

**BATTERY STATE OF HEALTH
DETERMINATION
THROUGH VARIOUS TECHNIQUES**

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Declaration

I hereby, declare that this manuscript, entitled “Battery state of health determination through various techniques”, is my own work but quotations and citations are done based on other scientists and them I referenced at the end of manuscript. I also declare that, to the best of my knowledge and belief, it has not been previously or concurrently submitted, in whole or in part, for any other degree or diploma at Nazarbayev University or any other national or international institution.



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Abstract

In the 21st century, there has been a significant increase in demand for electric vehicles and energy storage technology. To meet this demand, various technologies have been developed, including lithium-ion batteries, sodium-ion batteries, and vanadium flow batteries. However, many high-energy batteries face challenges related to material longevity and safety. As a result, it is crucial to incorporate a battery state determination algorithm into battery management systems. There are several parameters that determine the battery's state, such as its health, charge level, power status, function, and safety.

In this manuscript, a new algorithm is developed for assessment of the state of health of the battery through various techniques. The secondary and primary batteries were used for creating the state of health estimation model. As a secondary battery, a popular Li ion (NCM) cylindrical battery referred to as NCR18650 (Panasonic was selected and as a primary battery cylindrical lithium thionyl battery (Minamoto) was selected.

In this research work, the state of charge of a battery was determined based on the thermodynamics parameters of the battery which is fitted through equation: $SOC = \alpha + \beta * \Delta H + \gamma * \Delta S$, where ΔH – enthalpy, ΔS – entropy, SOC – state of charge, and α, β, γ – are coefficients which depend on state of health and chemistry of a battery [1]. on of the dependence of coefficients to the state of health of the battery was done. One of the problems during the thermodynamics parameters measurement includes its long measurement time. Therefore, more fast measurement method of entropy and enthalpy was developed.

Additionally, the state of health of the secondary battery was analyzed by and emerging technique of machine learning. A suitable algorithm and feature was chosen to assess state of health of the battery based on charge profile data.

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List of Abbreviations & Symbols

LIB	Lithium-ion battery
XRD	X-ray Powder Diffraction
XPS	X-ray Photoelectron Spectroscopy
SEM	Scanning Electron Microscopy
EDS	Energy Dispersive Spectroscopy
TEM	Transmission Electron Microscopy
ICP	Inductively Coupled Plasma analysis
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy
CE	Coulombic efficiency
Li	Lithium
Na	Sodium
ESS	Energy storage system
SEI	Solid electrolyte interphase
SOC	State of charge
SOH	State of health
ML	Machine learning
DL	Deep learning
AI	Artificial intelligence
SP	Spherical particle

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Chapter 1 – Introduction

1.1 The goal and objective of the work

The main idea of the research is to create model that can assess the state of health of the battery based on the non-destructive analysis. Therefore, the dependence of the state of health of the battery is analyzed for basic parameters such as temperature, voltage, current, and time. Lithium-ion batteries are very popular batteries in applications for electric vehicles, smartphones, and electronic devices. Consequently, all created state of health assessment methods will be analyzed on commercial lithium-ion batteries with the following types: secondary cylindrical battery and primary cylindrical battery. Generally, battery aging is classified as follows: standing aging and cycling aging. In this research work, only cycling aging will be considered by cycling the battery continuously. The cycling aging of the battery depends on the following factors: chemistry of the battery, current rate, depth of discharge, temperature of cycling, and the number of cycles. In this thesis, the following factors are considered: chemistry of the battery and the number of cycles.

1.1 Aims and objectives

The aim of the master's thesis is to explore and develop new features for determining the state of health of batteries using various techniques. To achieve this objective, the following research questions must be addressed in order to better understand the research topic:

1. What state of health estimation methods have been developed till?
2. What are the advantages and disadvantages of each method for determining the state of health?
3. In what ways can the entropymetry technique be utilized for determining the state of a battery?
4. How can the thermodynamic parameters of a battery be computed effectively?
5. What are the most efficient ways of applying artificial intelligence methods to estimate the state of health of a battery?

To accomplish the master thesis work, the overall work is divided into the following main tasks:

1. To construct the temperature chamber and to automate the experiment
2. To obtain thermodynamics profile of secondary battery at various cycles
3. To obtain thermodynamics profile of primary battery at various cycles
4. To apply the machine or deep learning for the state of health estimation
5. To create the state of health estimation model based on collected data.

1.1.1 The objectives of the work

The aim of the master's thesis is to explore and develop new features for determining the state of health of batteries using various techniques. Notably, the investigation can be divided into the following tasks:

- To construct the temperature chamber and to automate the experiment;
- To develop a new entropy evaluation method;
- To obtain thermodynamics profile of primary battery at various state of charge.
- To obtain thermodynamics profile of primary battery at various cycles based on developed new entropy evaluation method
- To apply the machine or deep learning for the state of health estimation
- To show some relationship of thermodynamics parameters to state of health

This research will be beneficial for the development of the battery management system.

1.1.2 The novelty of the research

This research developed the new method of estimation using entropy of a battery. Based on this method, thermodynamics profile for the primary and secondary battery is provided. In addition, the efficient way of determination state of health through artificial intelligence techniques and thermodynamics parameters is analyzed.

1.2 Methodologies and techniques

The initial research method involved developing a search strategy to conduct a literature review and achieve the research objectives. Firstly, the review considered numerous articles from different databases, such as Google Scholar, NU library, and Scopus. The experimental phase was carried out in the second step of the research. Prior to the

experimental phase of the master's thesis, the necessary equipment for thermodynamic computations was prepared.

