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Semi-empirical ageing model development of Traction battery

Master's thesis in Electric Power Engineering

Yidan Gao
Huijia Lei

DEPARTMENT OF ELECTRICAL ENGINEERING

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Supervisor: Sandeep Nital David, CEVT
Supervisor: Evelina Wikner, Chalmers University of Technology
Examiner: Torbjörn Thiringer, Chalmers University of Technology

Master's Thesis 2023: EENX30
Department of Electrical Engineering
Division of Electric Power Engineering
Chalmers University of Technology
SE-412 96 Gothenburg
Telephone +46 31 772 1000

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YIDAN GAO, HUIJIA LEI
Department of Electrical Engineering
Division of Electric Power Engineering
Chalmers University of Technology

Abstract

In this thesis work a semi-empirical model for lithium-ion battery calendar ageing and cycling ageing behaviour was built based on several ageing factors. For the calendar ageing, the factors include State of Charge (SOC), temperature and storage time. For the cycling ageing, the factors include Full Equivalent Cycles (FEC), temperature, Depth of Discharge (DOD), C-rate and middle-SOC. More than six groups of independent research data and two different chemistry of lithium-ion batteries, Lithium Nickel-Manganese-Cobalt Oxide (NMC) are included (NMC111 and NMC442). The developed ageing model can be used for several different type of cells.

The primary tool for data analysis and modelling is Matlab. This thesis investigates the relations of ageing factors and their influence on the degradation of batteries in the final model. Then the obtained model was validated and managed to be fitted for three different batteries' ageing data with minor adjustments.

An ageing model was acquired with separated calendar ageing and cycling ageing. The RMSE of each data sets is from 1.5-1.9 which is considered good to use for prediction. Besides, the stressed factors of the ageing model have been studied in order to provide input parameters for the required applications in a BMS. The research shows that the storage time has an important influence on the calendar ageing process. The storage temperature is more important than the storage SOC. Regarding cycling ageing, the FEC plays an important role in the ageing process. The cycling temperature and the SOC window are more important than the C-rate.

Keywords: lithium-ion battery ageing, semi-empirical model, NMC442, NMC111, ageing factors

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Contents

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis :

SOC	State Of Charge
DOD	Depth Of Discharge
FEC	Full Equivalent Cycles
BMS	Battery Management System
EV	Electrical Vehicles
NMCxyz	Lithium Nickel-Manganese-Cobalt Oxide (NixMnyCoz)
LFP	Lithium-Iron-Phosphate
HV	High Voltage
DOD	Depth of discharge
mid-SOC	middle SOC
SOH	State of Health

1
Introduction

1.1 Background

The structure of the energy demand has changed remarkably since the development of automobile technology.

In the vehicle industry, electric propulsion is gradually replacing internal combustion engines in the efforts to reduce carbon emissions and due to the legislative requirements. According to Jose[1], approximately 250,000 new plug-in cars were registered around the whole EU only in March 2022, which is a 10% increase compare to the previous year. The market share of plug-in cars in total sales is reaching 22% and will keep growing. An interesting discovery is that the plug-in share is only driven by Battery electric vehicles (BEVs), since the BEVs grow 47% while hybrids sales number declined noticeably.

In the current electric vehicle (EV) market, one of the most commonly used battery types is the lithium-ion battery. The Li-ion battery system provides the highest energy densities among the rechargeable battery systems currently available. It makes it the best candidate for electric vehicles. Until 2017, lithium-ion batteries took 37% of the total batteries market and reached over 120,000 MWh in sales around the world [2]. Thus, qualifying and quantifying the batteries production become a significant part for the researchers.

Among all the performances, ageing is one of the most vital parts for manufacturers and customers. However, the lifetime cycling tests of batteries are expensive and time-consuming. At the same time, there are strong demands from the vehicle industry, who asks for a reasonable estimation of battery cost in both the initial assembling and warranty period. Therefore, building an adequate model to simulate battery performance and ageing behaviour is essential.

Legislative requirement is also an important reason. More and more countries or regions are promising carbon neutralization, electrifying the transportation with energy from clean resources is a crucial part of this great process.

1.2 Previous work

Several methods to describe battery ageing have been developed in the past years, including using electrochemical models, data-driven models (empirical models), and semi-empirical models.

Electrochemical models are based on mathematical descriptions of the physical and chemical processes. This modeling strategy can identify the loss of lithium inventory, loss of active materials, loss of electrolytes, etc.. Parameterization is the most challenging part of this model. Many of the parameters need precise tests with different types of equipment. Lots of assumptions need to be made since it is quite impossible to simulate what is really happening in each particle in the electrodes. These assumptions can be very arbitrary. It also requires an accurate description of all the intrinsic degradation reactions in the cells. There are a few electrochemical models are used now, for example, P2D(Pseudo-two-dimensional) model, and SPM(single-particle model), but they are mainly used for battery performance instead of ageing process. These models could also bring a huge computation burden even with all the parameters collected, which made it complex to be integrated into an industrial application [3].

Data-driven models (empirical models) are more and more widely utilized with the development of AI technology. It is based on statistics and neural network theory, using the historical data on battery ageing to build the prediction model for the remaining capacity. This method can be easily applied in different situations. A considerable amount of input data is needed to build up the model. This method is also called a "black box" modeling which cannot indicate the influence of each ageing parameter [3]. Another issue with this kind of model is that it can be built only when there are already big amount of data input, which is not suitable for the beginning of a project. There are only very limited number of cells are tested and ageing data are not available for all the complex conditions.

The semi-empirical model simulates the ageing process from long-term cell tests, which usually are characterized as two different sections: calendar ageing and cycling ageing [3]. Calendar ageing is mainly evaluated by three factors: storage SOC, storage temperature, and duration time. While cycling ageing is parameterized by more factors including energy throughput or FEC, DOD, C-rate, Operation Temperature and mid-SOC. FEC is the Full Equivalent Cycle. DOD is the Depth Of Discharge, and refers to how much energy is cycled into and out of the battery on a given cycle. It is expressed as a percentage of the total capacity of the battery. A battery's C-Rate is defined by the rate of time in which it takes to charge or discharge. 1C requires 1 hour, 2C requires 1/2 hours. Mid-SOC is the midpoint of the cycling SOC window.

A semi-empirical model is developed with both experimental regression and derivations from the Arrhenius equation. Many classic models were proposed based on different research data sets, such as the Double Exponential Model, polynomial model, logistic model, or a combination of exponential and linear trend [4].

However, most of the existing semi-empirical models fail to interpret the multiple parameters in the function or do not have accurate enough results when trying to fit the same model to cells with different chemistry. It is crucial to create a universal model or a definite methodology to optimize the battery capacity fade for vehicle applications.

1.3 Purpose

The goal of the thesis is to identify the major factors contributing to the ageing of lithium-ion cells. Then build an empirical lithium-ion battery ageing model in simulation software and evaluate the significance of different ageing factors. Finally, offer input information to determine strategies that can be implemented to extend the battery lifetime in BMS of EVs.

The final model should be established with all stress factors in one formula for either cycling aging or calendar aging. It should be able to rebuild a proper model for different battery cells or projects. With this model, the manufacturer could easily predict battery degradation with multiple user behaviors, for example, different climate or driving habits. Or it can be simplified and integrated into BMS system in order to give feedback to drivers to extend the durability of their batteries.

1.4 Research Scope

The general research scope of this thesis work is to study lithium-ion battery ageing and develop a generic semi-empirical ageing model. The semi-empirical ageing model should be possible to apply to several different Li-ion batteries. In the current BEV market, nickel-based batteries take the most significant amount of share in GWh (79%) [5]. The most common nickel-based chemistry for BEVs is Lithium nickle manganese cobalt oxide (NMC). For this project, the focus has been on the NMC with higher nickle content NMC422 and also NMC111 due to lack of data.

NMC811 and NMC622 batteries are becoming prominent [6], and numerous researches are conducted on them. Their ageing mechanism is, however, different from other NMC batteries due to the high content of nickle [7]. Apart from SEI growing and Lithium plating, nickel-rich batteries have also been reported other ageing mechanisms, such as electrolyte oxidation(at cathode side)[8]; transition metal dissolution (from cathode); deposition (at anode side)[9]; O_2 release from cathode side[10]; the surface reconstruction at NMC[11]; and NMC particle cracking[12].
Batteries with silicon in the anodes are also excluded since the existence of silicon could cause severe accelerating of ageing because of the cracking of the anode material [13]. Several BEVs are using NMC811 and NMC622 already.

LFP is another type of lithium-ion battery that can provide reasonable expense from economic and environmental perspectives. Nevertheless, its low energy density caused by its relatively low average potential, lead to a dilemma between the capacity and the total mass of vehicles [14]. Its performance under extreme cold weather is also a concern for the industry [15]. Fewer companies are using it, although Tesla is one of them, which draws more attention and funding to the technical development. Among all chemistries, NMC111 and NMC442 with graphite anode are chosen for the modelling in this research.

2
Theory

2.1 Lithium-ion battery

As an energy storage device, batteries allow conversions between chemical energy and electricity. The main components of lithium-ion batteries are positive electrode material, current collector, separator, electrolyte, and negative electrode material. The cathode and anode are connected to the load circuit by electrode tabs. The processes during charging and discharging are shown in Figure 2.1. The electrolyte is usually composed with organic or inorganic solvent and lithium salts.

The mechanism of NMC lithium-ion batteries can be depicted: During the charging process, electrons are released from the NMC cathode, moving to the graphite anode through the external circuit. At the same time, lithium ions move from the cathode to the anode through the electrolyte. Electrons and Lithium ions arrive at the anode where the charge neutralization happens. The discharging process is the opposite of the charging process, during which electrons and lithium ions move from the anode to the cathode through external and internal circuits respectively.[14] [16]

2.2 Ageing Process

When batteries are used, or when stored, some irreversible and unwanted reactions occur in parallel. It cause the capacity to fade and the impedance to increase, in worst case scenario, leading to batteries failing thermo-cooling or even reaching thermal runaway.

The capacity degradation could be defined as reversible loss and irreversible loss [17]. It occurs during both storage and cycling [18].

Researches of ageing mainly focus on two aspects: the first is analyzing the relations between internal side-reactions and external properties during ageing, the second is building up the relations between ageing conditions and battery properties based on the experimental data. Currently, there are many challenges regarding battery ageing analysis or simulation because of the complex composition of the batteries and side-reactions interactions. Nevertheless, there is no direct method to detect or monitor these reactions without destroying the batteries. The external conditions that cause the ageing processes vary and makes it more difficult to analyze or quantify battery ageing.

In the past decades, researchers worked on unveiling the mechanisms of side reactions to build a clearer picture of batteries ageing. Arora [19]described the ageing mechanism with reaction equations, which introduced the theoretical framework for the degradation modelling. Aurbach [20] analyzed the reaction that happens at the interface between electrodes and electrolyte, and provided essential information for the SEI growth at anodes.

When lithium ion batteries are charged and discharged for the first time, a small amount of polar aprotic solvent in the electrolyte gets some electrons and reacts with lithium ions to generate an interface film with a thickness of about 100-120nm, which is called SEI. SEI is usually formed at the solid-liquid interface between electrode material and electrolyte.

When the lithium ion battery begins to charge and discharge, the lithium ion is removed from the active material of the positive electrode, enters the electrolyte, penetrates the SEI and then enters the electrolyte, and finally is embedded in the layered gap of the negative carbon material, then lithium ion completes a de-embedding behavior. Meanwhile, electrons from the positive electrode go along the outer loop, into the negative carbon material. Redox reactions occur slowly among electrons, solvent and lithium ions, increasing the thickness of the SEI until electrons cannot penetrate, forming a blunt layer and inhibiting the continuation of Redox reactions. Hence the batteries are highly aged.

Lithium plating is also another important part of losing lithium inventory. When a lithium-ion battery is being charged, the lithium ions are removed from the positive electrode and embedded in the negative electrode. But under some abnormal situation, such as the anode doesn't have enough space for lithium embedding, anode embedding resistance is too big, lithium ion taken off too quickly from the cathode but not in the same amount of lithium can get into the anode. When these exceptions occur, silver metal lithium is formed, which is called that lithium plating [21].

Agubra [22] summarized anodes ageing processes including Lithium precipitation, the SEI growth, loss of the lithium inventory, and loss of the active materials. While the influence of each mechanism that caused degradation differs, the loss of active lithium-ion inventory is the major factor [23]. Ageing can also be separated into two sections: calendar ageing and cycling ageing.

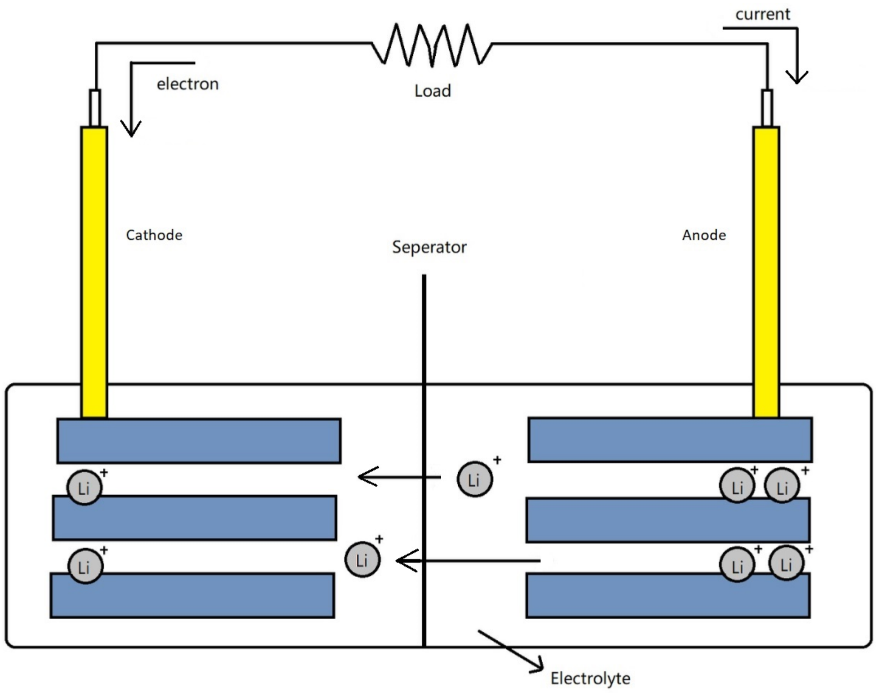

Figure 2.1: The electro-chemical reactions in Lithium-ion battery

2.2.1 Calendar Ageing

Many pieces of research indicate that the SEI growth under relatively low temperatures is the main reason that causes irreversible capacity loss. Another important reason is the transition metal in cathodes dissolving or structures changing under high temperatures and high SOC. Although calendar ageing is a slow process and it is not easy to be noticed, cars can be used for many years on the road, the accumulated amount of time could lead to a big degradation result. [24]

2.2.2 Cycling Ageing

During cycling ageing, the capacity is influenced by the change of electrode volume, and its change is caused by lithium-ion embedding and escaping. Besides the SEI growth, the cycling effect also contributes to the irreversible capacity fade. In general, cycling ageing is larger than calendar ageing. Researches show that charge or discharge current, temperature, and DOD are the major factors that impact the ageing process.[25]

2.2.3 Modelling Theory

Semi-empirical model refers to the model that trying to describe the established mathematical model, which needs to be tested by experiments, and the model based on theory is modified by adding experimental data, and its model parameters are determined. Since the reactions happen inside the battery cells are too complex to describe, semi-empirical model is a necessary way of simplify it. For the battery ageing process, both calendar ageing and cycling ageing contain 3 or more stress factors even with this modeling method.

3 Data collection and analysis

In this chapter, the selected data which are used in simulation development, and the relevant data information will be introduced. Additionally, the methodology of data selection and data modification will be presented.

3.1 Data collection

This thesis work was only using data from open sources. Traction batteries used in EVs usually have a large capacity, which varies from approximately 16 Ah to 150 Ah or even higher. Therefore, batteries with small capacities such as a battery in the 18650 will not be considered in this thesis work. All of the data used in the modelling development come from large NMC commercial cells.

It is commonly known that batteries with different chemical constitutions have different ageing mechanisms. NMC 111 is the first generation of the NMC cathode material which dominated the market for its high energy density and was popularly used in EV applications. NMC 532, after the short existence of NMC 442, replaced NMC 111 and became the most popular cathode material in 2021 [26]. NMC 532 is cheaper and it has a larger capacity. Nevertheless, the data of NMC532 used in EV are rare and most of them are confidential. Therefore, the data of NMC442 and NMC111 are utilized in the thesis work. NMC811 is another popular type to be used in the EV industry. As it is a quite new material, no ageing data could be found in open source publications and hence could not be included in this work. It is pretty new and is not as popular to be applied as NMC532, NMC111, and NMC442.

Batteries in which anode electrode components consist of silicon will also be neglected in the work because with silicon, the ageing process can be accelerated and its ageing mechanism is quite different from the type without silicon.

In summary, the restrictions which were set to select the valid data are listed as follows:

- Commercial cells tested should be with large capacity, mostly around 20 Ah.
- The chemical constitutions of the selected cells are determined and are restricted to NMC532, NMC111, NMC442, and NMC622.
- The ageing factors must remain constant throughout the whole test process. Specifically, in calendar ageing, the duration time of the degradation needs to be more than a year. The main influencing factors are SOC, T and days. In the cycling ageing, the dependency factors are restrained to depth of discharge (DOD), charging C-rate (C_{ch}), discharging C-rate (C_{dch}), middle-SOC (mSOC), full equivalent cycles (FEC), and Temperature (T). Only tests with

deep DOD are taken into consideration, shallow DOD tests, under 10 percent SOC window, will be neglected.

The literature referenced are listed in Table 3.1.

3.2 Data Analysis and Evaluation

Due to some test condition limitations, the test results may contain some errors. The raw data was acquired via a software named 'GetData' and was extracted by deleting some obviously unreasonable lines. In the following part, the data information and the changed contents will be introduced.

3.2.1 Calendar Tests

The calendar model developed is based on data from three different projects. The data mainly focus on the relationship between storage conditions and the capacity degradation of the cell.

