16,371	16,388
4/25/2023	kl 13	16,461	16,459	16,461	16,464
5/9/2023	kl 10	16,389	16,376	16,399	16,369
5/9/2023	kl 14	16,466	16,497	16,407	16,470
5/22/2023	kl 09.30	16,413	16,396	16,366	16,398

Acceptable voltage zone [V]		(16.550-16.600)	(16.550-16.600)	(16.550-16.600)	(16.550-16.600)
Voltage level for recharge [V]		16.460	16.460	16.460	16.460
		Room	Heat chamber	Room	Heat chamber
Date	Time	Battery 9	Battery 10	Battery 11	Battery 12
3/31/2023	kl 13.30	16,577	16,554	16,552	16,560
4/11/2023	kl 10.10	16,456	16,385	16,442	16,396
4/11/2023	Kl 10.20	16,457	16,386	16,443	16,395
4/11/2023	kl 12.20	16,582	16,562	16,559	16,549
4/25/2023	kl 09.20	16,474	16,417	16,462	16,417
4/25/2023	kl 13	16,474	16,553	16,559	16,554
5/9/2023	kl 10	16,403	16,404	16,448	16,410
5/9/2023	kl 14	16,575	16,539	16,559	16,544
5/22/2023	kl 09.30	16,484	16,402	16,460	16,435

- **PnP logging (real value)**

Date	3/31/2023								
Time	13.20								
Battery	Voltage [mV]	Current [mA]	Relative SOC [%]	Remaining capacity [mWh]	Absolute SOC [%]	Full charge capacity [mWh]	Max error [%]	Cycle count	Temperature [°C]
1	16473	1266	91	82220	88	90350	1	2	22.8
2	16465	1365	91	81140	87	89360	1	2	22.6
3	16470	1284	91	79480	85	87680	1	2	22.4
4	16479	1244	91	78160	84	86340	1	2	22.2
5	16527	739	97	89130	96	91850	1	2	22.4
6	16579	440	99	90830	98	92000	1	2	22.7
7	16544	689	97	90140	97	92530	1	2	22.9
8	16544	729	97	87700	94	90360	1	2	22.6
9	16552	0	97	90130	97	90130	1	2	25.9
10	16549	0	100	91200	98	91200	1	2	25.0
11	16554	0	100	90870	98	90870	1	2	25.3
12	16558	0	100	90060	97	90060	1	3	25.6

	Date	4/11/2023							
	Time	kl 10.20							
Battery	Voltage [mV]	Current [mA]	Relative SOC [%]	Remaining capacity [mWh]	Absolute SOC [%]	Full charge capacity [mWh]	Max error [%]	Cycle count	Temperature [°C]
1	16466	1348	90	82780	89	91510	1	2	22.1
2	16454	1511	91	81640	88	90170	1	2	21.8
3	16485	1338	91	80830	87	88850	1	2	21.8
4	16467	1406	91	79800	86	87790	1	2	21.6
5	16496	978	94	86770	93	91830	1	2	21.7
6	16522	1001	96	89200	96	93020	1	2	22.1
7	16522	948	96	88490	95	92050	1	2	21.9
8	16498	1118	96	86320	93	89720	1	2	21.8
9	16430	0	97	87430	94	90440	1	2	22.2
10	16383	0	96	87330	94	91250	1	3	21.7
11	16444	0	97	87600	94	90330	1	2	21.9
12	16403	0	96	86010	92	89410	1	3	22.2

	Date	4/25/2023							
	Time	kl 10.45							
Battery	Voltage [mV]	Current [mA]	Relative SOC [%]	Remaining capacity [mWh]	Absolute SOC [%]	Full charge capacity [mWh]	Max error [%]	Cycle count	Temperature [°C]
1	16465	1565	89	81320	87	90940	1	2	22.2
2	16448	1716	89	78990	85	88470	1	2	22.6
3	16467	1490	90	80580	87	89390	1	2	22.0
4	16473	1612	88	78400	84	88850	1	2	22.5
5	16493	1232	92	84640	91	91830	1	2	22.0
6	16527	1060	97	89290	96	92480	1	2	22.8
7	16517	997	95	86850	93	91800	1	2	22.0
8	16524	1051	95	84950	91	89040	1	2	22.7
9	16446	0	97	87640	94	90400	1	2	22.5
10	16412	0	97	88230	95	91180	1	3	22.2
11	16462	0	97	87780	94	90040	1	2	21.9
12	16412	0	97	86150	93	89100	2	3	22.8