Following the preparation of the equipment, thermodynamic parameters of the NCR 18650 cylindrical battery and lithium thionyl cylindrical battery were analyzed at various states of health and states of charge. Furthermore, the collected charge-discharge profile of the battery was used to evaluate the state of the battery using artificial intelligence technique.

The BT2000 Arbin battery tester was used to test the batteries. To measure the temperature, UT320 thermometers were used. The results of the thermodynamic parameters and charge-discharge profile of the battery were processed using MATLAB (a software with a Nazarbayev University license for students) and Python 3.10 (an open-source software).

The primary objective of the research was to identify features of the state of the battery that could be useful for battery management system applications. The research was conducted from June 2021 to April 2023, and the main steps of the research are shown in Figure 1.1.

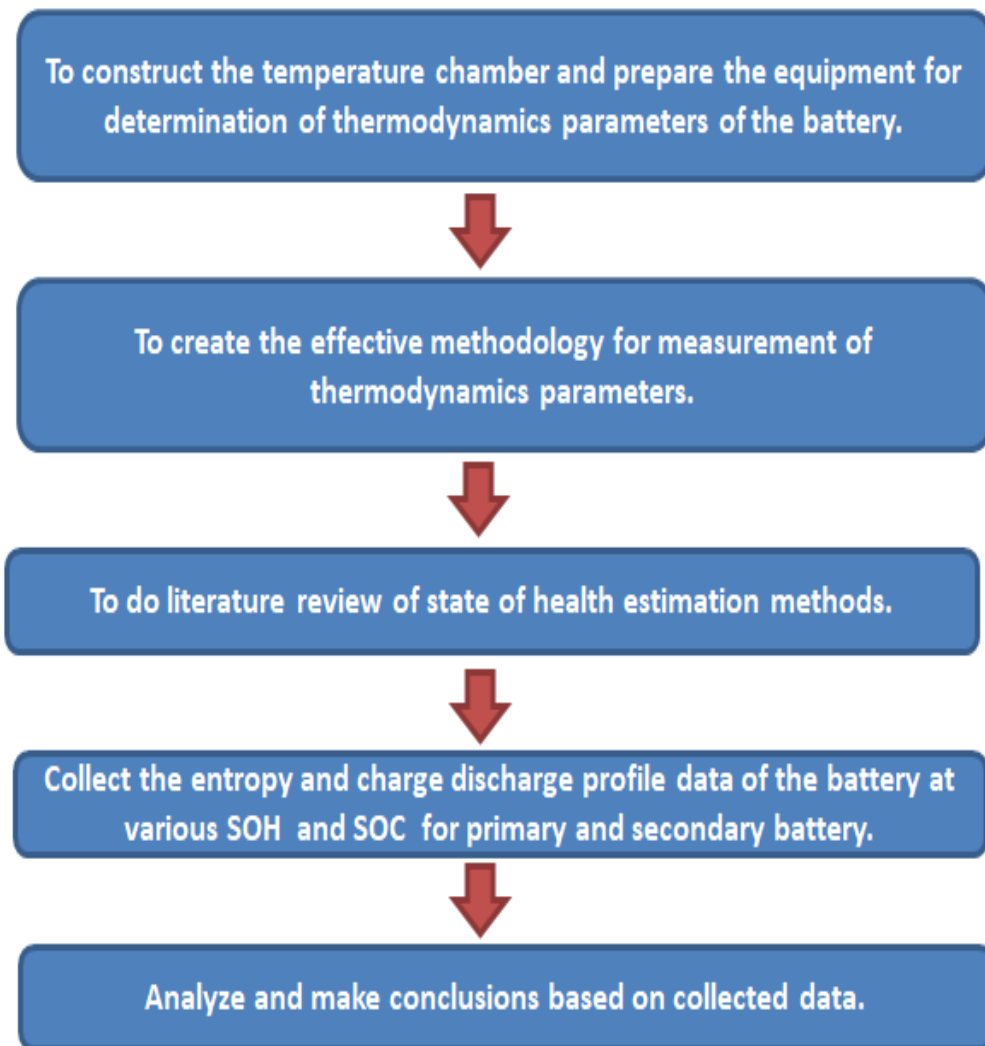


Figure 1.1: Flow process work chart of the master's thesis

1.3 Benefits of the research to Kazakhstan and wide community

This research work will provide the state of a health assessment method of the battery. Nowadays, batteries are used in a lot of applications. Generally, most batteries are just thrown away even if they can be used for further applications due to the wrong estimation of the state of health of the battery. Our model with high precision can assess which battery indeed is not reusable. Moreover, the created model can provide the good planning of purchase of new batteries for enterprises which use batteries. And the created model can be helpful for the basis for the battery management system production in Kazakhstan.

1.4 Scope and constraints

Constraints of this research are that the data of thermodynamics profiles of the batteries are limited. This is because there is no effective methodology to measure the entropy of the battery. Therefore, effective methodology for entropy measurement was developed and emerging artificial techniques were used on charge discharge profiles to obtain more insights from data.

1.5 Thesis structure

The outline of this research work is shortly defined as follows:

Chapter 1 represents the overall data, primary challenges of SIBs, and the structure of this thesis.

Chapter 2 presents a literature review on state of health estimation methods, comparing it with other techniques .

Chapter 3 indicates the following moment experiment procedures: description methodology of the analysis, software and equipment processing the data, and samples description.

Chapter 4 describes the results of experimental work with figures and tables. It is divided into 3 main points: Thermodynamics profile of thionyl primary battery, thermodynamics profile of NCR 18650 battery, and the artificial intelligence (AI) techniques.

Chapter 5 has conclusions of the experimental work and the future prospects.