The first project is Battery 2020 [27], where the ageing tests were performed at static conditions. The cells used in the tests are NMC422 cathode-based pouch cells with graphite anodes. They have a Nominal capacity of 20 Ah, and they are commercial cells for EV. The nominal characteristics of the cell are listed in Table 3.2. 30 cells were tested under 10 different conditions and the longest storage duration is approximately 600 days. Parts of the raw data were extracted from the literature. Some parts were neglected in the thesis. For example, when the test was conducted under the condition of 35 degree Celsius and 20 percent SOC value, the data in the literature show that the ageing process only lasted less than 100 days and there were few data being recorded. So those test results were filtered. The experimental matrix is presented in Table 3.3.

Finally, the data used to develop the ageing model in this Thesis are presented in Figure 3.1.

The second project is Mat4Bat [29]. This project tests two different kinds of cells. One selection is the Kokam battery with its Li-ion cells reference of 'SLPB78205130H'. Its electrical characteristics are specified in Table 3.4. In the literature, the cell's exact chemical composition is not specified. However, since the project was conducted at an early age (the end of 2013), and at that time, it is assumed that new types of batteries, such as NMC 811 or Nickle-rich cathode material, have not come out, the data from the projected were selected for the following modelling development. Also, the cells tested in the project were EV commercial cells with large capacity, therefore, the data meet the selection requirements mentioned previously. The cells' ageing trend data were only extracted ranging from 100 percent to 80 percent in State of Health (SOH) from the open source data. The tests' longest storage duration is approximately 800 days. When the testing condition is under 5 degree celsius in temperature and 100 percent in SOC, the testing results seem unreasonable. Because in the figure, it shows that its State of Health (SOH) tends to increase when the time passed, which is unreasonable. Therefore, this trend was deleted from the extracted data. The final tests matrix in the thesis

Table 3.1: Literature compilation for large commercial cells

No.	Author or Project	Cell chemistry	Cell Capacity $[Ah]$	Manufacturer	Cycling Tests	Storage Tests	Factors included	Ref.
1	**Batteries 2020**	**NMC442**	20	**EIG**	124	-	**SOC, T Days**	[27]
2	**Batteries 2020**	**NMC442**	20	**EIG**	-	32	**DOD,** C_{ch} C_{dch}**, mSOC FEC, T**	[28]
3	**Mat4Bat**	**NMC111 (GEN1)**	16	**Mat4Bat**	26	12	**DOD,** C_{ch} C_{dch}**, mSOC FEC, T**	[29]
4	**Mat4Bat**	**NMC**	16	**KOKAM**	46	-	**DOD,** C_{ch} C_{dch}**, mSOC FEC, T**	[29]
5	**Mat4Bat**	**NMC**	16	**KOKAM**	-	30	**SOC, T Days**	[29]
6	**S. L. Hahn, et al.**	**NMC111**	50.8	**Litec battery GmbH**	-	56	**SOC, T Days**	[30]

[a] Cells included means the cells those are selected in this thesis work.
[b] All the battery cells have graphite as anode material.No information specify the geometry of the cells or electrolytes.

Table 3.2: Battery 2020 cell Electrical characteristics

Electrical characteristics	
Nominal voltage [V]	3.65
Nominal capacity [Ah]	20
AC impedance (1 kHz) [mOhm]	< 3
Specific energy [Wh· kg-1]	174
Energy density [Wh· L-1]	370

Table 3.3: Calendar ageing tests matrix

Temperature	SOC					
	100	80	65	50	35	20
25 °C		2		2		
35 °C	3	3	3	3	3	
45 °C		3		3		

is presented in Table 3.5. And the data used to develop the model can be found in the Appendix.

Table 3.4: Mat4Bat cell Electrical characteristics

Electrical characteristics	
Chemistry	NMC / Graphite
Nominal capacity	16Ah
Measured capacity at C/2-C/2, 25°C	16.2Ah +/- 0.1Ah
Measured resistance at SOC=0.5 25°C	0.87$m\Omega$ +/- 0.02$m\Omega$
Nominal specific energy	148Wh/kg
Measured specific energy	150.1Wh/kg 281.3Wh/L

Another type of cell tested in this project is the lab cell. They are artificial cells and are generated according to the relevant parameter of Kokam cells. However, it shows unstable ageing characteristics, so the relevant data were also been neglected in this thesis.

The third database used is from the literature 'Quantitative validation of calendar ageing models for lithium-ion batteries' [30], written by S L. Hahn, et al. The cell used for the ageing experiment was the HEA50 pouch cell by Litec Battery GmbH with a nominal capacity of 50.8 Ah. And it can be mentioned that these cells were commercially fitted in the EV Smart Electric Drive by Daimler. The cells' cathode active material is defined as $Li_yNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC111) and its anode composition is graphite (Li_xC_6). The cells' electrical characteristics are shown in Table 3.6. The calendar ageing tests were performed at different ageing conditions. Only one test was performed. The storage duration is approximately 280 days. The cells' ageing trend data were only extracted ranging from 100 per cent to 80 per cent State of Health (SOH) from the open source data. Apart from that, the conditions under the SOC value of 100 and under the SOC value of 0 per cent will not be taken into consideration, due to that under the highest SOC and lowest SOC,

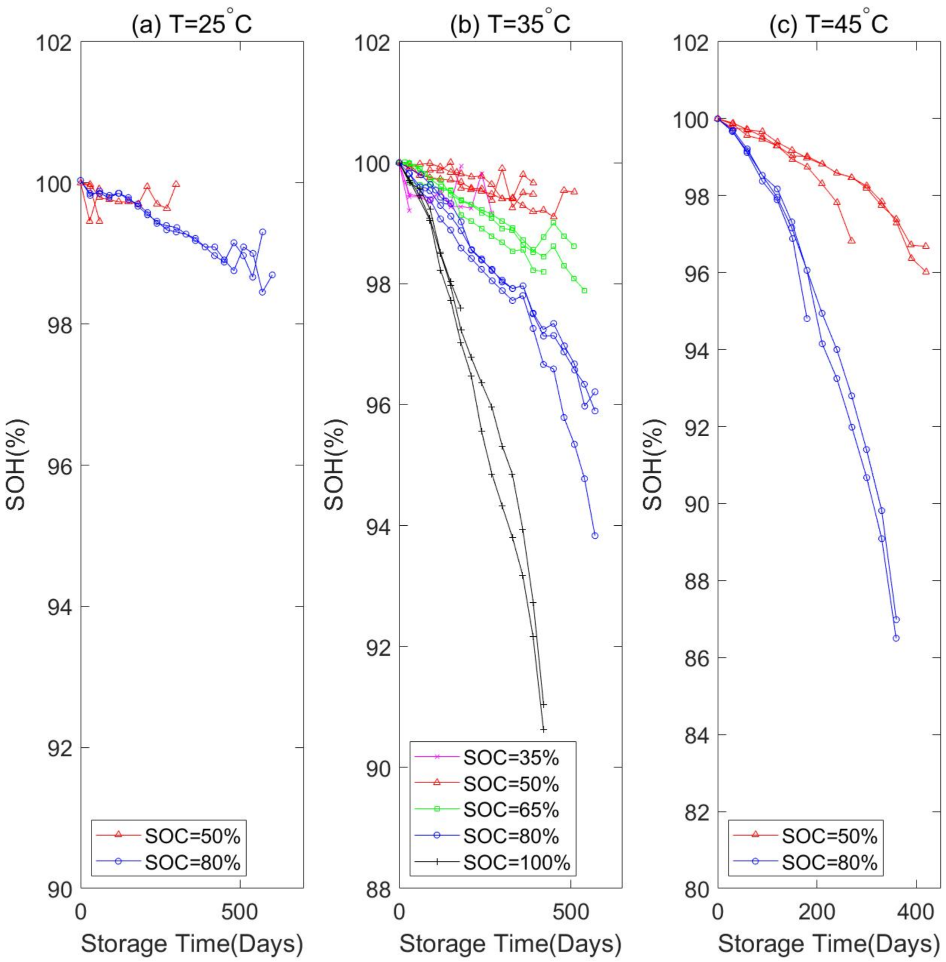

Figure 3.1: Calendar ageing data in battery2020 project. (a)Temperature = 25°C; (b)Temperature = 35°C; (c)Temperature = 45°C

the developed model's performance is not in line with reality. The predicted results showed unreasonable trends. Therefore, the used data extracted from the literature database is limited to the range from 15 per cent to 95 per cent. Its experimental matrix can be found in Table 3.7. Testing data under the temperature condition of 50 degree were presented in Figure 3.2. Other testing data can be found in the Appendix.

Table 3.5: Calendar ageing tests matrix

Temperature	SOC		
	100	90	50
5 °C	1	1	1
25 °C	1	2	1
45 °C	2	2	1
60 °C	-	2	2

Table 3.6: Electrical characteristics

Electrical characteristics	
Chemistry	NMC111 / Graphite
Nominal capacity	50.8 Ah
Operating Window	3.0 V $\sim$ 4.2 V

3.2.2 Cycling Tests

Cycling ageing is affected by several factors. This thesis will mainly look into the relevant effective influence on the battery ageing process and its influenced factors: FEC, T, DOD, mid-SOC, and C-rate. The data collected from the literature will mainly focus on the relationship between the battery SOH and FEC.

Apart from the calendar ageing tests, in the project Battery 2020 [31], cycling tests are also been conducted. The cells are of the same type as the ones used in the calendar ageing tests. They are large commercial cells with a capacity of 20 Ah. The testing pouch cells have NMC422 cathodes and graphite anodes. The cells' electrical characteristics are presented in Table3.2. In the cycling ageing tests, a total of 124 cells were cycled under different conditions. Several different influential factors are investigated, including operating temperature, DOD, mSOC, and the charging and discharging C-rate. The testing results can be accurate since under each condition, several tests were conducted, and there were more than one thousand points recorded. Therefore, it is easy to filter some trends which are not in line with the other trends for the same condition. The testing matrix of this thesis is specified in Table 3.8. The cells were characterised every 4000 Ah (100 FECs), and under each testing condition, at least 3 cells were tested. The data presented in the literature have already been processed and the data used in the thesis can be found in the Appendix.

The second data used for the cycling model development are extracted from project Mat4Bat. The cells' information is introduced in the previous parts and can be found in Table 3.4. The testing matrix is presented in Table 3.9. Some of the tests have reached around 6000 cycles under certain conditions. The raw data certainly exist some errors. For example, the trends seem unreasonable when the testing temperature is 5 degree. The trend will not decline after around 500 FECs, and after several cycles, the battery SOH even increases. Another unreasonable part is that the trend will go straight down after the battery SOH reaches a value of around 80 percent. It is assumed that the cell electrolyte was the breakdown reason. Therefore, the parts where the value of SOH was below 80 percent were neglected.

Table 3.7: Calendar ageing tests matrix

Temperature				**SOC**					
40 °C							85		
42.5 °C							85		
45 °C							85		
47.5 °C							85		
50 °C	15	22	30	40	55	70	85	90	95
52.5 °C							85		
55 °C					55		85		
60 °C							85		

Except for those reasons, some other trends which do not fit the ageing general law were deleted from the used database. The raw data can be found in the Appendix.

The third data used for the cycling model development are extracted from the generation cell's raw data in the project Mat4Bat. The cells were generated by the project lab itself based on the data of the Kokam cells. It mentioned that the lab focused on the battery electrolyte, so in this thesis, it is assumed that the anode and cathode components are almost the same as the Kokam cells. However, most of the trends seem not reasonable. Many of the trends lack a smooth characteristic and suddenly go down after some cycles. Only a few promising trends were saved for the modelling verification use. The preserved trends are presented in Table 3.10 and the rest of the reserved figure can be found in the Appendix.

Table 3.8: Battery 2020 Cycling ageing tests matrix

Temperature		25 °C			35 °C						45 °C
C-rate[C] (charge - discharge)		**C/3-1C**	**1C-1C**	**C/3-C/3**	**C/3-1C**	**C/3-2C**	**C/2-1C**	**1C-1C**	**2C-1C**	**2C-2C**	**C/3-1C**
DOD	**Mid-SOC**										
100	50	3	-	-	2	-	-	-	-	-	3
80	50	6	3	4	5	3	3	6	3	2	4
65	50	3	-	-	3	-	-	-	-	-	4
50	65	-	-	-	3	-	-	-	-	-	-
	50	3	-	-	5	-	-	-	-	-	3
	35	-	-	-	2	-	-	-	-	-	-
35	50	-	-	-	2	-	-	-	-	-	3
20	80	-	-	-	6	-	-	-	-	-	3
	65	-	-	-	3	-	-	-	-	-	-
	50	3	-	-	6	-	-	-	-	-	3
	35	-	-	-	-	-	-	-	-	-	-
	20	-	-	-	3	-	-	-	-	-	-
10	80	-	-	-	3	-	-	-	-	-	-
	65	-	-	-	1	-	-	-	-	-	-
	20	-	-	-	3	-	-	-	-	-	-

Table 3.9: Mat4Bat Kokam Cycling ageing tests matrix

Temperature		5 °C			25 °C			45 °C				
C-rate[C] (charge - discharge)		**1C-1C**	**2C-1C**	**3C-1C**	**1C-1C**	**2C-1C**	**3C-1C**	**1C-1C**	**2C-1C**	**2C-2C**	**3C-1C**	**3C-3C**
DOD	**Mid-SOC**											
80	60	-	-	-	-	-	-	1	2	-	1	-
80	50	-	-	-	1	1	2	2	-	2	2	2
80	40	-	-	-	-	-	-	2	2	-	1	-
100	50	-	-	-	-	-	-	2	-	-	2	-

Table 3.10: Mat4Bat Gen1 Cycling ageing tests matrix

Temperature		5 °C			25 °C			45 °C		
C-rate[C] (charge - discharge)		**1C-1C**	**2C-1C**	**3C-1C**	**1C-1C**	**2C-1C**	**3C-1C**	**1C-1C**	**2C-1C**	**3C-1C**
DOD	**Mid-SOC**									
80	60	-	-	-	-	-	-	-	-	-
80	50	2	1	2	2	-	2	1	-	1
80	40	-	-	-	-	-	-	-	-	-
100	50	-	-	-	-	-	-	-	-	1

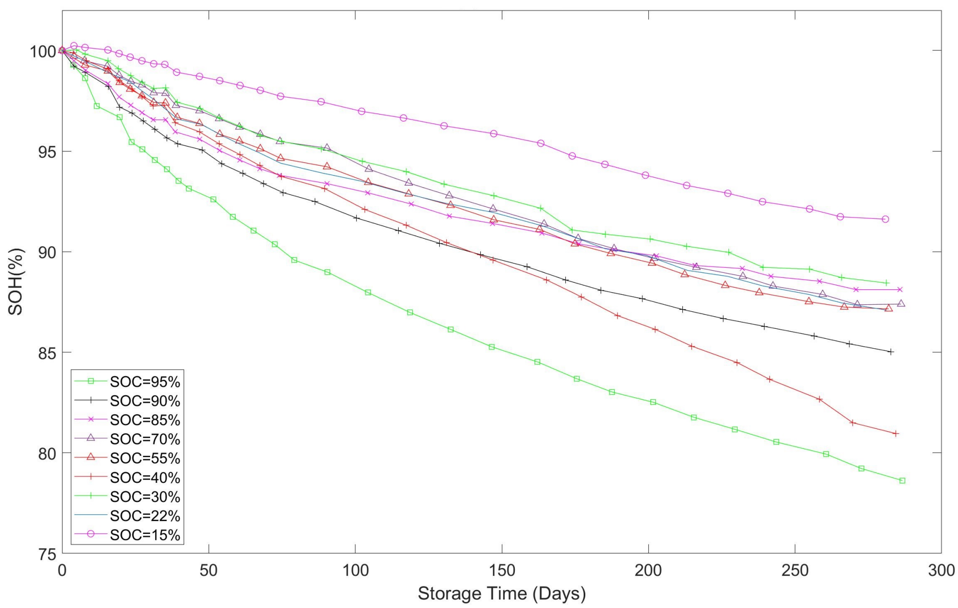

Figure 3.2: Calendar ageing data of LBG cells when the testing temperature is 50 degree

4
Method

4.1 Method Description

In this work, the main purpose is to model battery degradation. The term SOH is used. SOH is defined as a percentage of the current capacity compared to the original capacity. Most of the researchers conducted experiments for calendar ageing and cycling ageing separately. There is an important assumption the degradation from storage and cycling can be added directly without considering their interactions. There are a few projects trying to reveal the connections between these two ageings, while the experimental set-ups are not enough to achieve any precise conclusion about the interaction mechanisms. Although many creative analyses or assumptions are made, it is still not feasible to predict the interactions. In this thesis work, SOH is defined as:

$$SOH = 100 - \Delta SOH_{calendar} - \Delta SOH_{cycling} \qquad (\%) \tag{4.1}$$

$\Delta SOH_{calendar}$ and $\Delta SOH_{cycling}$ will be evaluated independently with the following factors:

$$\Delta SOH_{calendar} = func(SOC_{storage}, T_{storage}, time) \qquad (\%) \tag{4.2}$$

$$\Delta SOH_{cycling} = func(FEC, T_{cycling}, DOD, C_{ch}, C_{dch}, m_{SOC}) \qquad (\%) \tag{4.3}$$

4.2 Modelling Method

The semi-empirical model is a mixture of data-based model and electro-chemical model. There is a function used to describe the ageing behavior corresponding to multiple stress factors. It will be discussed in the Method chapter to decide which factors that should be included in the model.

Matlab is the main tool used in this work. The "least square regression" method is utilized. It can help to achieve the curve for an existing data set with the best fit, which means the sum of the square of residuals is minimum. Residual represents the difference between results obtained by observation and by computation model. It is widely applied in many fields in data analysis for both linear and non-linear fit.

The iterative method is used in the cycling ageing modelling. For model validation, each data set's Root-mean-square deviation (RMSE) was evaluated. It is a standard parameter to describe the accuracy of a model compared to the experimental data set.

4.3 Linear Model

On the first attempt, the linear model was taken into consideration, since the function could be clearly defined with a second or even higher order of each factor. The data sets from Battery2020 project[27] showed that the degradation curve has linear behavior to some extent which can be seen in Figure 4.1.