Date	5/9/2023								
Time	kl 10.00								
Battery	Voltage [mV]	Current [mA]	Relative SOC [%]	Remaining capacity [mWh]	Absolute SOC [%]	Full charge capacity [mWh]	Max error [%]	Cycle count	Temperature [°C]
1	16441	1711	88	79800	86	91060	1	2	22.7
2	16475	1443	94	82440	89	87590	1	2	22.9
3	16448	1664	88	79190	85	89530	1	2	22.6
4	16482	1345	94	81180	87	86140	1	2	22.6
5	16496	1068	95	87080	94	91910	1	2	22.4
6	16524	1043	97	89020	96	91870	1	2	23.1
7	16530	977	96	88510	95	91930	1	2	22.6
8	16515	1076	98	87740	94	89620	1	2	22.9
9	16493	994	94	84840	91	90040	1	2	22.7
10	16401	0	97	88120	95	91260	1	3	22.6
11	16450	0	97	87660	94	90390	1	2	22.2
12	16408	0	97	87350	94	90030	2	3	23.1

Date	5/22/2023								
Time	kl 09.45								
Battery	Voltage [mV]	Current [mA]	Relative SOC [%]	Remaining capacity [mWh]	Absolute SOC [%]	Full charge capacity [mWh]	Max error [%]	Cycle count	Temperature [°C]
1	16505	1212	92	84700	91	91670	1	2	23.3
2	16459	1588	90	81510	88	90690	1	2	25.0
3	16486	1080	92	82290	88	89460	1	2	23.0
4	16475	1517	91	80670	87	88810	1	2	24.8
5	16516	934	96	88030	95	91960	1	2	22.7
6	16544	939	97	89890	97	93000	1	2	24.6
7	16510	1153	94	86730	93	91900	1	2	23.1
8	16546	948	97	88170	95	90720	1	2	24.6
9	16455	0	97	87770	94	90290	1	2	23.2
10	16397	0	97	87720	94	90670	1	3	24.4
11	16460	0	97	87800	94	90400	1	2	22.6
12	16429	0	98	87570	94	88910	3	3	24.5

- **PnP logging (after recharge)**

Date	4/11/2023								
Time	12.20								

Battery	Voltage [mV]	Current [mA]	Relative SOC [%]	Remaining capacity [mWh]	Absolute SOC [%]	Full charge capacity [mWh]	Max error [%]	Cycle count	Temperature [°C]
1	16473	1266	91	82220	88	9035	1	2	22.8
2	16465	1365	91	81140	87	8936	1	2	22.6
3	16480	1284	91	79530	85	8768	1	2	22.4
4	16479	1244	91	78160	84	8634	1	2	22.2
5	16527	739	97	89130	96	9185	1	2	22.4
6	16579	440	99	90830	98	9200	1	2	22.7
7	16544	689	97	90140	97	9253	1	2	22.9
8	16544	729	97	87700	94	9036	1	2	22.6
9	16552	0	100	90130	97	9013	1	2	25.9
10	16549	0	100	91200	98	9120	1	3	25.0
11	16554	0	100	90870	98	9087	1	2	25.3
12	16558	0	100	90060	97	9006	1	3	25.6