Chapter 2 – Literature Review

2.1 Basic concepts

Based on the literature review, methods for estimating the state of health can be categorized into three main groups: experimental, model-based, and data-driven. The experimental method involves measuring parameters that are sensitive to aging. For example, the state of health can be determined by analyzing the battery's internal resistance, which increases as the number of cycles increases due to the growth of the solid electrolyte layer. This increase in resistance results in a decrease in the battery's energy storage capacity. The most precise measuring the state of health of the battery is ampere *hour counting method which is defined by the following equation [1]:

$$SOH = \frac{Q_f}{Q_i} * 100 \quad (1)$$

Where, SOH – the state of health of the battery, Q_i – the initial nominal capacity of the battery, Q_f – the final capacity of the battery.

The initial nominal capacity of the battery is determined by charging and then discharging of the battery at 0.05 C – rate and ambient temperature. An equation 1 is a very simple formula, but in practice it is hard to assess the state of health because there is often no information about the initial capacity and past experience of the battery.

In general, experimental methods are not ideal for the implementation in a battery management system due to their limitations, such as the time-consuming assessment process and the fact that many of these methods are destructive. Thus, experimental methods are primarily utilized for scientific purposes, such as understanding the degradation mechanism. As a result, the literature has focused on the use of model-based and data-driven methods for battery management. Model-based methods can be categorized into various groups, including electrochemical models, electric circuit models, and mathematical models. On the other hand, data-driven methods rely on emerging technologies such as deep learning and machine learning.

2.2 Model based state of health estimation

Another way to determine a battery's state of health is through model-based estimation, but this method requires enough pre-existing experimental data [1]. Essentially, this technique involves identifying how crucial battery characteristics - such as current,

voltage, and capacity - are related to the battery's aging. Once the model has been validated with a series of experimental results, it becomes possible to estimate the battery's state of health without damaging it. As a result, this method is useful for battery management systems, where it would not be cost-effective to destroy the battery during the estimation process. One key difference between this method and the experimental estimation method is that the latter can also serve scientific purposes. According to a survey of academic papers, there are several main categories of model-based estimation, including Kalman-based filters, equivalent circuit model-based methods, electrochemical model-based methods, empirical fitting methods, machine learning methods, and deep learning methods.

2.2.1 Kalman-based filters

The standard Kalman filter is an algorithm that uses the minimum root-mean-square variance to filter measurements of the state of linear systems whose errors follow a Gaussian distribution [2, 3]. However, many real-world systems exhibit nonlinearity in their state or measurement equations, which means that the standard Kalman filter algorithm may not produce satisfactory results [4]. In such cases, a linear approximation of the nonlinear relationship can be used to convert the problem into a linear one. For battery health assessment, the extended Kalman filter algorithm is used to estimate the model parameters based on the initial health value [5]. The first step in the health status estimation process is to create a model, which involves inserting the model parameters, operating current, and voltage into the recursive equation of the extended Kalman filter. The model parameters are then updated in real-time based on the improved battery state of health [6]. Next, the findings are analyzed using a prediction approach, which requires a filtering method to identify dependencies and eliminate noise from the results. In battery characterization, adaptive Kalman filtering is often used, and there are several variations of Kalman filtering available, such as dual unscented Kalman filtering, linear regression filtering support, and double-scale particle filtering [2, 7]. Additionally, Kalman filtering can be used to simultaneously assess the state of charge and state of health of the battery.

2.2.2 Equivalent circuit model-based methods

In this model, the battery is considered as the electric circuit which can contain elements such as, inductor, capacitor, and resistor (connected by parallel or series). According

to [7], the electric circuit model illustrated in Figure 2.1 was applied. The precision of the model was checked for LiFePO₄/C coin cell battery.

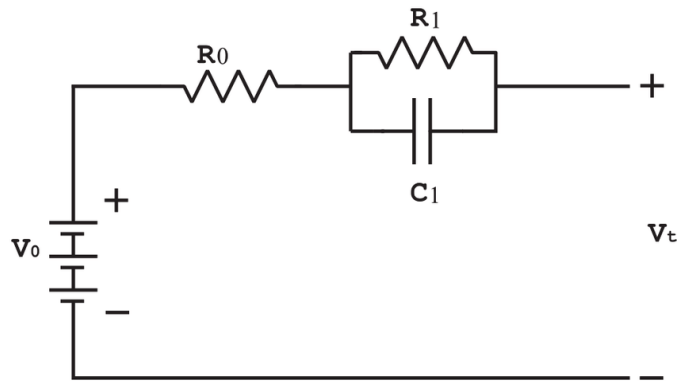


Figure 2.1 Equivalent circuit model consisting two resistor and capacitor

Another study proposed a similar circuit model to represent the self-healing mechanism. Pei et al. used two schemes for the aging and self-healing processes [8]. The model consisted of a self-healing process in a standing state and an aging process in a discharged state, as illustrated in Figure 1 [9]. The circuit model used in the study by Xia and Abu Kahuk consisted of a series of resistors and capacitors, and electrochemical impedance data were collected during accelerated battery aging [10]. This equivalent circuit model is depicted in Figure 2.2. The collected data were used to create an equivalent circuit model, which showed that increasing the aging process's acceleration led to an increase in the resistance value and a decrease in the capacitance value. To reduce acquisition time, some researchers have suggested using a circuit model that includes a double resistance and a capacitor with hysteresis in one state [11]. This equivalent circuit model is depicted in Figure 2.3. The Sobol method was used to study the battery's aging characteristics in one study, and it was concluded that this method requires only half the aging results, reducing acquisition time. Finally, the equivalent circuit model has been found to be useful for estimating SOH for lead-acid batteries in low voltage applications. Topan et al. used recursive least squares and Kalman filtering based on the Thévenin circuit model and found that the Kalman filtering results were better than those obtained using RLS [12 -14].