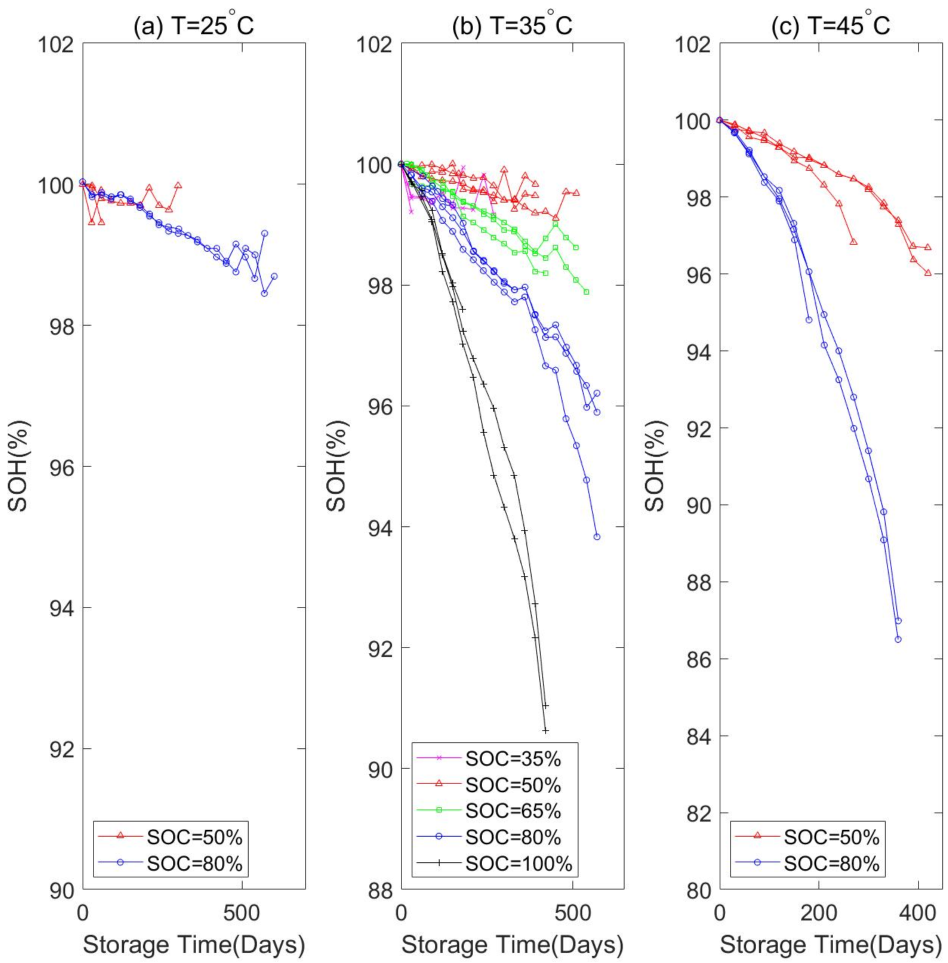

Figure 4.1: Calendar ageing data in battery2020 project.(a)Temperature = 25°C; (b)Temperature = 35°C; (c)Temperature = 45°C

On the other hand, the weightage of all the parameters is also easy to be evaluated. Take calendar ageing for example, (4.2) can be specified as:

$$
\begin{aligned}
SOH_{calendar} &= 100 - \Delta SOH_{calendar} \qquad (\%) \\
&= b_{10} - (b_1 SOC_{storage} + b_2 T_{storage} + b_3 time + b_4 SOC^2_{storage} \\
&+ b_5 T^2_{storage} + b_6 time^2 + b_7 SOC_{storage} T_{storage} \\
&+ b_8 SOC_{storage} time + b_9 T_{storage} time) \qquad (\%)
\end{aligned}
\tag{4.4}
$$

First-order and Second-order terms are used for every single factor. Interactions between every two factors are included as well to achieve higher accuracy. b_1, b_2,..., b_9 are the coefficients for all the monomials, b_{10} is the interception. Battery2020 project data set was tested first. The regression results are shown in Chapter 5: Result.

4.4 Non-linear Model

Linear models are rarely used in the current research, but it is still a reasonable attempt to see the outcome of different methods. To achieve a more accurate simulation, non-linear models were developed for battery degradation. The modelling process is explained in the following figure.

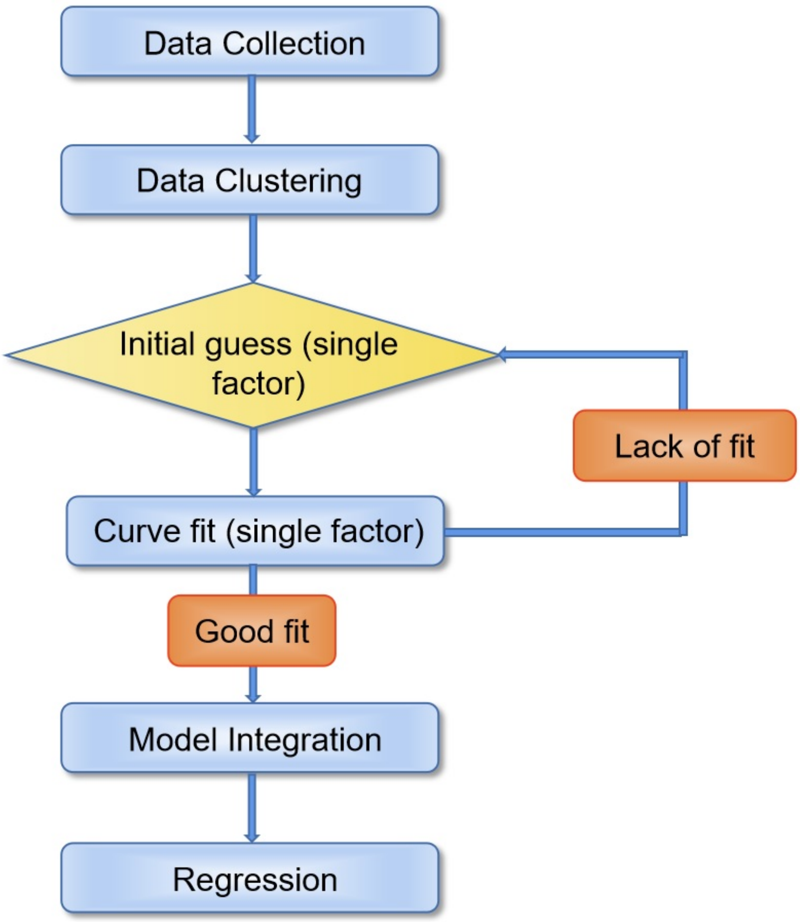

Figure 4.2: The process for Non-linear model

The first step is collecting data from existing research and projects which has NMC111, NMC442 as battery chemistry. Large-capacity commercial cells are preferred because they are similar to industrial use and more stable when trying to duplicate tests. For some ageing factors, there are not enough data sets, then a few smaller cells are included.

The second step is clustering the data into different groups regarding the ageing factors that they are focusing on. For example, when considering the factor: $Temperature_{storage}$, the other factors($SOC_{storage}$ and $time$) should remain the same value.

After clustering the data sets, the analysis for each ageing factor started one by one, in accordance with the following procedures. Step 3 is making an initial guess for each factor that how it can be expressed in a certain form(or equation), then trying to fit the clustered data into this form. The initial guess usually comes from research or simplified theories. If this form has a good fit, integrate it into the final model, and move to the next factor; if it is a bad fit, go back to the initial guess step and try with other possible types of equations until a good fresearchhed.

The fourth step is integrating each equaLarge-capacityfactor into one full model.

The final step which follows, regression, is achieved by using Matlab or iterative methods in order to gain the best coefficieares with the best fit. RMSE is the parameters used to evaluate the fit of the model. If RMSE is smaller than 2%(out of 100%), the model is acceptable. This is an arbitrary threshold.

$$RMSE = \sqrt{\sum_{i=1}^{n} \frac{(\hat{y} - y)^2}{n}} \tag{4.5}$$

4.4.1 Calendar ageing

Calendar ageing has three important stress factors, degradation time(Days), storage SOC and storage temperature. According to previous researches, the loss of capacity over time was commonly described with $\sqrt{Days}$ i.e. [32] [33]. In order to make the equation more adjustable, the exponential form of Days is kept.

On the other hand, no linear trend is in the ageing process observed regarding SOC. Exponential expression of SOC was suggested by previous researches [34], which is similar to the storage time. It could also keep a unified form of the integrated equation.

Temperature is another significant factor. Since both the two ageing processes (lithium plating and SEI growing) are related to chemical reactions, it is reasonable to believe storage temperature will influence ageing speed as it does in most of the reactions. The degradation process should follow Arrhenius's behavior as shown in 4.8 [35], k is the reaction rate constant, A is the pre-exponential factor, Ea is the activation reaction energy, and R is the gas constant. k indicates how fast the reaction would be conducted, thus how fast the battery would age. This form of ageing model (about the temperature parameter) is also widely found in many modelling works. Although using a reference temperature to integrate into the ageing function is a common method, see (4.9), the regression result was not satisfying in the selected data sets. So (4.10) was kept for modelling.

$$SOH_{SOC} = 100 - b^{*}SOC^{b2} \tag{4.6}$$

$$SOH_{Days} = 100 - b^{*}Days^{b3} \tag{4.7}$$

$$k = Ae^{\frac{-Ea}{R(T+273)}} \tag{4.8}$$

$$e^{\frac{Ea}{R(T-T_{ref})}} \tag{4.9}$$

$$SOH_{T} = 100 - b^{*}e^{\frac{-b4}{8.314(T+273)}} \tag{4.10}$$

$$SOH_{calendar} = 100 - b1SOC^{b2}Days^{b3}e^{\frac{-b4}{8.314(T+273)}} \tag{4.11}$$

As described before, after regressing all the equations for each single factor, multiple sets of coefficients are found. However, the coefficients from these regressions are not able to be used directly, since they have different b* values. By integrating all the equations together, the final equation, (4.11) was obtained. With this whole calendar ageing model, the whole data sets could be applied into regression to get a completed result.

4.4.2 Cycling ageing

As discussed in the Theory chapter, compared to calendar ageing, the mechanisms of cycling ageing is more complicated and caused by more factors.

Energy throughput is the most influential one among them all[36], which could also be described as FEC. Since the battery capacity will decrease while cycling, 1 FEC is defined as 1 cycle's energy throughput at the beginning of life, and it will remain the same in the rest of the tests. According to literature study, FEC doesn't show a linear behavior, it could be assumed to have an exponential format as (4.12). It is an interesting observation that some battery cells' ageing accelerate while the driving cycles/FECs are increasing, and some decelerate. The coefficient b_6 could be over 1 or below 1 accordingly based on the performance of different cells.

In this thesis work, the concept of DOD is slightly different. It is defined as the size of the cycling window in between two SOC level. To describe this SOC window, two separate factors are utilized: DOD is the range of the SOC window; mid-SOC is the locator: the middle point of the SOC window.

The reason that DOD should be included in the ageing model came from many tests and practices. It was clearly shown that DOD factor couldn't be simulated in linear functions. Two different functions were tried to express DOD factor: (4.13) and (4.14). Both of these two worked in the model, but to unify the format of the final whole equation, (4.13) is kept.

On the other hand, mid-SOC as a locator is more difficult to integrate into the ageing model. According to [37], mid-SOC can be expressed as (4.17). It was found feasible in this model. In (4.17), $mSOC_{ref}$ is a reference middle SOC value, which could vary for different cells. it could be considered as another parameter, but to lower the dimensions of final model, the best way to acquire this value is manual fitting while the other coefficients are already fixed.

There are still many assumptions about how the driving cycles are impacting the capacity degradation. Some researchers believe the cycling process could be considered as an accelerated storage ageing process. Thus temperature, as usual, is another factor that can't be neglected in the ageing side reactions,

$$SOH_{FEC} = 100 - b^* FEC^{b_6} \tag{4.12}$$

$$SOH_{DOD} = 100 - b^* e^{b_3 DOD} \tag{4.13}$$

$$SOH_{DOD} = 100 - b^* DOD^{b_3} \tag{4.14}$$

$$SOH_{C_{ch}} = 100 - b^* e^{b4 C_{ch}} \tag{4.15}$$

$$SOH_T = 100 - b^* e^{-b2(\frac{1}{T} - \frac{1}{T_{ref}})} \tag{4.16}$$

$$SOH_{mid-SOC} = 100 - b^*[1 - b7mSOC(1 - \frac{mSOC}{mSOC_{ref}})] \tag{4.17}$$

$$\begin{aligned} SOH_{cycling} =& 100 - b1e^{-b2(\frac{1}{T} - \frac{1}{T_{ref}}) + b3DOD + b4C_{ch} + b5C_{dch}} FEC^{b6} \\ & [1 - b7mSOC(1 - \frac{mSOC}{mSOC_{ref}})] \end{aligned} \tag{4.18}$$

4.4.3 Modelling validation

The developed model needs to be validated to confirm its validity. Around fifteen percent of the testing points were extracted from the initial training data. Then, the model was parameterized with the rest of the data points. After the regression, the fifteen percent data was fed into the regressed model in order to see if the model is able to predict these data. The predicted values were compared with the actual tested values. If the RMSE value is small enough(below 2% out of 100%), the model is considered acceptable.

According to the above described method, for the calendar ageing model, it is shown that the the RMSE of the model, which was developed from the rest of the data, is 0.4489%. The RMSE value of the model which was developed from the extracted data is 1.32%. For the cycling ageing model, it shows that the RMSE of the model which was developed from the rest of the data is 1.50%. The RMSE value of the model which was developed from the extracted data is 1.51%. The RMSE value mentioned above can flow variably because the fifteen percent of the data were extracted randomly. Since the RMSE values are below 2%, the model works properly.

5

Result

5.1 Calendar model development

5.1.1 linear model

Only Batter2020 Data set(calendar aging part) was tested with this method. The regression results are shown in Table 5.1.
Which gives a final calendar ageing function as:

$$
\begin{aligned}
SOH_{calendar} &= 100 - \Delta SOH_{calendar} \qquad (\%) \\
&= b_{10} - (b_1 SOC_{storage} + b_2 T_{storage} + \\
b_3 &- b_4 SOC_{storage}^2 \\
&- b_5 T_{storage}^2 + b_6 time^2 \\
&- b_7 SOC_{storage} T_{storage} \\
&- b_8 SOC_{storage} time - b_9 T_{storage} time)(\%)
\end{aligned}
\tag{5.1}
$$

This linear model gave an R-square of 0.8610% and an RMSE of 0.7871% out of 100 %, which are both in an acceptable range. While the figure regarding the experimental value and the predicted value from this model raised some controversy as shown in Figure 5.1.

Table 5.1: The coefficients of linear model(Battery 2020 project data set: calendar ageing)

Coefficient	Value
b1	**0.3114**
b2	**1.0063**
b3	**0.0443**
b4	**-0.0009264**
b5	**-0.009456**
b6	**6.6599e-6**
b7	**-0.004878**
b8	**-0.0003487**
b9	**-0.0008813**
b10	**72.0400**

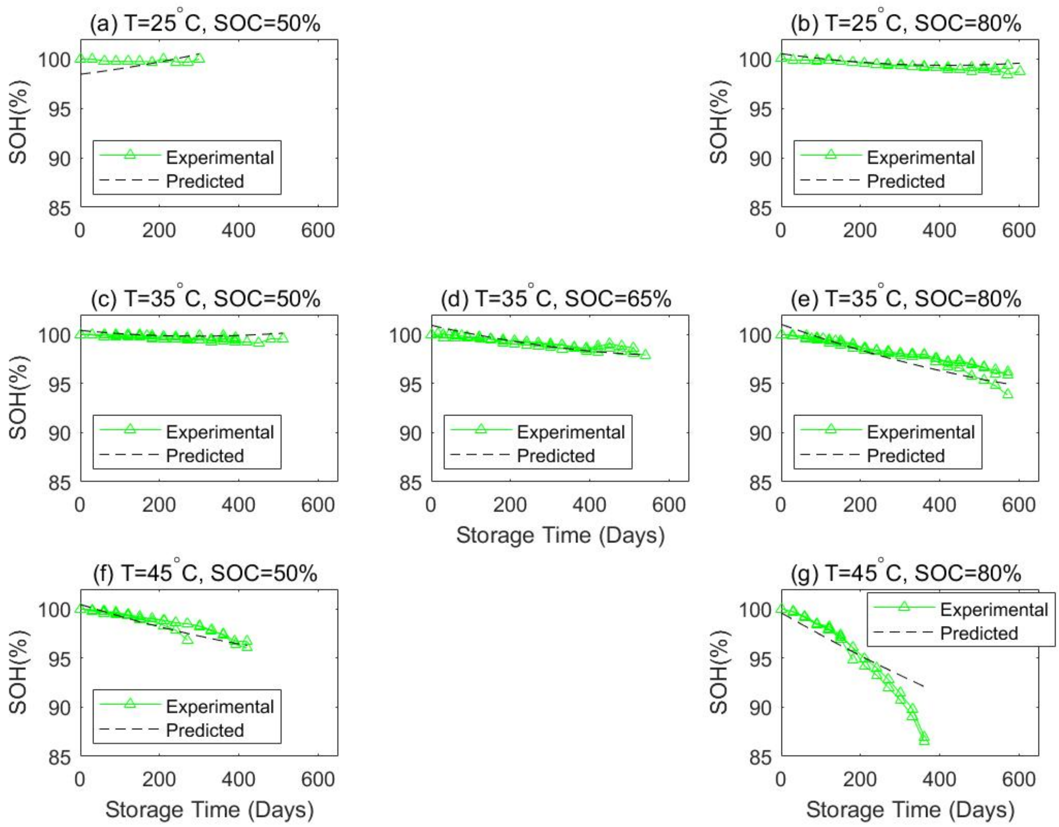

Figure 5.1: Linear model(Battery 2020 project data set: calendar ageing)

It is clearly shown in the figure that the predicted values couldn't simulate the ageing behavior with an accelerated speed. The batteries are mildly degrading at a stable pace. It caused some outliers in the BOL which are higher than 100% capacity. And this simulated degradation process abnormally slows down after longtime storage. According to the reasons above, although the RMSE and R-square values are decent, the linear model was excluded from the calendar ageing simulation. Since the cycling ageing process has less linear behavior while more factors, the linear model is even more impossible to be applied in cycling ageing.