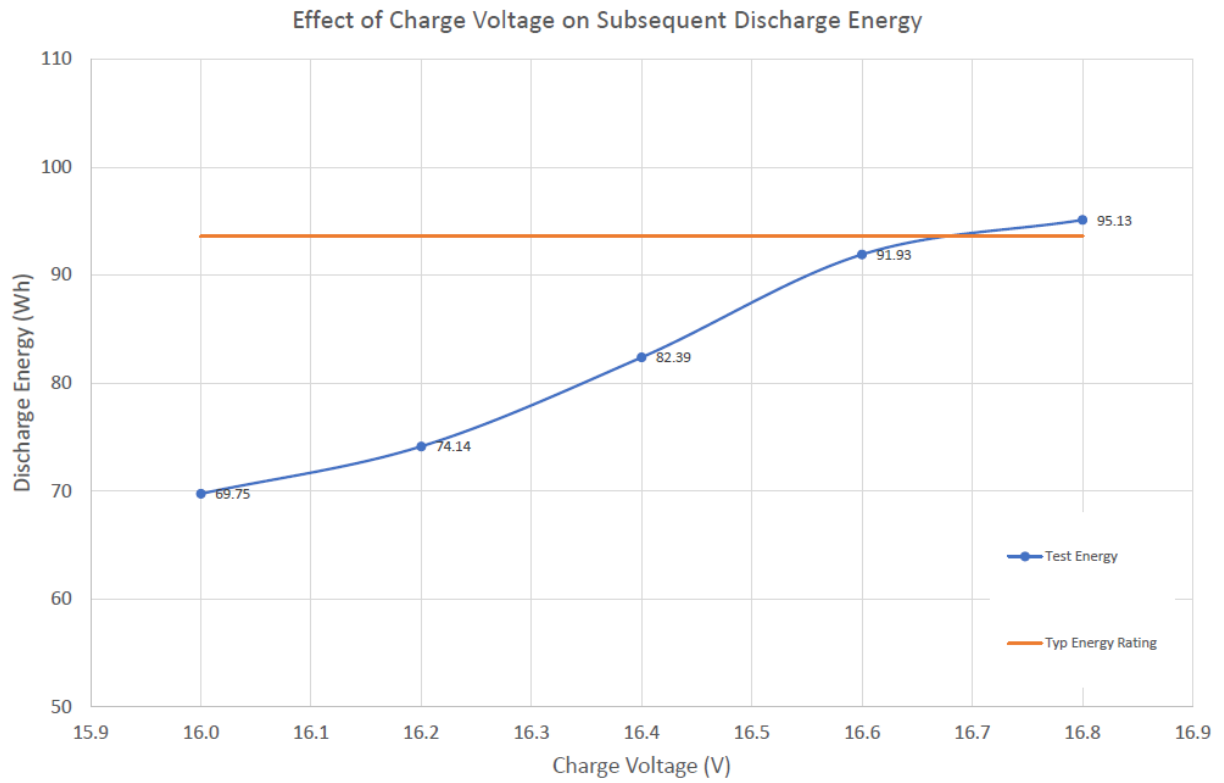| Date	4/25/2023								
Time	13.00								

Battery	Voltage [mV]	Current [mA]	Relative SOC [%]	Remaining capacity [mWh]	Absolute SOC [%]	Full charge capacity [mWh]	Max error [%]	Cycle count	Temperature [°C]
1	16469	1531	90	81450	88	90940	1	2	22.6
2	16501	1189	96	85000	96	88470	1	2	22.8
3	16468	1488	90	80720	87	89390	1	2	22.4
4	16506	1130	95	84170	90	84170	1	2	22.4
5	16531	723	97	88810	95	91830	1	2	22.5
6	16561	688	98	91040	98	92480	1	2	22.7
7	16554	702	98	90270	97	91800	1	2	22.6
8	16557	508	98	87590	94	89040	1	2	22.5
9	16448	0	97	87650	94	90450	1	2	22.9
10	16552	0	100	90950	98	90950	1	3	22.2
11	16559	0	100	90990	98	90990	1	2	22.4
12	16549	0	100	90040	97	90040	2	3	22.7

Date	5/9/2023							
Time	14.00							

Battery	Voltage [mV]	Current [mA]	Relative SOC [%]	Remaining capacity [mWh]	Absolute SOC [%]	Full charge capacity [mWh]	Max error [%]	Cycle count	Temperature [°C]
1	16490	1098	96	87450	94	91060	1	2	23.1
2	16486	1231	95	82910	89	87590	1	2	22.6
3	16490	1147	96	85620	92	89530	1	2	22.7
4	16477	1299	94	81290	87	86140	1	2	22.1
5	16522	671	98	89720	96	91910	1	2	22.8
6	16576	450	99	90950	98	91870	1	2	22.6
7	16515	783	96	88620	95	91930	1	2	22.6
8	16572	431	99	88290	95	89190	1	2	22.4
9	16549	0	100	90130	97	90130	1	2	22.7
10	16538	0	100	91050	98	91050	1	3	22.1
11	16563	0	100	91050	98	91050	1	2	22.2
12	16543	0	100	89970	97	89970	2	3	22.6

Date	5/22/2023							
Time	17.45							

Battery	Voltage [mV]	Current [mA]	Relative SOC [%]	Remaining capacity [mWh]	Absolute SOC [%]	Full charge capacity [mWh]	Max error [%]	Cycle count	Temperature [°C]
1	16539	0	100	90210	97	90210	1	3	23.7
2	16548	0	100	88140	95	88140	1	3	24.8
3	16552	0	100	88910	95	88910	1	3	24.6
4	16539	0	100	87320	94	87320	1	3	23.1
5	16530	0	100	90700	97	90700	1	3	24.8
6	16570	0	100	90100	97	90100	1	3	25.5
7	16564	0	100	91260	98	91260	1	3	24.8
8	16568	0	100	89310	96	89310	1	3	25.4
9	16520	0	100	91390	98	91390	1	3	24.3
10	16531	0	100	91410	98	91410	1	4	22.9
11	16534	0	100	91450	98	91450	1	3	23.6
12	16538	0	100	90000	97	90000	3	4	24.7

A3. Information by Accutronics

Effect of Charge Voltage on Subsequent Discharge Energy

A4. Test station