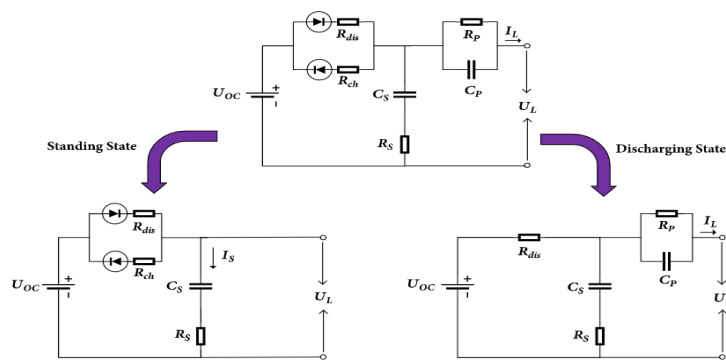


Figure 2.2 The equivalent circuit model scheme of the battery's self-healing process

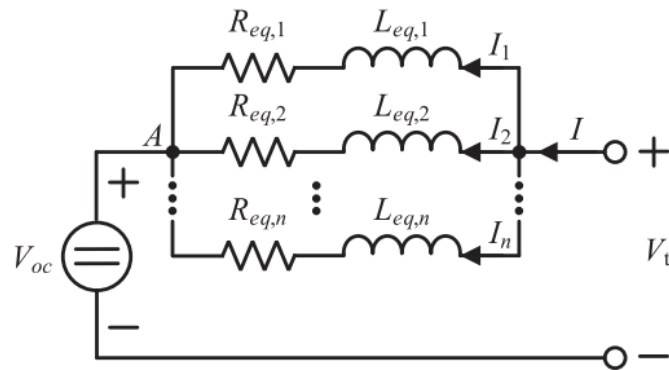


Figure 2.3 The equivalent circuit model consists of parallel connected resistance and inductor

2.2.3 Electrochemical model-based methods

The electrochemical model is based on describing the chemical processes happening in the battery. For instance, intercalation and deintercalation processes happening in the LiCoO_2/C battery are shown in figure 2.4. According to the literature review, most chemical models are describing the solid layer formation on the interphase of electrolyte and cathode material [4-6].

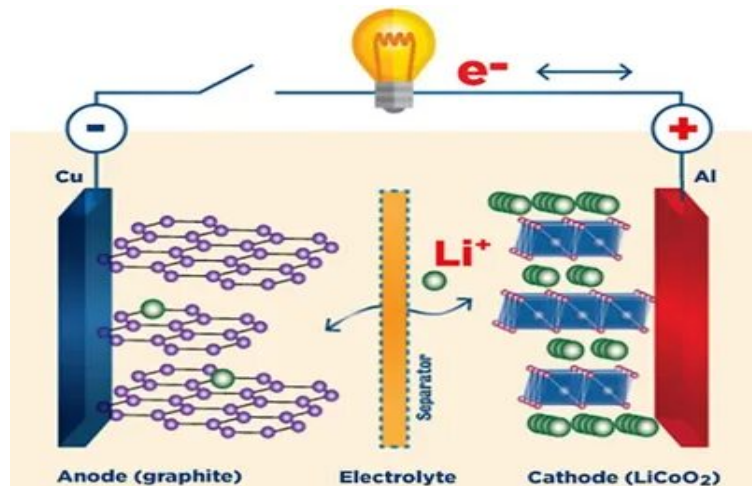


Figure 2.4 the description of the chemical processes in the LiCoO₂/C battery [4].

Understanding battery operation processes is necessary to assess battery condition using an electrochemical model. The study discussed in the article showed that battery aging results in reduced battery capacity and increased internal resistance. The first electrochemical model of a lithium-ion battery was developed by Doyle, Fuller, and Newman and is abbreviated as the DFN model [15 - 18]. This model analyzes battery parameters with high accuracy, but is too complex to be used in a Battery Management System (BMS). The DFN model is developed based on the differential form of the mass and charge conservation equations in the solid and electrolyte phases, and it describes the chemical process that occurs before the formation of the Solid Electrolyte Interfacial Layer (SEI). The formation of the SEI reduces the capacity of lithium-ion batteries due to the formation of non-consumable lithium ions. The DFN model equations are presented in table 2.1:

Table 2.1: Equations of the electrochemical model

	Description	Equation
Equations based on mass balance and diffusion		
1	The diffusion equation, where C_s – concentration of lithium in solid phase, r – radius of spherical particle in SP model	$\frac{\partial C_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_s}{\partial r} \right)$
2	Boundary conditions of the diffusion equation. Where j_{Li} – the volume specific rate of the chemical reaction, $a_s = \frac{3\varepsilon_s}{R_s}$ – specific surface area of spherical particle, R_s - radius of spherical particle, ε_s – the active material volume fraction.	$\frac{\partial C_s}{\partial r} (r = 0) = 0,$ $D_s \frac{\partial C_s}{\partial r} (r = R_s) = \frac{j_{Li}}{a_s * F}$
Equations based on charge balance		
3	Charge flux equation	$\frac{\partial}{\partial x} \left(\sigma_{eff} \frac{\partial \varphi_s}{\partial x} \right) = j_{Li}$
4	Where, A – is the surface area of the electrode, i_{app} – applied current, φ_s - the potential of solid phase, L – the	$\sigma_{eff} \frac{\partial \varphi_s}{\partial x} (x = 0) = \frac{i_{app}}{A};$ $\frac{\partial \varphi_s}{\partial x} (x = \delta_-) = 0;$