5.1.2 non-linear model

With the method introduced in the last chapter, the final predicted ageing model was developed in (5.2). Each parameter, from b1 to b4, is different in each case. The parameters are given for each case in Table 5.2.

From the table, it can be noticed that with different types of battery data applied, the parameters change as well in the model. Influential factors, including the storage time, the storage temperature, and the storage SOC, are involved. The value of the RMSE indicates the modelling predicted errors. From the results, the values are no more than 2%, and the authors of this article considered that this deviation is acceptable for the prediction results. The model can be used to predict battery ageing trends, and this will be detailed in the following section.

$$SOH_{calendar} = 100 - b_1 \cdot SOC^{b_2} \cdot Days^{b_3} \cdot e^{\frac{-b_4}{8.314 \cdot (T+273)}} \tag{5.2}$$

Table 5.2: The comparison of each parameter in the Developed calendar model

Coefficient	b1	b2	b3	b4	RMSE
Battery2020	$3.5 * 10^9$	3.56	1.29	$1.13 * 10^5$	0.45
Mat4Bat	$2.36 * 10^6$	1.02	0.74	$5.58 * 10^4$	0.449
S. L. Hahn, et al.	$2.22 * 10^6$	0.296	0.625	$4.49 * 10^4$	1.33

5.1.3 Modelling Performance

Three cases are involved in the analysis of the calendar ageing prediction performance. They are the project battery 2020, the project Mat4Bat and LBG battery cells tests. The modelling performances are presented in Figure 5.2, Figure 5.3, and Figure 5.4. Since the database is too large to present here, only selected parts are specified per case. The complete compilation of the data for the cases and the model performance can be found in the Appendix. The colored lines refer to the experimental data, while the black dashed lines refer to the predicted value. From the figures, two types of lines fit well in general, no big deviations or offsets are observed from these figures. This means that the model has a good performance. Among all, the case battery 2020 shows the best performance, and the RMSE value also shows merely slight error exists.

The modelling performance of the cells in the project Mat4Bat is acceptable as well, though it is not as good as the performance of the cells in project 2020. Furthermore, it is found that the prediction value may exist larger errors if the storage temperature is higher. Also, one should avoid to predict the battery ageing trend in a high SOC level. The actual state of health of the lithium-ion battery can drop quicker than the prediction value for a high SOC condition, however, not as quick as the prediction for high storage temperature.

The modelling performance of the LBG battery cells is acceptable, though its performance is not better than the previous two cases generally. There are large discrepancies in this case, are seen in the figure 5.4. The LBG battery cells are NMC 111 lithium-ion battery cells, so the ageing process may be different from that of the NMC 442. Also, it can be seen from the figure that when the testing temperature is high, the actual ageing process is quicker than the predicted one.

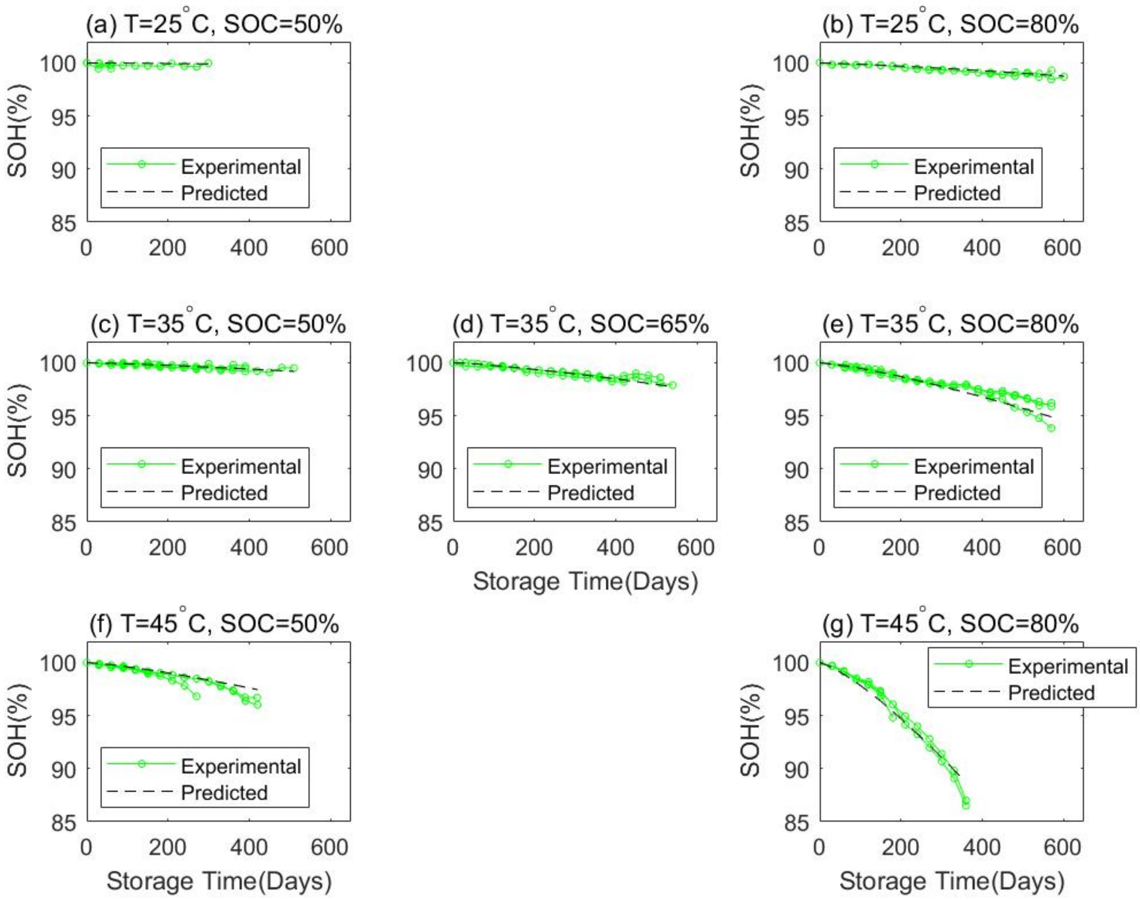

Figure 5.2: Calendar Modelling performance in project battery2020

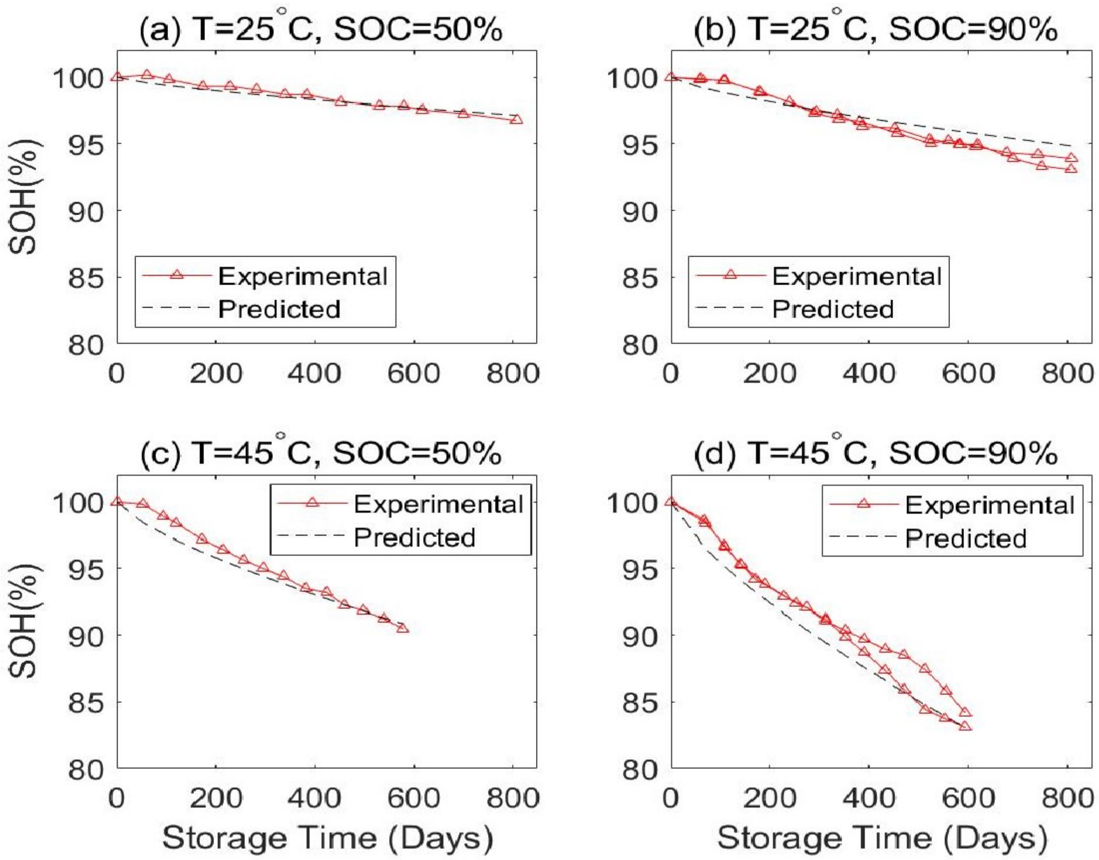

Figure 5.3: Calendar Modelling performance in project Mat4Bat

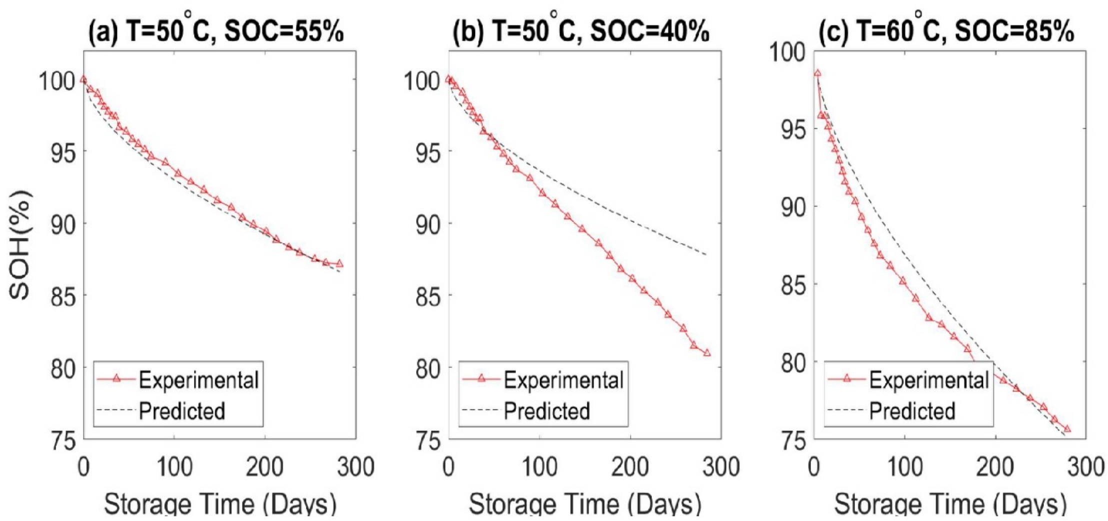

Figure 5.4: Calendar Modelling performance of the LBG battery

5.1.4 Ageing factor significance comparison

The significance of the stressed factors is evaluated from the equation form, the equation parameters (from b1 to b7) and the modelling performance, etc. The storage time plays an important role on the ageing process. Compared with the storage SOC, the storage temperature has more influence on the battery ageing. The evaluation results are presented in Table 5.3.

In Figure 5.5, one can find the SOH value of the tested battery after one year under different SOC levels when the testing temperature is 25 degree. Also, one can find the remaining SOH after one year storage under different storage temperature levels in the appendix. From the figure, it can be found out that the higher the storage SOC level, the more the batteries degrade. Also, it is good to store the battery in a place in low temperature. After 25 degree, the SOH of the battery may drop dramatically.

Table 5.3: The significance of each factor for calendar ageing

Stressed factors	Significance
Storage time (Days)	++++
Storage Temperature	+++
Storage SOC	++

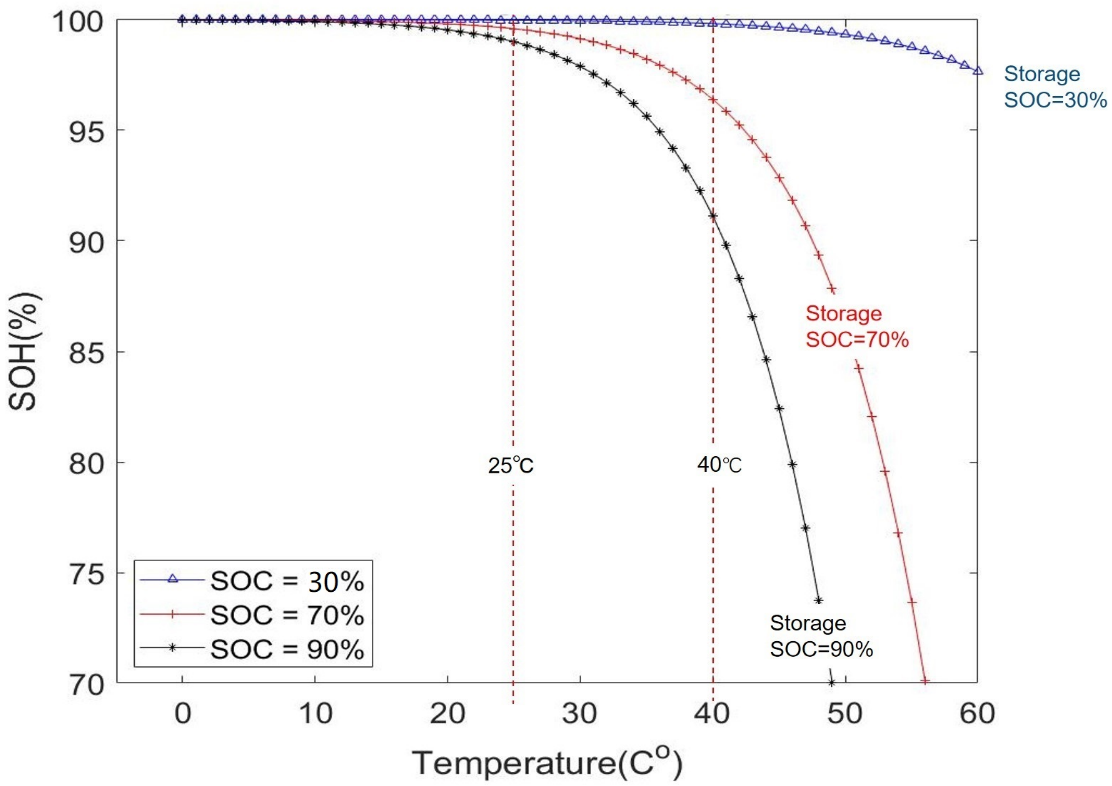

Figure 5.5: State of Health (SOH) after storageing 1 year under different SOC

5.2 Cycling model development

With the method introduced in the last chapter, the final predicted ageing model was developed in (5.3). Each parameter, from b1 to b7, is given in Table 5.4.

From Table 5.4, it can be noticed that with different types of battery data applied, the parameters change as well in the model. Influential factors, including temperature, FEC, DOD, Mid-SOC, charging rate and discharging rate, are involved. However, as to the tests of the Kokam cells and the generated cells, the discharging rate were not considered as an influencial factor. Therefore, b5 cannot be specified in those cases. The value of RMSE indicates the modelling predicted errors. From the results, the values are no more than 2, which means that the results are acceptable for the prediction results. The model can be used to predict the battery ageing trends, which will be describe more in details in the following.

$$\begin{aligned} SOH_{cycling} =& 100 - b_1 e^{[-b_2(\frac{1}{T}-\frac{1}{T_{ref}})+b_3 DOD+b_4 C_{ch}+b_5 C_{dch}]} \\ & FEC^{b_6}[1-b_7 mSOC(1-\frac{mSOC}{mSOC_{ref}})] \end{aligned} \tag{5.3}$$

Table 5.4: The comparison of each parameter in the Developed cycling model

Coefficient	b1	b2	b3	b4	b5	b6	b7	RMSE
Battery 2020	0.006	6800	0.0242	0.155	0.139	0.907	0.0215	1.5
Gen1	0.1574	0.9807	0.0054	0.5205	-	0.3514	0.1137	1.487
Kokam	0.0223	2400	0.037	0.0651	-	0.8055	0.042	1.41

5.2.1 Modelling Performance

The modelling performances are presented in Figure 5.6, Figure 5.7, and Figure 5.8. Since the database is too large to present here, only selected parts are specified per case. The red lines refer to the experimental data, while the black dash lines refer to the predicted value. From the figures, two types of lines fit well in general. For the battery 2020, more than one thousand points were extracted from the raw data, and the RMSE value also shows that only slight error exists.

The modelling performance of the generated cells is acceptable as well, though is not as good as the performance of the cells in project Battery 2020. What is more, it is found that the prediction value may have larger errors if the testing temperature is higher. The actual state of health of the lithium-ion battery can drop quicker than the prediction value.

The modelling performance of the Kokam cells is acceptable, though its performance is not better than that of the generated cells generally. This is because the number of tests for the Kokam cells are higher than the tests of the generated cells. It can be seen from the figure that when the testing temperature is high, the actual ageing process is quicker than the predicted one. If the charging rate is high, the ageing process can be too quick to trace its ageing process.

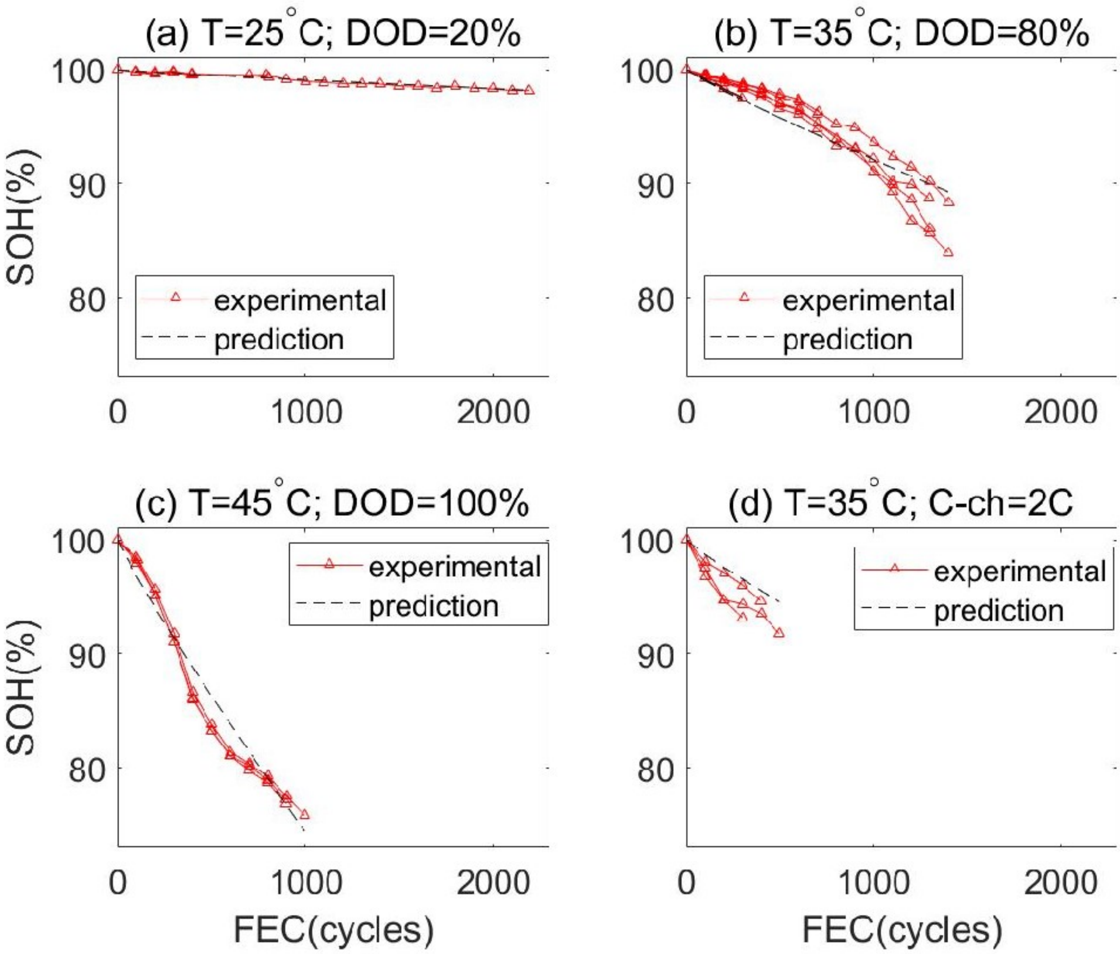

Figure 5.6: Cycling Modelling performance in project battery 2020

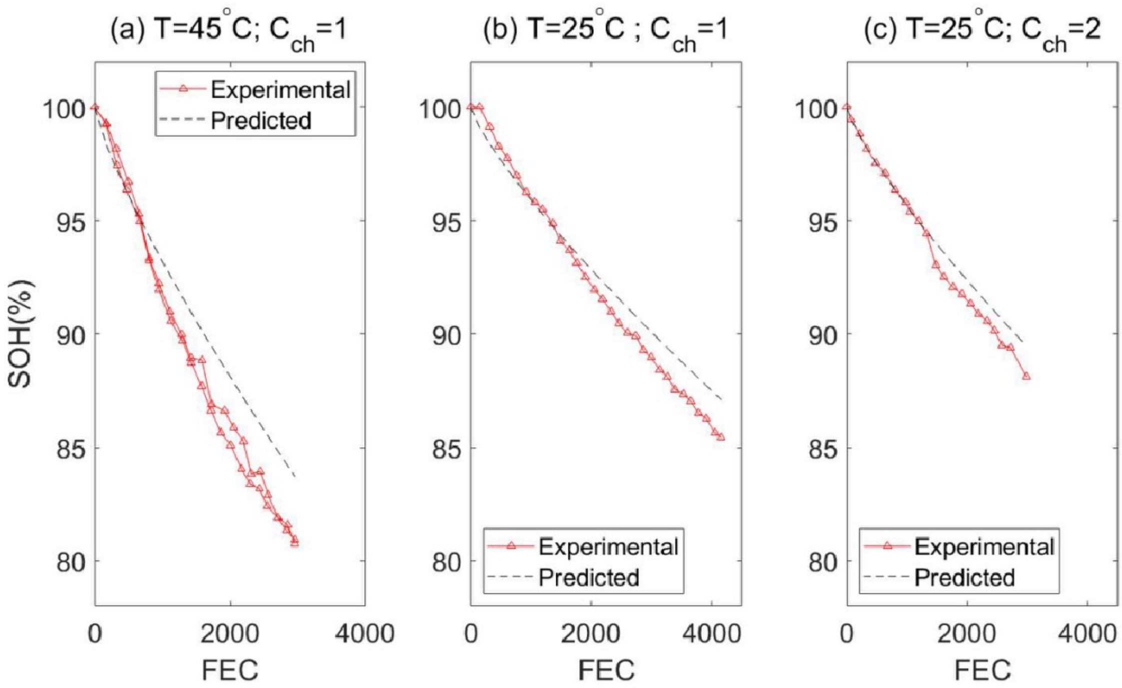

Figure 5.7: Cycling Modelling performance of the Generated cells in project Mat4Bat

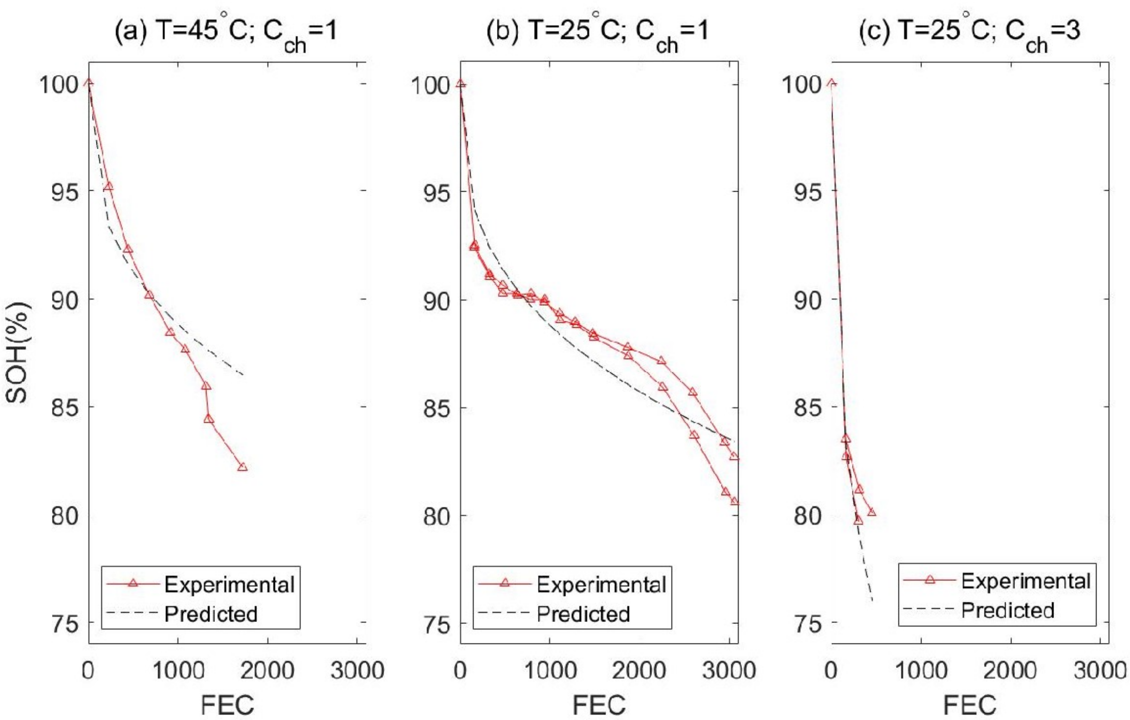

Figure 5.8: Cycling Modelling performance of the Kokam cells in project Mat4Bat

5.2.2 Ageing factor significance comparison

The significance of the stressed factors is evaluated from the equation form, the equation parameters (from b1 to b7) and the modelling performance, etc. The FECs plays an important role in the ageing process. It is an interesting observation that some battery cells' ageing accelerate while the driving cycles/FECs are increasing, and some decelerate. The more the battery is cycled, the more it ages. Compared with the C-rate, the cycling temperature and the SOC-window also have a huge influence on the battery ageing. The evaluation results are presented in Table 5.5.

In Figure 5.9, one can find the SOH value after 1000 cycles under different SOC-windows when the testing temperature is 25 degree. The first four SOC-window group, whose DOD values are all 20 percent, show high SOH after numerous cycles. The second three SOC-window group, whose DOD values are 50 percent, ranks the second. When the DOD value is 100 percent, the SOH shows the lowest. It also verifies the significance of the SOC-window, which cannot be ignored when it comes to the battery ageing process.

Table 5.5: The significance of each factor

Stressed factors	Significance
Full Equivalent Cycles (FEC)	+++++
Cycling Temperature	++++
SOC-window	++++
C-rate (charge)	+++
C-rate (discharge)	++

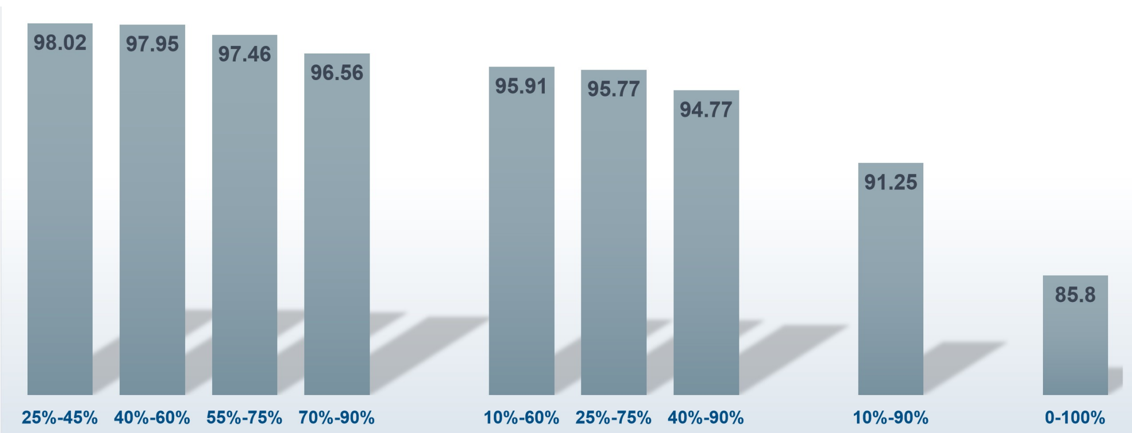

Figure 5.9: State of Health (SOH) after 1000 cycles under different SOC-window

5.3 Degradation functions

The degradation functions of all the researched projects throughout the thesis are listed in Table 5.6.

Table 5.6: Degradation functions for large commercial cells

No.	Author or Project	Cell chemistry	Cell Capacity $[Ah]$	Manufacturer	Degradation Function	Ref.
1	**Batteries 2020**	**NMC442**	20	**EIG**	$SOH_{cycling} = 100 - 0.006$ $e^{[-6800(\frac{1}{T}-\frac{1}{T_{ref}})+0.0242DOD+0.155C_{ch}+0.139C_{dch}]}$ $FEC^{0.904}[1 - 0.0215mSOC(1 - \frac{mSOC}{mSOC_{ref}})]$	[27]
2	**Batteries 2020**	**NMC442**	20	**EIG**	$SOH_{calendar} = 100 - 3.5 * 10^{9} SOC^{3.56}$ $Days^{1}.29e^{\frac{-1.13*10^{5}}{8.314(T+273)}}$	[28]
3	**Mat4Bat**	**NMC111 (GEN1)**	16	**Mat4Bat**	$SOH_{cycling} = 100 - 0.1574$ $e^{[-0.9807(\frac{1}{T}-\frac{1}{T_{ref}})+0.0054DOD+0.5205C_{ch}]}$ $FEC^{0.3514}[1 - 0.1137mSOC(1 - \frac{mSOC}{mSOC_{ref}})]$	[29]
4	**Mat4Bat**	**NMC**	16	**KOKAM**	$SOH_{cycling} = 100 - 0.0223$ $e^{[-2400(\frac{1}{T}-\frac{1}{T_{ref}})+0.037DOD+0.0651C_{ch}+]}$ $FEC^{0.8055}[1 - 0.042mSOC(1 - \frac{mSOC}{mSOC_{ref}})]$	[29]
5	**Mat4Bat**	**NMC**	16	**KOKAM**	$SOH_{calendar} = 100 - 2.36 * 10^{6} SOC^{1.02}$ $Days^{0.47}e^{\frac{-5.58*10^{4}}{8.314(T+273)}}$	[29]
6	**S. L. Hahn, et al.**	**NMC111**	50.8	**Litec battery GmbH**	$SOH_{calendar} = 100 - 2.22 * 10^{6} SOC^{0.296}$ $Days^{0.625}e^{\frac{4.49*10^{4}}{8.314(T+273)}}$	[30]

[a] Cells included means the cells those are selected in this thesis work.
[b] All the battery cells have graphite as anode material.No information specify the geometry of the cells or electrolytes.

6
Conclusion and Future Work

6.1 Conclusion

In this thesis, the latest lithium-ion battery ageing data, including the calendar ageing data and cycling ageing data, were collected, filtered, classified, and analyzed. A prediction ageing model was developed and can be used to predict the ageing trend of a certain type of lithium-ion battery. The researched types are listed in Table 5.6 as a quick look.

During the process of the literature study, different major factors contributing to the ageing of lithium-ion cells were identified. As to the calendar ageing, they are the SOC, the storage temperature and the storage time. As to the cycling ageing, they are the cycling temperature, the SOC-window, the charging rate and the FECs. In the thesis, two factors, the DOD and the mid-SOC, are used to identify the SOC-window.

The battery ageing model was developed by using the semi-empirical method. The model was developed based on the open-source data. After the initial data was utilized, the model was trained and got a general prediction equation, which can be used to predict the trend of the battery ageing. After the modelling development, the model was also validated. The modelling performance was evaluated, and each stressed factors were established.

It is found that different ageing factors weigh differently. As to the calendar ageing process, storage time has the most influence on the reduction of the battery SOH. The storage temperature weighs more than the storage SOC. As to the cycling ageing process, the FECs weighs the most. Then the factors cycling temperature and the SOC-window rank the second. C-rate, including the charging rate and the discharging rate, is also influential for the ageing process.

Regarding to the EV battery maintenance, it is good to store the battery in a place with low temperature and with a low SOC level in the batteries. It is also good to charge daily by using small DOD during driving that can help reduce the pace of degradation and also to use the regenerated power more efficiently.

The study can be applied when someone has a certain type of battery and wants to predict the future ageing trend of the battery. The prediction results can be used for a battery simulation and can be utilized as the battery ageing reference data.

6.2 Discussion

6.2.1 Sustainability

Energy is the dominant contributor to climate change. With electrification growing, the electric drive system is replacing the traditional combustion engine. This project contributes to the theory and the application of the EV development field and pushes forward the access to affordable, reliable, sustainable, and modern energy.

Pure electric vehicle only uses electricity as its propulsion power. This technology improves dramatically the transportation system and leads to building resilient infrastructure, promote sustainable industrialization and foster innovation. Electric charging station will take place of the gas station in the future, and transportation modernization will be influential to everywhere in our daily life.

6.2.2 Ethics

This thesis is based on experimental data from the open source. It is crucial to claim the source and its authors, and cite it correctly. A tool named 'GetData' was used to gain the trending figure. This meets the demand in the IEEE code of Ethics 'to seek, accept, and offer honest criticism of technical work, to acknowledge and correct errors, to be honest and realistic in stating claims or estimates based on available data, and to credit properly the contributions of others'.

The thesis was completed with the help of CEVT. After the thesis is finished, one copy should be sent to CEVT to make sure that some confidential data are not disclosed and will not do harm to the benefit of the company. This meets the demand in the IEEE code of Ethics 'to avoid real or perceived conflicts of interest whenever possible, and to disclose them to affected parties when they do exist.

6.3 Future Work

This thesis does not take the interaction between calendar ageing and cycling ageing into consideration, though in fact, the two types of ageing process can influence each other, and sometimes dramatically. For example, the calendar ageing may also happen during the cycling ageing tests. Moreover, though the initial unreasonable testing data have been filtered, there may still exist some errors. The prediction results may be influenced when the testing condition is of a too high or too low temperature. Another reason of the existing errors is that the limitation of the amount of the open-source data. The research of the lithium-ion batteries is still a new field for the EV technology, so the data related to the EV-used batteries, for example, the batteries with huge capacity, are still limited.

Based on those limitations that exist during the research, some further studies may be required. As the two types of ageing processes can influence each other, a combined ageing model deserves being considered, which is able to present the calendar ageing process and the cycling ageing process simultaneously.

During the modelling development, Matlab can only automatically train the models which contain less than five stress factors. When the stress factors are over six, the model needs to be trained manually. The code can be optimized by setting a function which enables the model being trained automatically when the stressed factors are over six.

With the time passing by, more and more tests related to the battery ageing may be brought out. A more accurate model with a wider temperature range and a wider SOC-window can be realized.