	thickness of electrolyte.	$\frac{\partial \varphi_s}{\partial x}(x = L - \delta_+) = 0 ;$ $-\sigma_{eff} \frac{\partial \varphi_s}{\partial x}(x = L) = \frac{i_{app}}{A}$
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Based on the equations described in Table 2.1, the voltage of the battery can be defined as follow:

$$V(t) = \varphi_s(L, t) - \varphi_s(0, t) - \frac{R}{A} i_{app}(t) \quad (2)$$

The electrochemical model has several considerations. First, the Butler-Volmer equation describes the electrochemical reaction happening at the interface between the solid and liquid phases. Second, the mass transfer of lithium-ion in the electrode is defined only by diffusion. The single-particle (SP) model is a simplified model that assumes the electrode material has a spherical shape and that the charge is uniformly distributed over the solid phase [19]. This model is precise at low C-rates because it doesn't consider particles' cracking and volume expansion during lithium-ion intercalation. However, the accuracy of the SP model can be improved by assuming fracture propagation in the electrode material. The model hypothesizes that the solid electrolyte interface layer is created in four stages, and the SEI layer's growth on fractures has a more significant impact on the battery's health than the SEI layer's growth on the original SEI layer. The model's precision is tested by observing the voltage profile results of a LiFePO₄ cathode material at different temperatures, C-rates, and cycle numbers [20]. The battery's physical characteristics can be extracted from the SP model's equations and tested in real-time. The SP model's final equation can be enhanced by specifying physical parameters, such as applied current, time, average concentration of lithium in the positive and negative electrodes, etc. This leads to simplifying equations and estimating parameters in real-time [21]. The magnitude of lithium-ion loss and diffusion into the liquid is chosen as the state of health indicators from the physical parameters due to their sensitivity to aging. The electrochemical model consists of partial differential equations that cannot be solved analytically and require numerical solution methods. Therefore, to solve these equations the following mathematical tools can be used: Euler's, Heun's, and nth order Runge kutte method. The diffusion parameter is evaluated at different levels of charge to improve the prediction of the state of health empirically, demonstrating high precision with a relative error of 2%. Additionally, the electrochemical model can be used to determine the

battery's state of charge (SOC). The adaptive filtering approach is used to evaluate the battery's physical properties' dynamic behavior in the equivalent circuit model for evaluating the state of health. The Sigma Point Kalman Filter adaptive filtering approach, coupled with the electrochemical model, is utilized to demonstrate the simultaneous evaluation of the SOC and state of health.

2.2.4 Empirical and fitting methods

This model is just related to the mathematical fitting dependence of the state of health of the battery to various aging sensitive features. In contrast to fitting the state of health battery with mathematical functions such as polynomial and exponential, the mathematical model for describing the battery's capacity considers variables such as C-rate, depth of discharge, temperature, storage time, number of cycles, and state of charge. Two different mathematical models for calendar ageing and cycling ageing are used to clearly define the battery's state mathematically. Deshpande and Bernardi propose equation 3 to develop a mathematical model that accounts for both calendar and cycle ageing by specifying the capacity of the model with depth of charge, number of cycles, and storage duration [25].

$$Q(t) = Q_0 (1 - B \times DOD_2 \times n - Kt) \quad (3)$$

where B - is the coefficient that characterizes the cycling ageing; Kt - is the coefficient that characterizes the calendar ageing; $Q(t)$ - is the real-time capacity of the battery; Q_0 - the initial capacity of the battery; t - the calendar time. The advantage of this equation is that cycling and calendar aging both considered in one equation

Analogically with previous discussed equation, other scientists suggest another approach in which, the state of health of the battery was defined by the following equation 2:

$$Q_{\text{loss}} = B * \exp\left[\frac{-31700+370.3*C\text{-rate}}{RT}\right] * (Ah)^{0.55} \quad (4)$$

$$Ah = \text{cycle}_{\text{number}} * DOD * 2$$

Where, B - is coefficient which depends on C- rate, DOD - depth of discharge, T - temperature. So this equation can assess the state of health of the battery considering the following aging factors: C-rate, DOD, temperature, cycling number.

The phase transition region during charge and discharge can be identified through incremental capacity (IC) analysis, which is the differential form of the capacity-voltage relationship [27]. This analysis produces several peaks that correspond to specific phase transitions, and these peaks are sensitive to the battery's state of health. Therefore, they can be

used as parameters for assessing the battery's state of health, as confirmed in various studies [28]. For instance, a study found that the cylindrical lithium ion battery exhibits four peaks in its incremental capacity analysis, and the second and fourth peaks were selected as parameters for assessing the battery's state of health. Based on this, a mathematical model was developed, as follows [29]:

$$h_2 \text{ or } h_4 = a \times \ln (SOH - b) + c \quad (5)$$

where h_2 or h_4 are height of peaks. a , b , c – constants of equations.

To improve the visibility of IC analysis peaks, the experiment should be conducted at a C-rate that is equal to or lower than 0.05 C. However, this approach can be time-consuming and impractical within a BMS. Li et al analyzed "Nickel Manganese Cobalt" batteries using IC at different C-rates resulted in four peaks at 0.05 C and two peaks at 13 C [30]. The study showed that the peaks obtained at 13 C were more sensitive compared to those at 0.05 C by analyzing four peaks at various SOH of the battery and depth of discharge. Therefore, a low C-rate is no longer necessary to determine the battery's health condition. The article employed a linear regression model to establish a mathematical model for SOH rely on height of the peak.

$$SOH = a - b \times h \quad (5)$$

where a and b are parameters of the model; h –peak intensity.