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A
Appendix 1

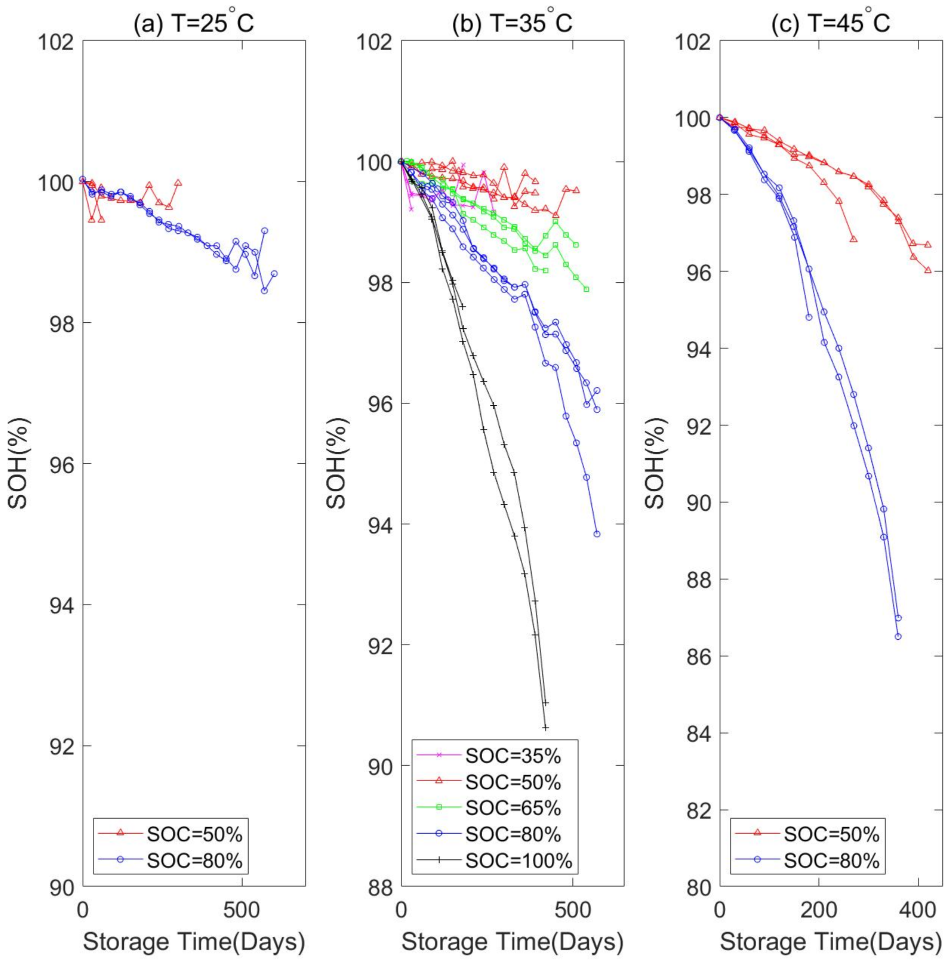

Figure A.1: Calendar aging data in battery2020 project.(a)Temperature = 25°C; (b)Temperature = 35°C; (c)Temperature = 45°C

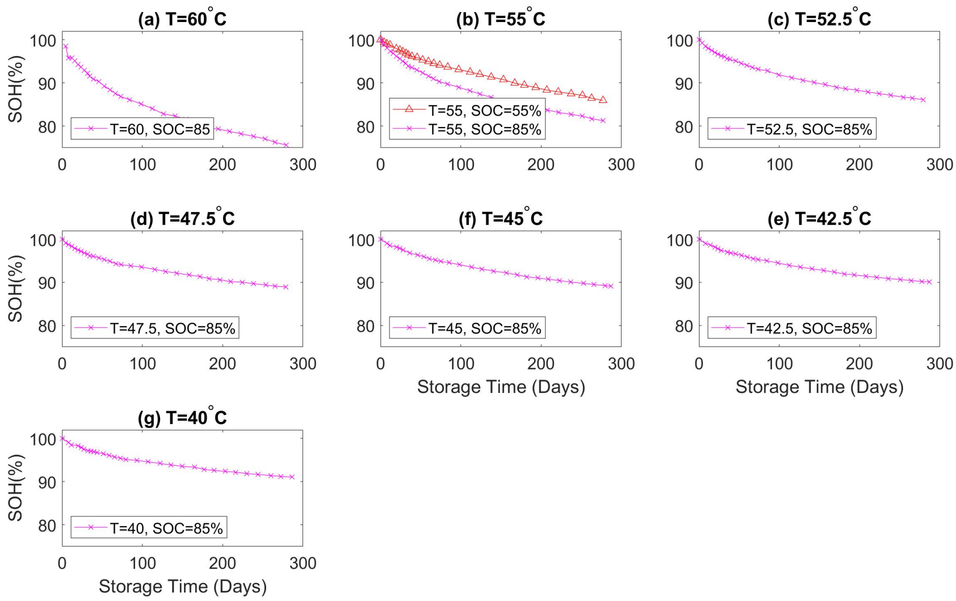

Figure A.2: Calendar aging data of the LGB cells under other temperature conditions

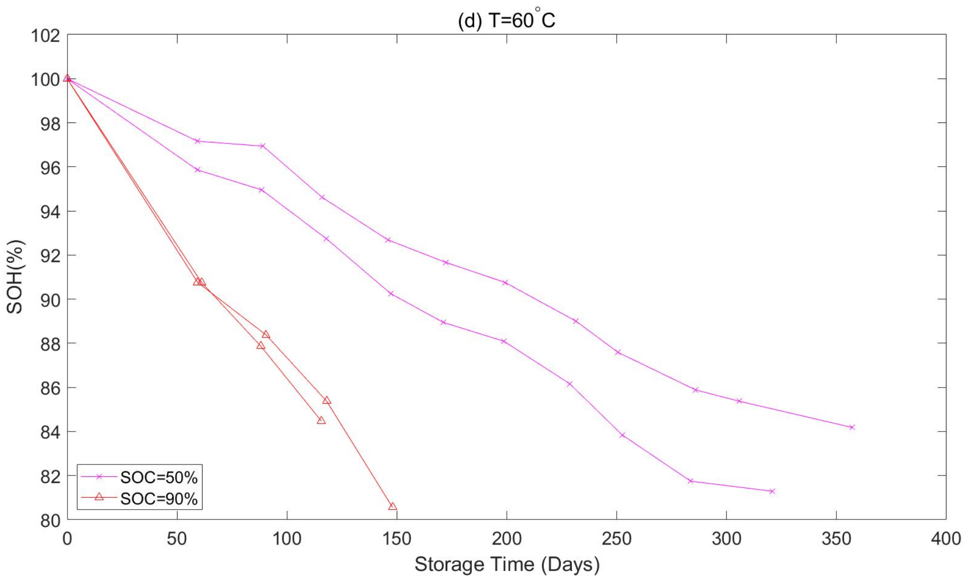

Figure A.3: Kokam Calendar aging data under testing temperature of 60 degree

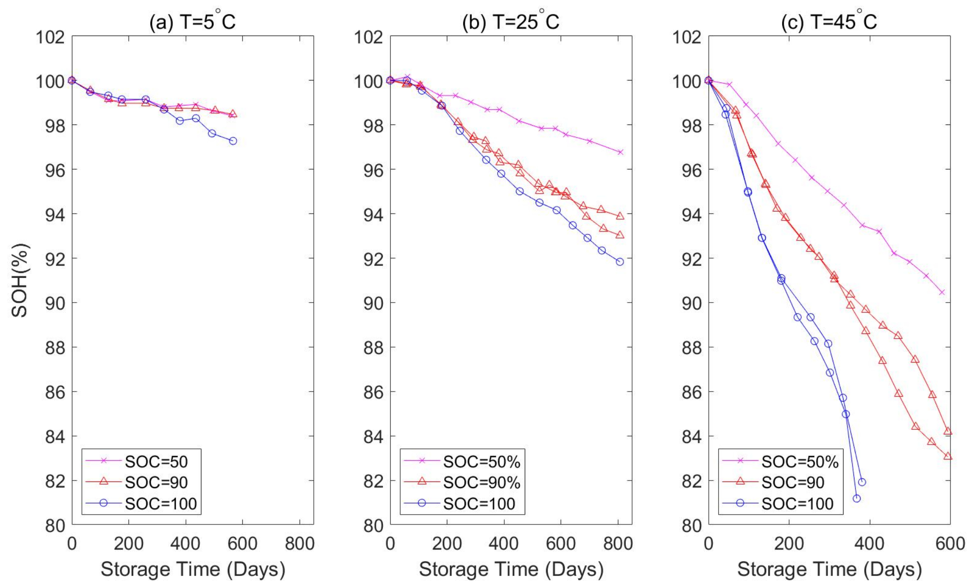

Figure A.4: Kokam Calendar aging data under testing temperature of 5, 25, 45 degree

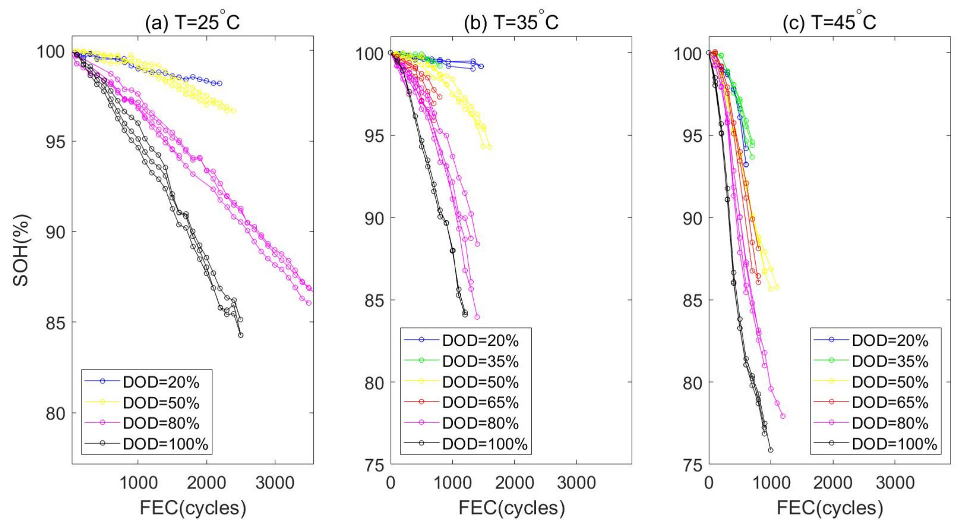

Figure A.5: Kokam Calendar aging data under testing temperature of 5, 25, 45 degree

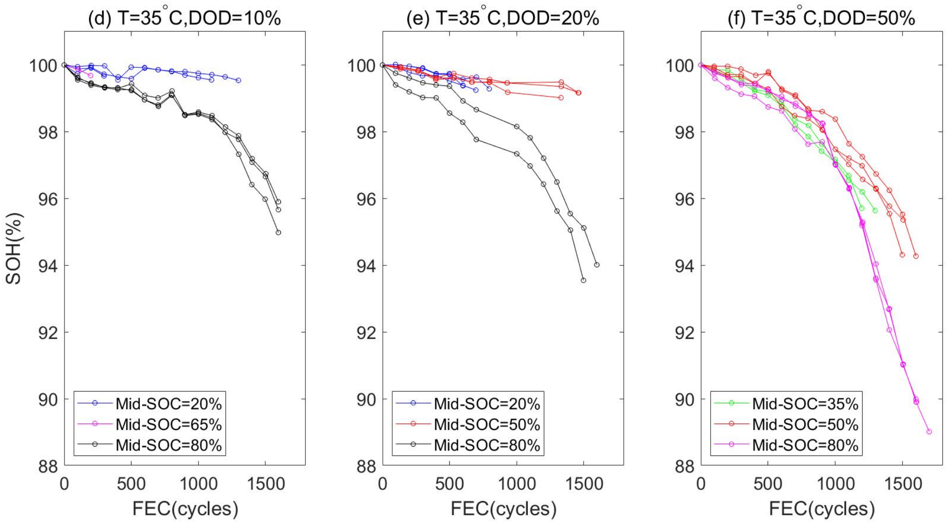

Figure A.6: Cycling test raw data in Battery2020

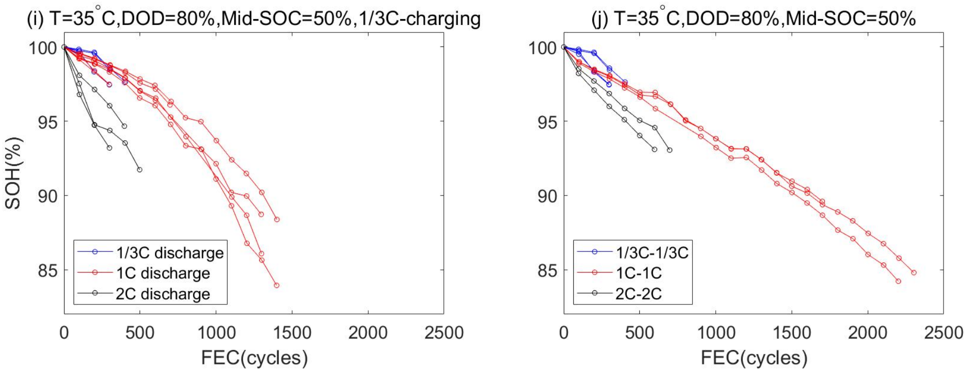

Figure A.7: Cycling test raw data in Battery2020

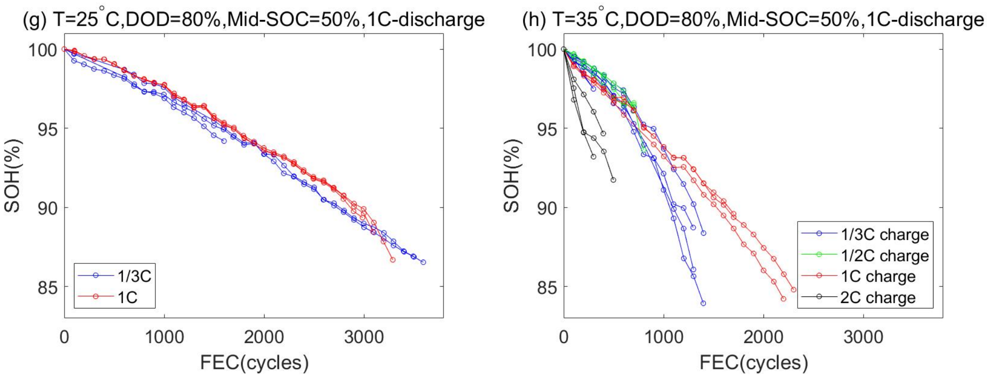

Figure A.8: Cycling test raw data in Battery2020

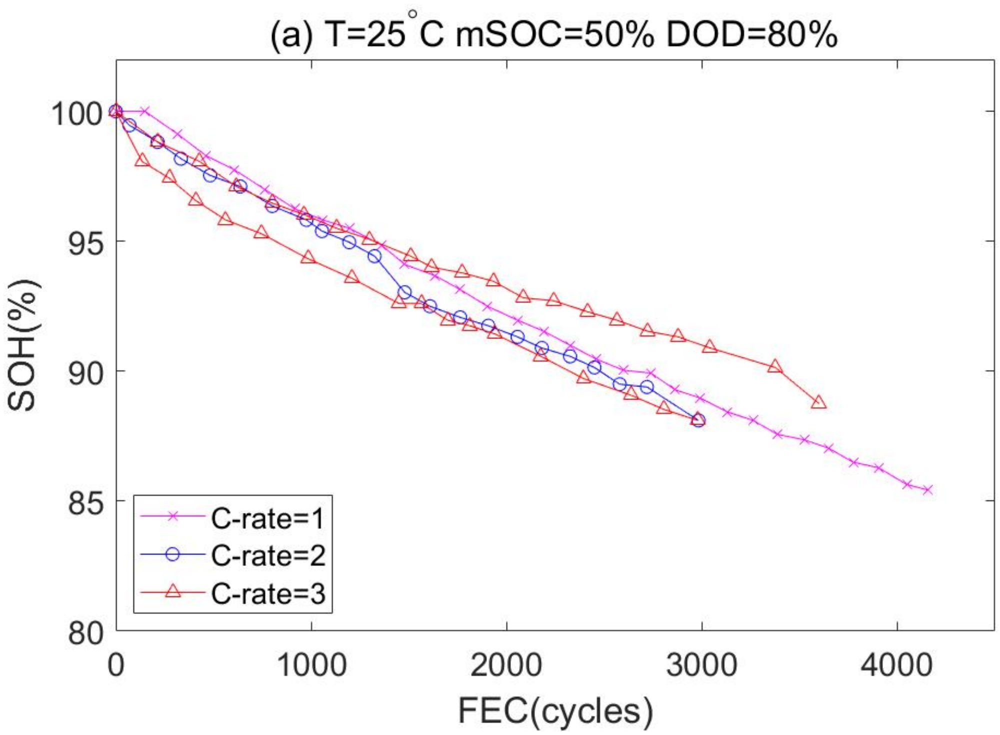

Figure A.9: Cycling test raw data of the Kokam cell

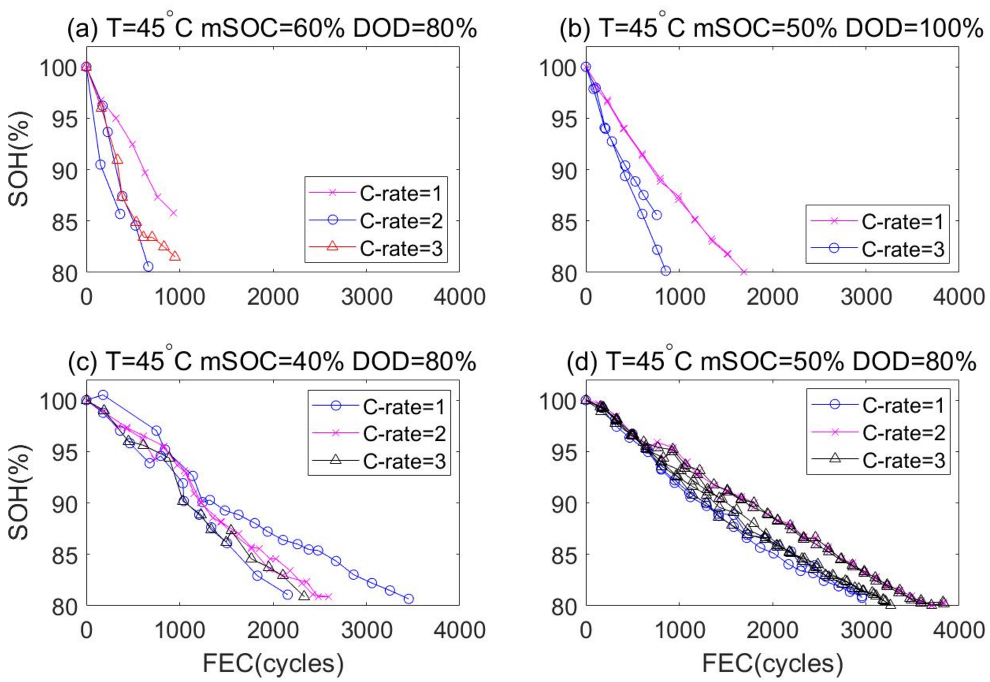

Figure A.10: Cycling test raw data of the Kokam cell

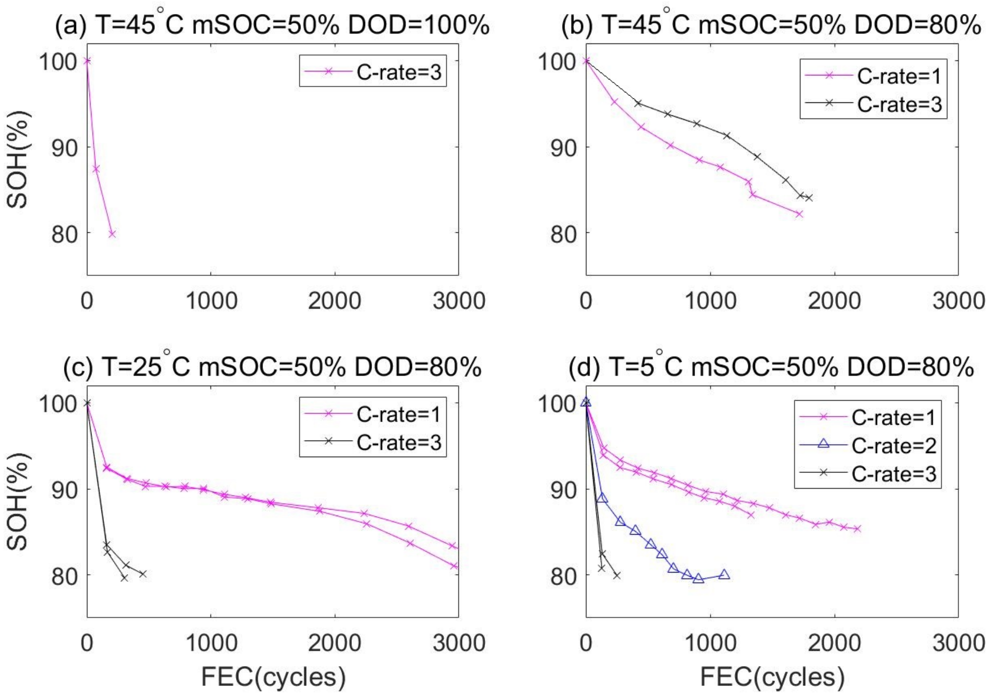

Figure A.11: Cycling test raw data of the generation cell in Project Mat4Bat

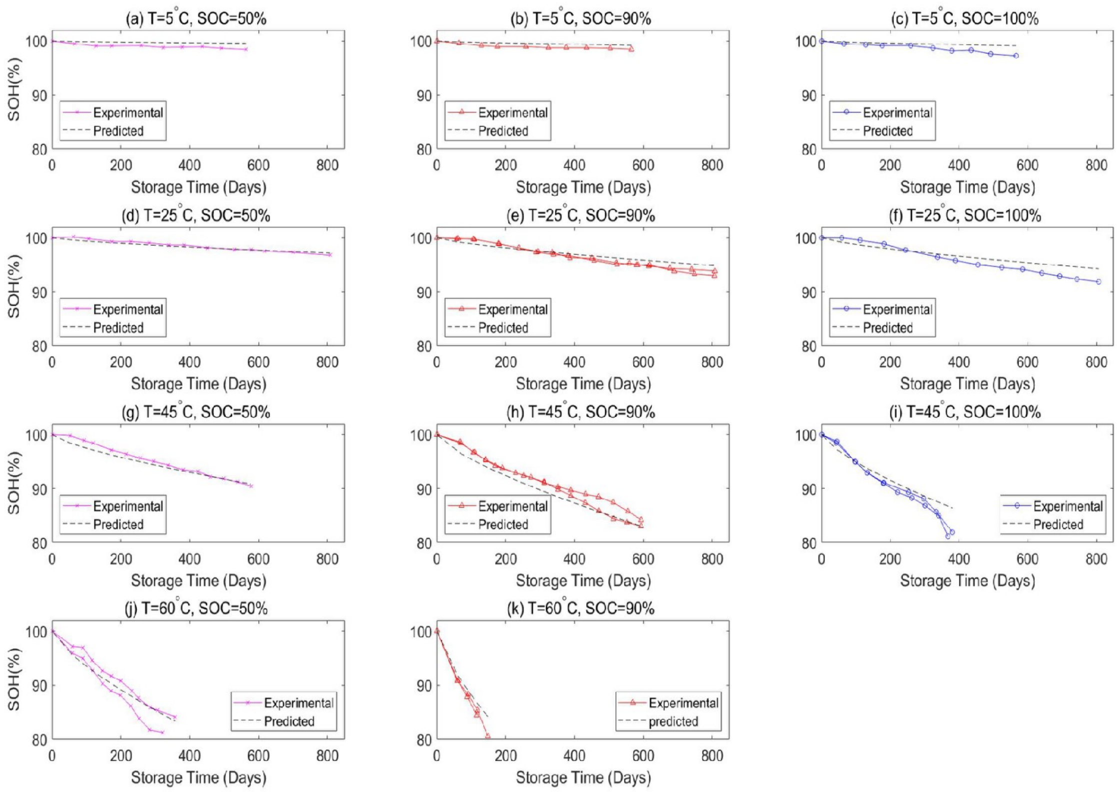

Figure A.12: Cycling modelling predicted performance of the cells in Project Mat4Bat

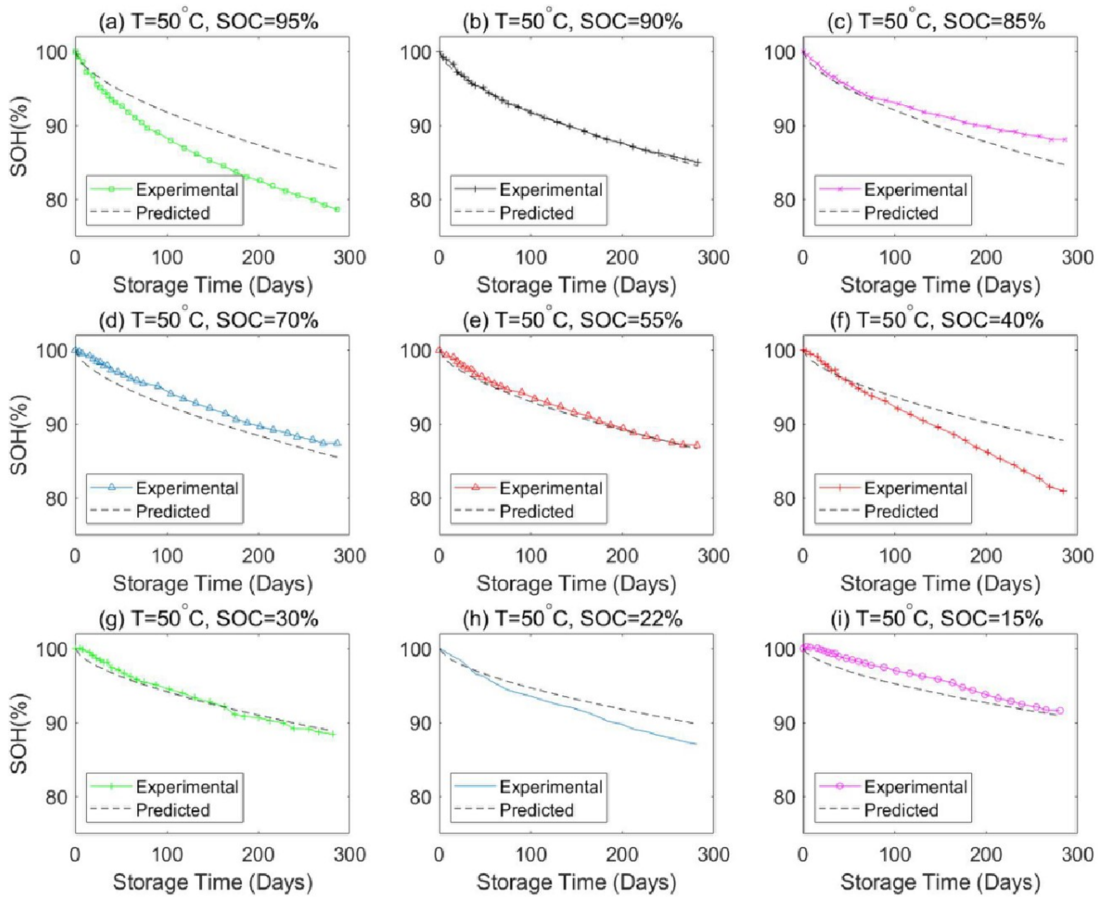

Figure A.13: Calendar modelling predicted performance of the LBG cells in 50 degree

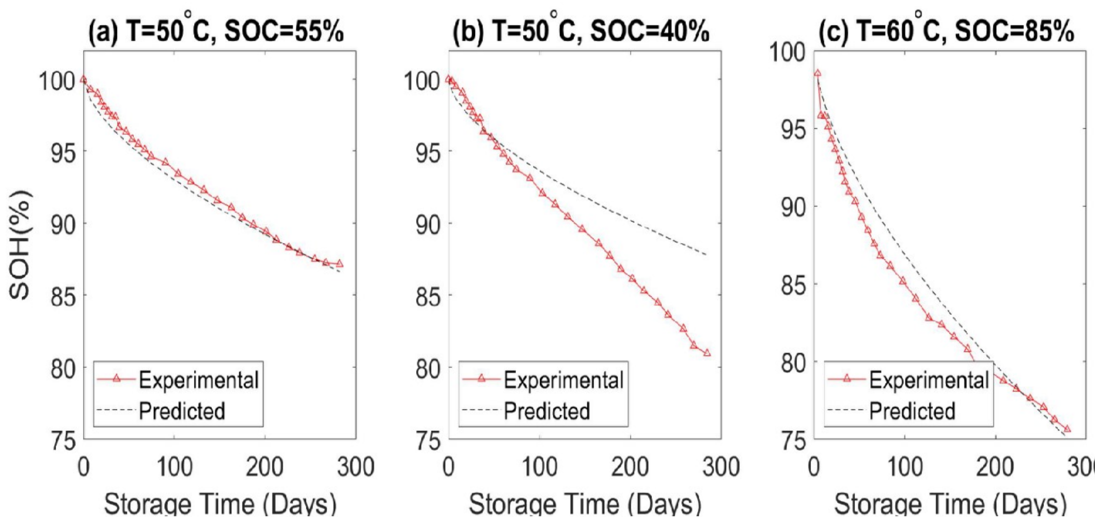

Figure A.14: Calendar modelling predicted performance of the LBG cells in Other temperature

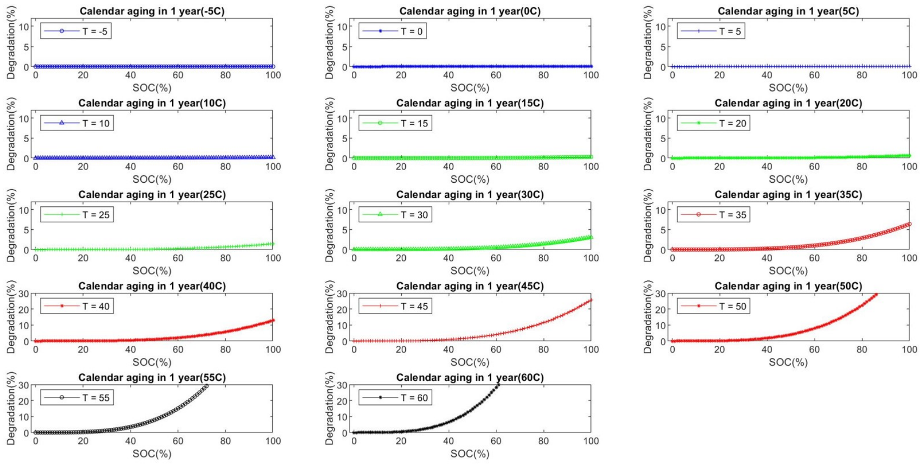

Figure A.15: Battery degradation in one year in different storage temperatures

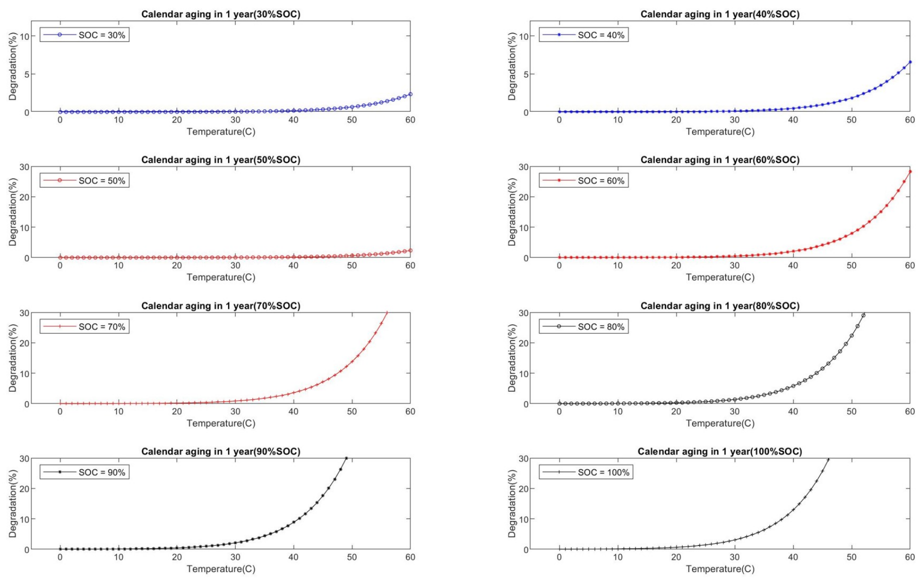

Figure A.16: Battery degradation in one year in different storage SOCs

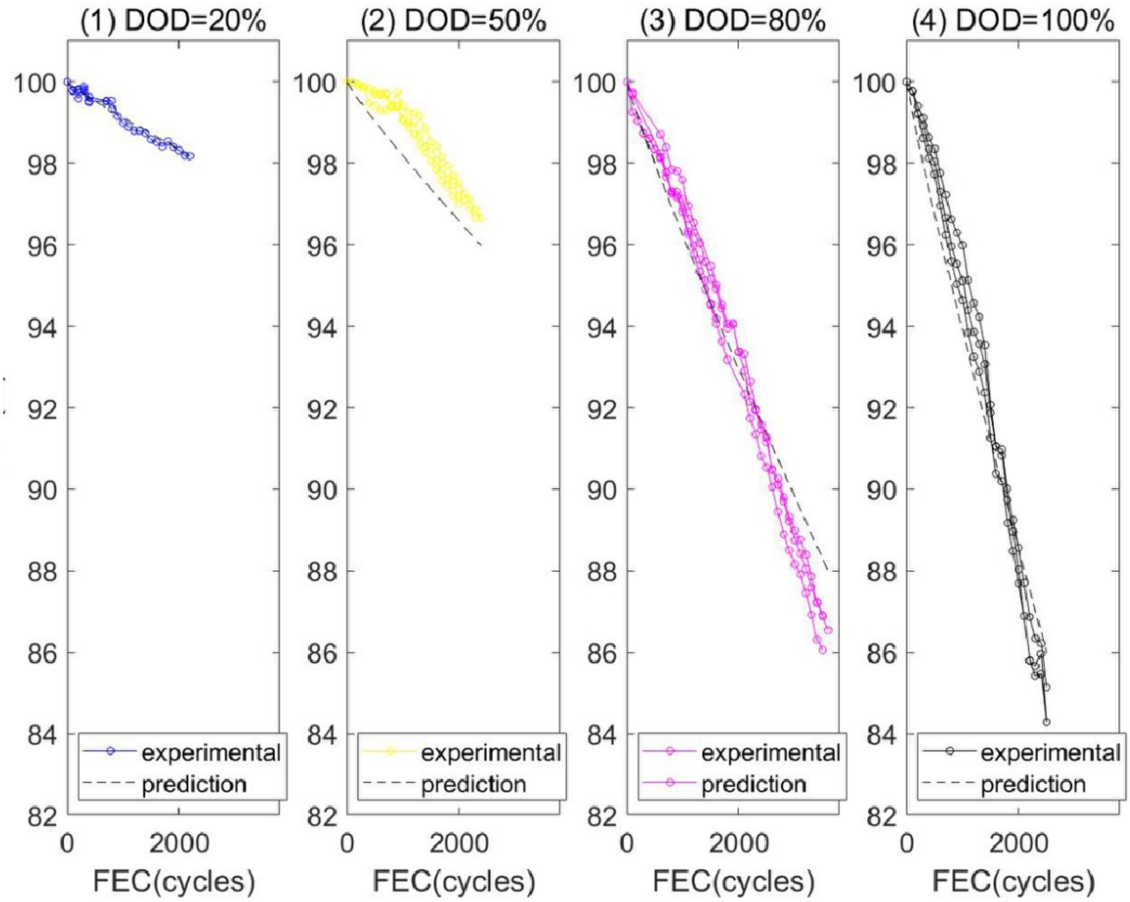

Figure A.17: Cycling modelling predicted performance of the cells in Project Battery 2020