Previous studies have explored the development of mathematical models based on the height of IC analysis peaks [31,32]. However, alternative approaches have been proposed where the area of peaks is used to create the mathematical model [33]. To this end, several articles have employed the linear regression model using the peak area, which has been successfully tested on 60 Ah and 74 Ah LiFePO₄/C cells, yielding an error rate of only 4%. Zhou, Huang, and Pecht found that the data obtained from constant current charging of the battery profile within the terminal voltage to upper cut-off voltage range is highly sensitive to the battery's SOH [34].

$$IV = \int_{t_0}^{t_1} v dt \quad (6)$$

where IV – integrated value of charge discharge profile, v – voltage at time t , t – time, t_1 – is the time when the battery reaches the upper cut-off voltage, and t_0 – is the time when the battery reaches the terminal voltage. Finally, they found a linear relationship between the area of the charge-discharge profile and the SOH of the battery. The high precision of this linear dependence was verified by testing four LiCoO₂ cathode-based batteries [34]. In summary,

the reviewed model-based methods are listed below in Table 2.2 with their benefits and drawbacks.

Table 2.2: Advantages and disadvantages of model based method

Method	Advantage	Disadvantage
Equivalent circuit model	Noninvasive The estimation requires only analysis of direct measurements such as current, voltage, and temperature, the rate of each process could be investigated through Kinetic model.	It is not possible to determine the ongoing chemical processes within the battery, thus necessitating a high level of control over the battery's characteristics to identify the aging parameter.
Electrochemical model	Noninvasive Besides the state of health of the battery, the model gives the exact description of chemical processes proceeding in the battery. And these processes can be manipulated at various charge discharge conditions such as, C-rate, temperature, and voltage range.	The state of health estimation needs high computational efficiency to solve multi-partial differential equations
Mathematical fitting	Noninvasive Due to the straightforwardness of the mathematical equations involved, there is no requirement for high computational efficiency.	It is not possible to determine the ongoing chemical processes within the battery. Mostly requires direct analysis of the battery such as incremental capacity, and differential voltage capacity analysis

2.3 Data – driven method

Previous methods for estimating the state of health of batteries involve developing physical or mathematical models that require an understanding of the chemical and physical processes taking place within the battery. However, data-driven methods such as machine learning and deep learning have recently emerged as alternative approaches. Machine learning and deep learning algorithms have been successfully applied in various fields such as drilling, medicine, image recognition, and finance.

In a study by Huang, Liu, Sun, and Liao, the deep learning method was used to estimate the state of health of Lithium iron phosphate batteries based on charge-discharge data, achieving precise results with 10-minute sampling data [50].

2.3.1 Data – driven method

Machine learning has been increasingly utilized in the estimation of the state of health of batteries. This method involves creating a program that is trained to predict the state of health of a battery using past aging data. Machine learning algorithms have been applied in various fields such as genetics, cancer prediction, mineral processing, economics analysis, and image recognition. One of the advantages of this method is that it does not require information about the electrochemical model of the battery. Instead, it relies on large amounts of battery data collected from testing under different variables such as depth of discharge, temperature, and cycling number. By training the machine learning program with this data, it can accurately predict the state of health of a battery with a relatively low error rate. This approach has shown promise in improving the efficiency and accuracy of state of health estimation for batteries, and it is expected to become more widely adopted in the future. This approach has been increasingly utilized in various fields such as genetics and genomics [35], cancer prediction for patients [36], mineral processing [37], economics analysis [38], and image recognition [39].

As discussed in previous sections, predicting the state of health of a battery without an electrochemical model can be time-consuming and challenging without sufficient data. However, advancements in big data technologies have enabled the collection of large amounts of battery data from testing 700 vehicles under different variables such as depth of discharge, temperature, and cycling number [40]. For training purposes, data from the state of charge regions of 20-80% was selected due to its sensitivity to aging. After utilizing big data, articles have demonstrated the estimation of state of health with a relative error of 4.5%. Based on literature analysis, machine learning methods can be classified into the following categories:

1. The estimation of state of health (SOH) for batteries can be based on direct measurements of temperature, voltage, and current. Researchers such as Roman et al. have used the gradient boosting regression tree model with these direct measurements to estimate the SOH of batteries, achieving relatively accurate results with a relative error of 7% [41].

2. Another approach to estimating the SOH of batteries is by analyzing the battery's charge-discharge profile. In this method, data on the battery's charge-discharge profile is collected and selected from the training data in a specific charge region. Researchers have used long short-term memory and convolutional neural networks to forecast the battery's health based on this data, achieving accurate results. Roman et al. also used this method and achieved a relative error of 4.4% [41]

3. SOH estimation is based on processed results of charge-discharge profiles such as IC analysis and DV analysis. As discussed earlier in chapter 2.5, the peaks of IC and DV analysis are sensitive to the ageing of batteries. The processed results of these analyses can be used as inputs to machine learning algorithms for SOH estimation. For example, in a study by Kim et al., a machine learning model was developed based on the IC analysis results of lithium-ion batteries to estimate their SOH. The model was trained using support vector regression and achieved an accuracy of 97% [41].

Machine learning mixed with IC analysis has been used in several ways for state of health (SOH) estimation of batteries. Direct measurements such as temperature, voltage, and current can be used to estimate SOH using machine learning algorithms such as gradient boosting regression tree models. Charge-discharge profiles can also be used, with long short-term memory and convolutional neural networks being used to forecast battery health. Processed results of charge-discharge profiles, such as impedance spectroscopy and differential voltage analysis, can also be mixed with machine learning methods, such as support vector machines.

Other algorithms that have been used for SOH estimation include feedforward neural networks, bi-directional LSTM, adaptive boosting, multilayer perceptron, and convolutional neural network. The training data can vary, from only current discharge profiles to including additional data such as impedance and temperature. To validate the accuracy of the model, tenfold cross-validation is used. Tenfold cross-validation scheme is well described in Figure 2.4.

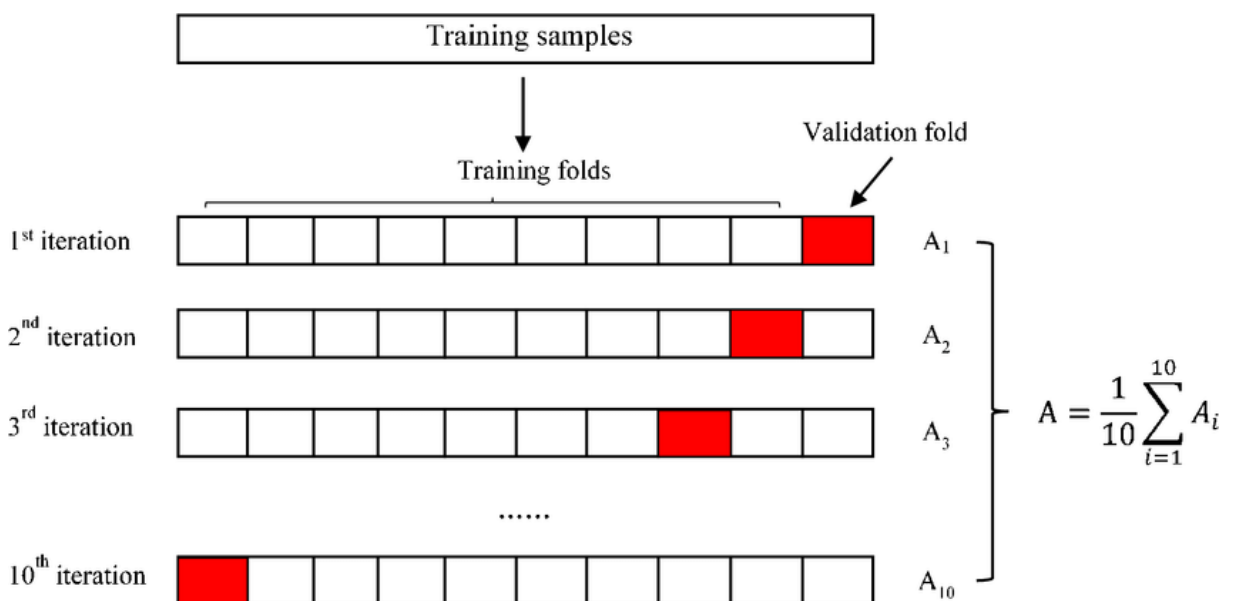


Figure 2.4 The 10 fold cross –validation illustration [41]

2.3.2 Deep learning method

From the traditional machine learning method. Deep learning algorithms, such as convolutional neural networks (CNNs) and recurrent neural networks (RNNs), are designed to automatically learn hierarchical representations of the input data. These algorithms are trained on large amounts of data and can identify complex patterns and relationships between the input data and the target output.

One of the advantages of deep learning methods is their ability to handle high-dimensional data, such as images and audio. For example, in image recognition tasks, CNNs have achieved state-of-the-art performance on various benchmarks. In the context of battery SOH estimation, deep learning methods have also shown promising results. For instance, in one study, a deep convolutional neural network was trained on a large dataset of battery cycling data to estimate the SOH of lithium-ion batteries, achieving an accuracy of over 99% [49].

However, deep learning methods require a large amount of training data and computational resources. Additionally, they can be difficult to interpret, and it can be challenging to understand how they arrive at their predictions. Therefore, the choice of method should be based on the available data and the specific requirements of the application.

The major drawback of the aforementioned methods is their time-consuming process for estimating SOH due to the limited availability of peaks in differential capacity analysis and charge-discharge profile with 20-60% state of charge (SOC) in real-world Battery Management System (BMS) applications. To overcome this limitation, Tian et al. developed a deep neural network model that can estimate SOH at different voltage windows of the charge-discharge profile, which significantly reduces the estimation time to 10 minutes by using a 300 mV voltage window with 2.28% inaccuracy [50]. However, the mechanisms of battery deterioration, such as fracture propagation in the electrode, side reaction, and collector corrosion, are primarily explored in half-cells, and it is challenging to determine if the whole cell battery is deteriorating due to cathode or anode deterioration. To address this issue, Tian et al. used a convolutional neural network model that can estimate the battery's SOH and detect the aging status of each electrode. Another promising deep learning approach is the encoder-decoder model that uses recurrent neural networks for sequence-to-sequence forecasting problems, as applied by Gong et al. for the publicly available dataset of NASA

and Oxford [62-63]. One of the significant advantages of deep learning is that it can calculate SOH based only on the charge-discharge profile recorded by the battery's BMS chip without requiring any specific data, such as impedance or differential capacity analysis, and can be computed in the appropriate high C-rate mode. However, deep learning requires a vast amount of accurate data for training, which is why scientists often begin by building models using publicly available datasets and then apply them to their proprietary battery tester dataset.

One of the limitations of deep learning is that it requires a substantial amount of accurate data for training. To overcome this limitation, many researchers start by building models using publicly available and verifiable datasets. Once a model is developed, it can be applied to their own sample dataset, which was collected using their own proprietary battery tester.

2.4 Universal state of charge law method.

Manane, et. al used the thermodynamics parameters of the battery to evaluate the state of charge of the battery by values of entropy and enthalpy. The exact equation of this model is well described in experimental section. Because, in this research work the universal SOC law was used to determine state of the battery.

The coefficients of the above-mentioned linear regression model depend on the nature of the battery, and the state of health of the battery. In this model, values of coefficients can be considered as feature for state of health estimation.