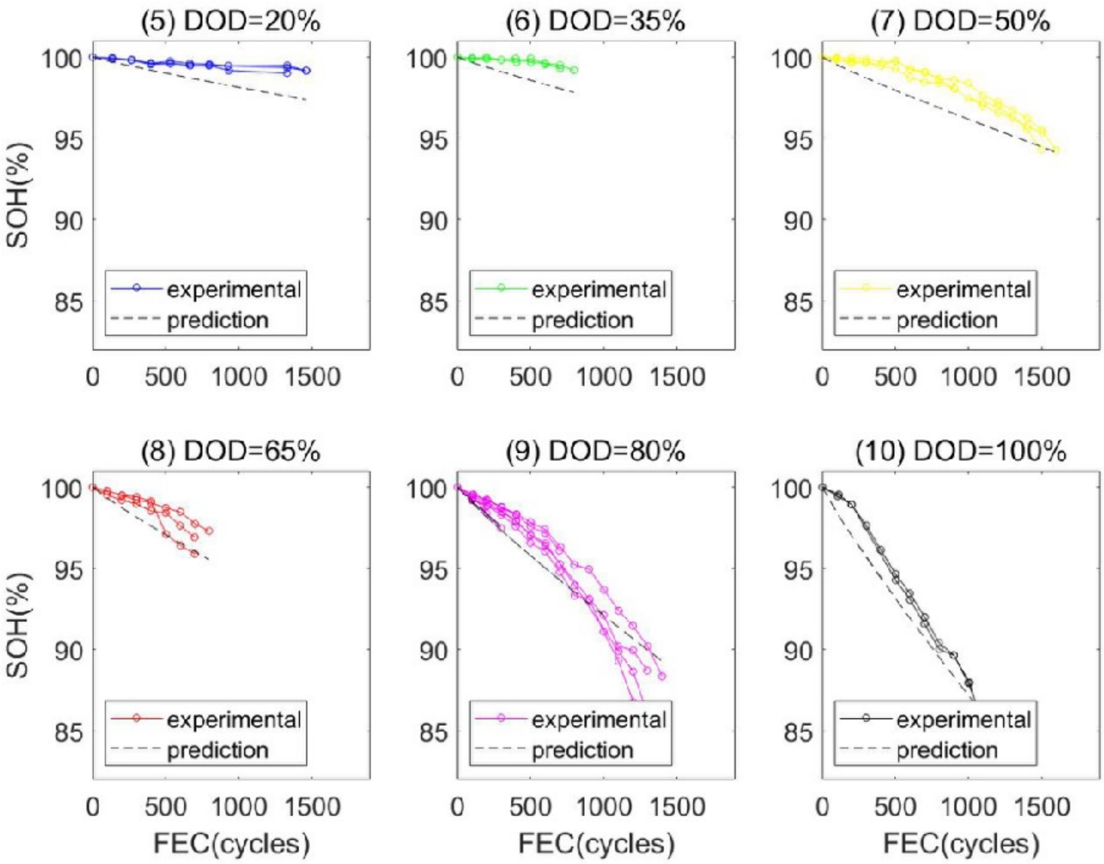

Figure A.18: Cycling modelling predicted performance of the cells in Project Battery 2020

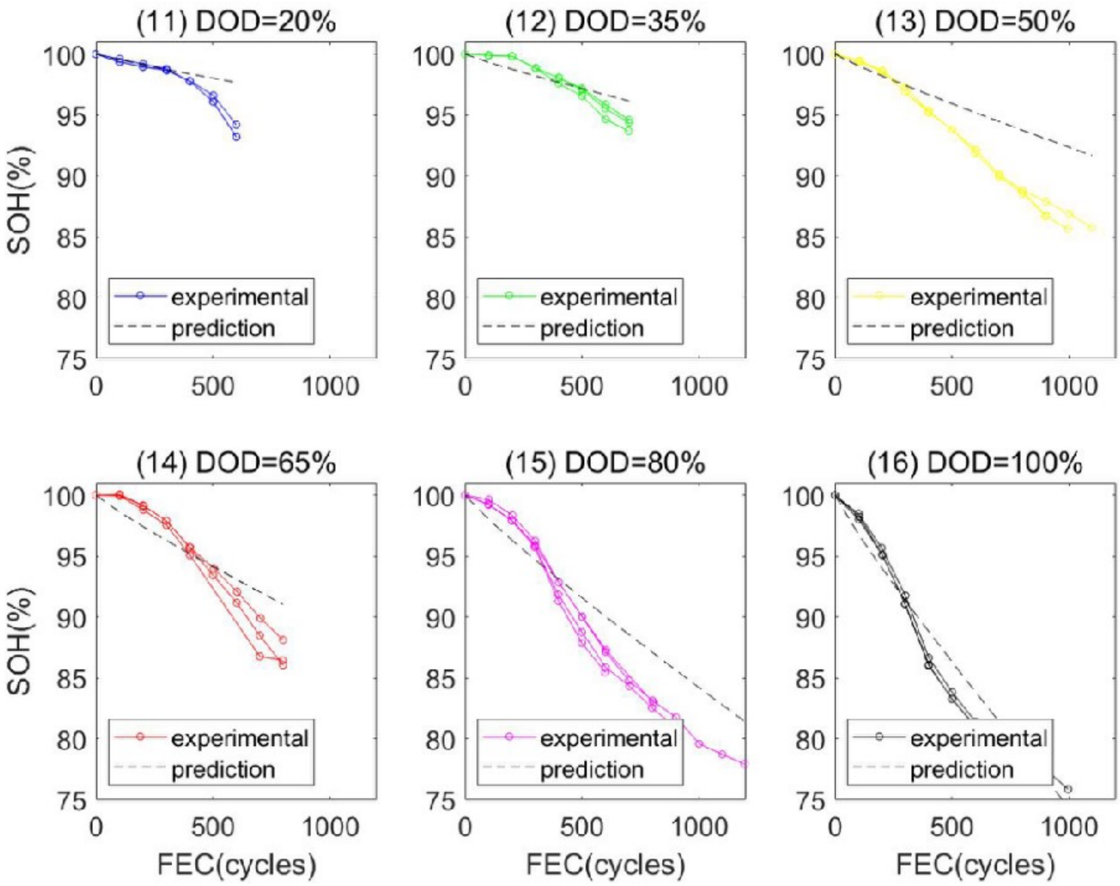

Figure A.19: Cycling modelling predicted performance of the cells in Project Battery 2020

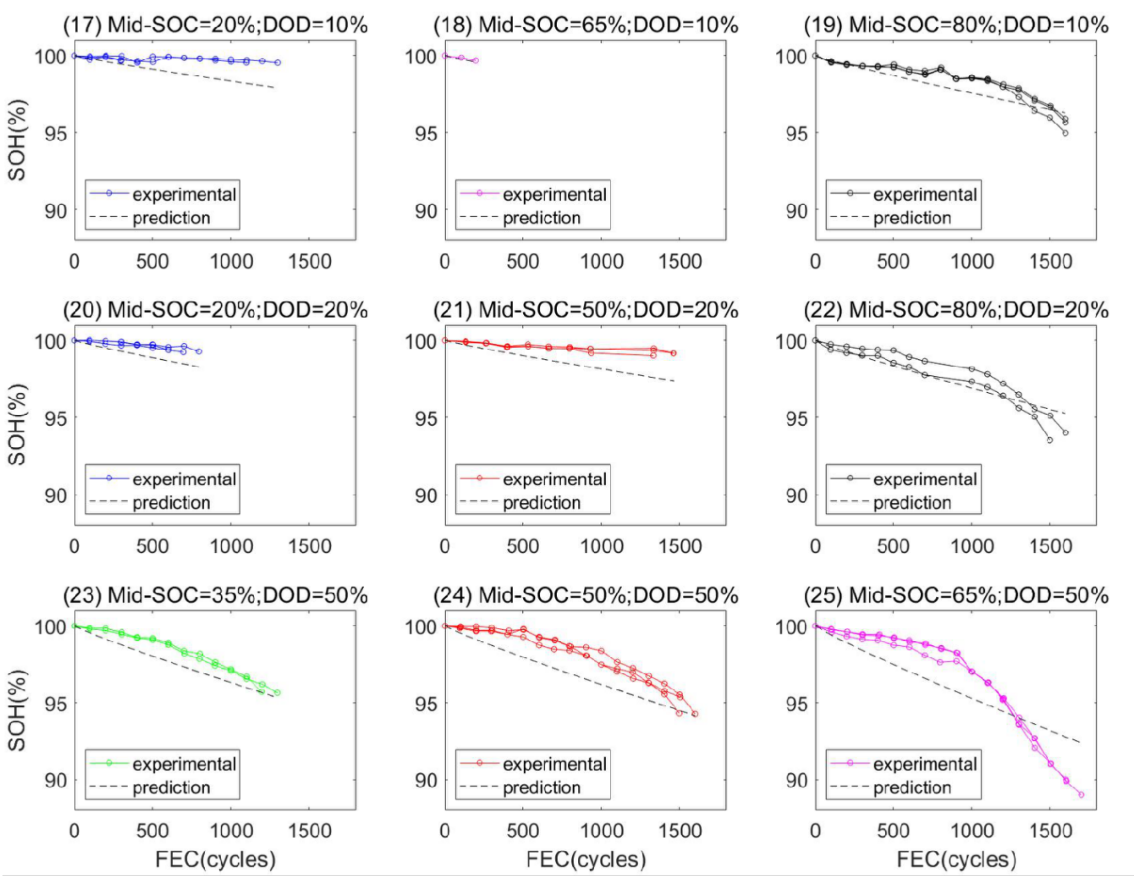

Figure A.20: Cycling modelling predicted performance of the cells in Project Battery 2020

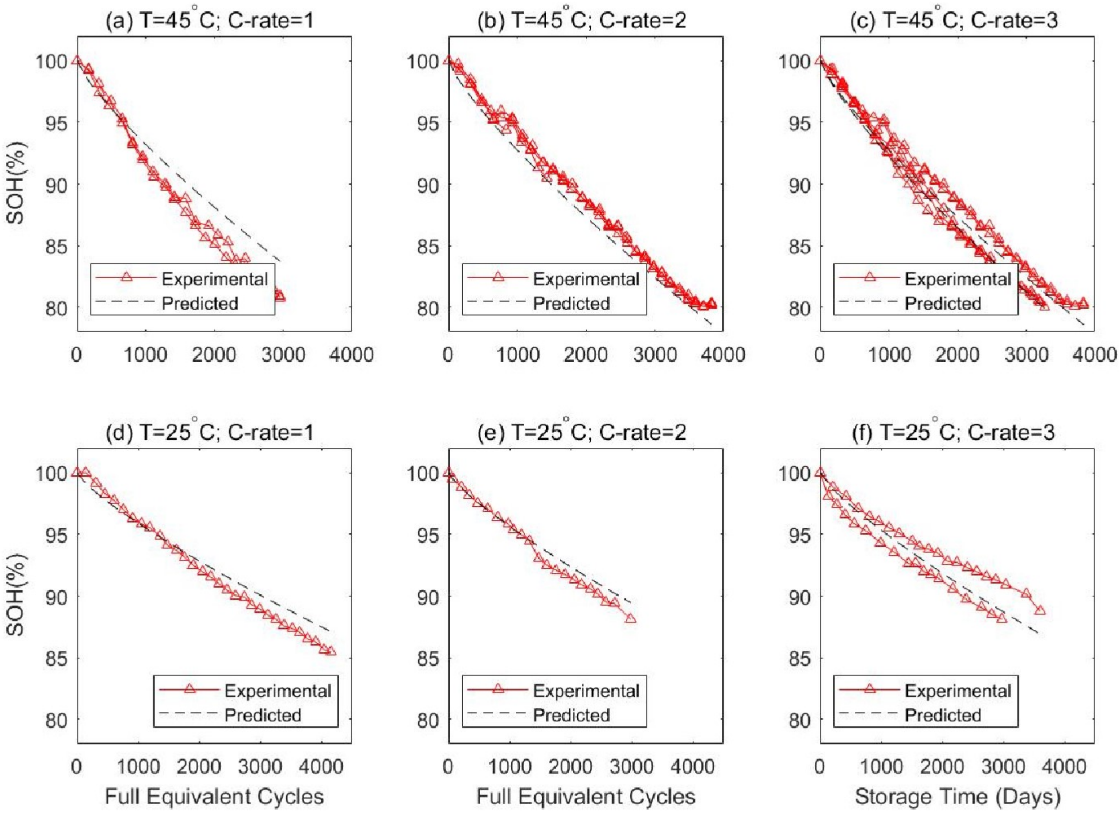

Figure A.21: Cycling modelling predicted performance of the Kokam cells

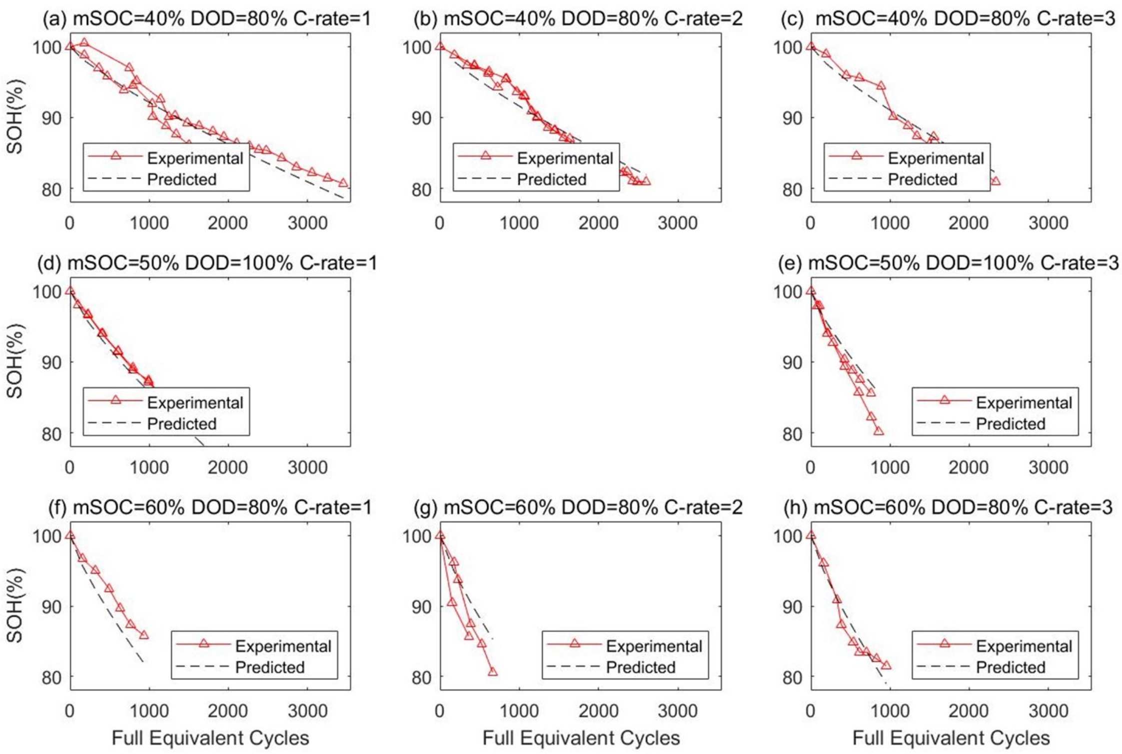

Figure A.22: Cycling modelling predicted performance of the Kokam cells

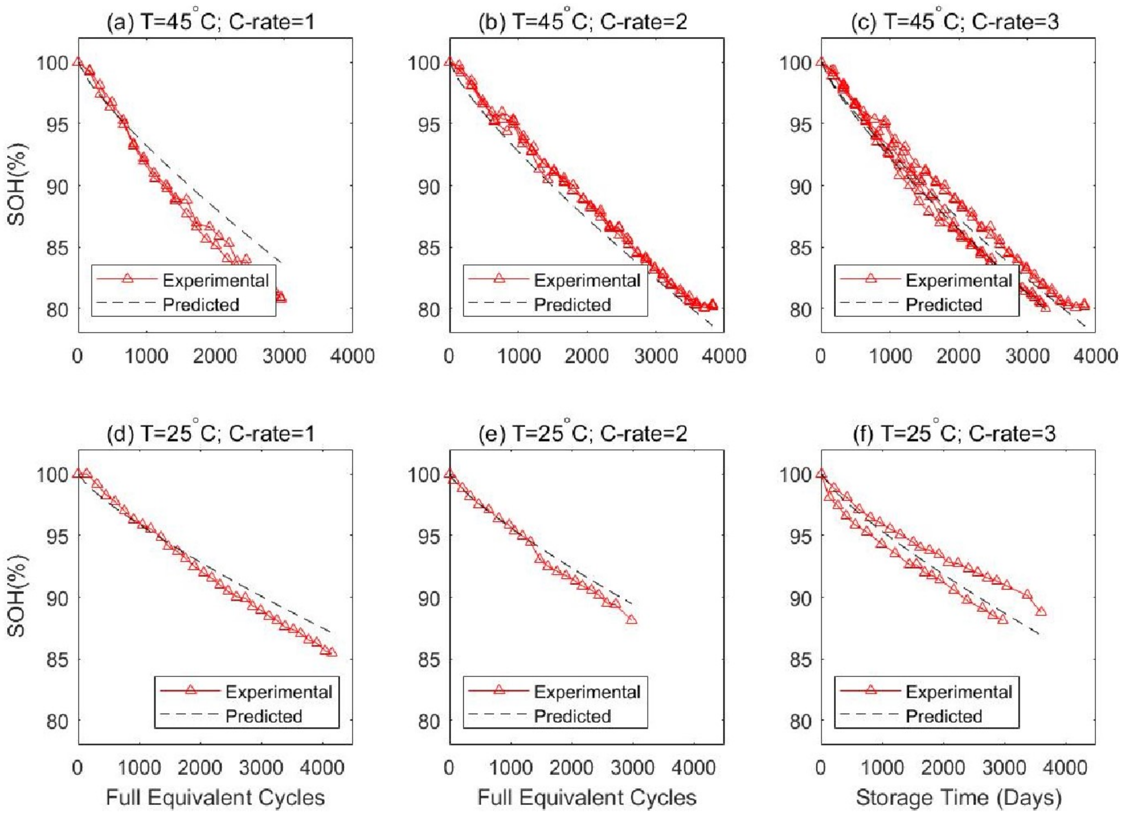

Figure A.23: Cycling modelling predicted performance of the generated cells

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