The SOC evaluation model was firstly investigated by them for secondary lithium ion batteries. It surprisingly applies to primary batteries too despite cathode processes are irreversible in nature. They suggested the method may extend to online SOC assessment introduced to an imbedded chip, which process and collect the thermodynamics data of battery. In addition, the model can be used to characterize MnO₂ materials from the thermodynamics properties perspective and to trace Li/MnO₂ cell manufacturer [57].

Chapter 3 – Experimental procedures

3.1 Overview

Two types of batteries were tested: a primary lithium thionyl chloride battery (Minamoto) and a cylindrical NCR 18650 (Panasonic) battery. The thermodynamics profile of the primary battery was obtained using a simple potentiometric method, while the profile of the cylindrical battery was obtained using a developed fast method. However, before using the fast developed method, its precision was verified by comparing it with the simple potentiometric method. This was necessary because despite the long estimation time of the simple potentiometric method, it is a precise estimation method for the entropy of the battery. All batteries were analyzed using a battery tester Arbin BT2000. The temperature of batteries was analyzed in programmed temperature chamber. The data of the charge-discharge profile of the NCR 18650 was used for the purpose of AI technique and all data was processed using Python 3.10 and MATLAB. The work flow of experiment procedures is depicted in figure 3.1.

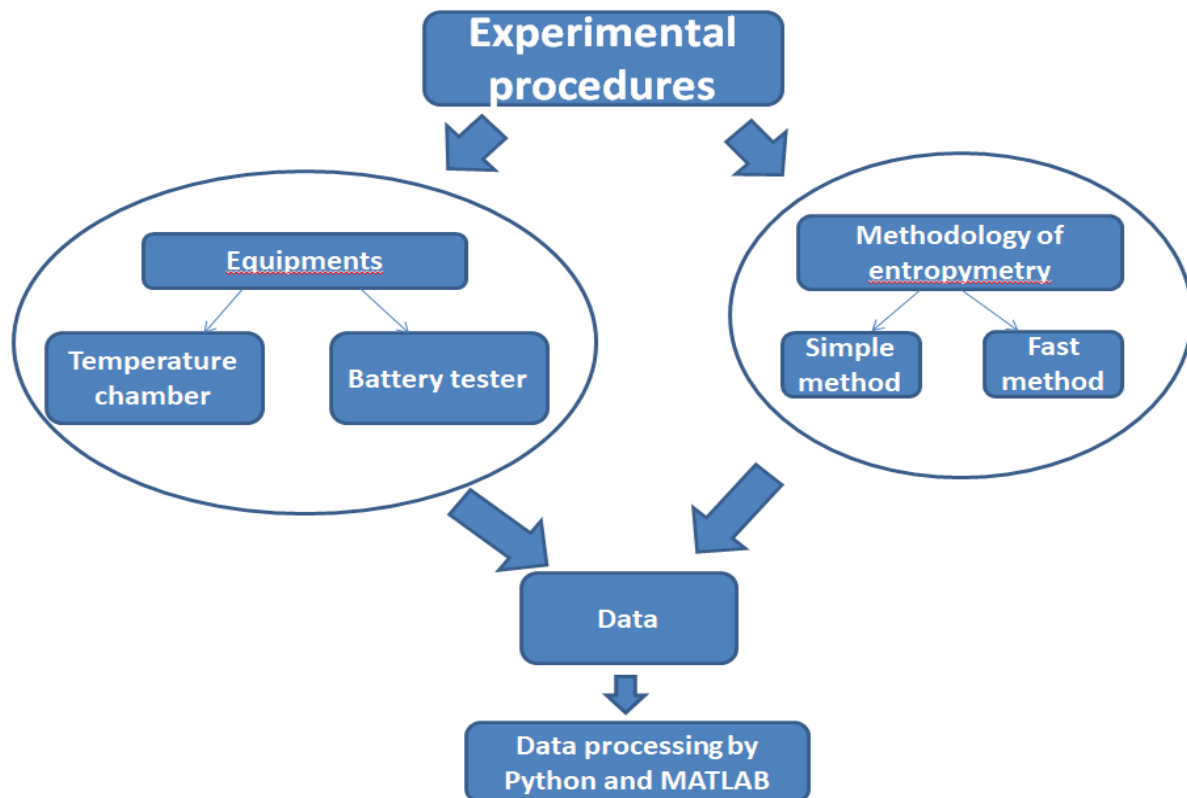


Figure 3.1: Experimental procedures of Master's thesis

3.2 Battery types and model

3.2.1 The secondary battery: NCR 18650 Panasonic

The Panasonic NCR 18650 battery is a type of cylindrical lithium-ion battery that is commonly used in various electronic devices such as laptops, power banks, and flashlights. It has a diameter of 18 mm and a length of 65 mm, hence the name “18650”. This type of battery is known for its high energy density. It has the following characteristics: the nominal voltage 4.2 V, capacity = 3200 mah. It also has a long cycle life, meaning it can be charged and discharged many times before losing its capacity. The Panasonic NCR 18650 battery also has a high discharge rate, which makes it suitable for high-drain applications. This battery is depicted in figure 3.2.



Figure 3.2: NCR 18650 cylindrical battery.

3.2.2 The primary battery: Lithium thionyl battery

Lithium thionyl chloride (Li-SOCl₂) battery is a type of primary battery that utilizes a combination of lithium as an anode and thionyl chloride (SOCl₂) as the cathode. This type of battery is known for its high energy density, long shelf life, and excellent performance in a wide range of temperatures. The Li-SOCl₂ battery is commonly used in applications that require long-lasting, reliable power sources such as military and aerospace systems, medical devices, and industrial sensors. They are also used in some consumer devices like digital cameras and remote controls. One of the key advantage of Li-SOCl₂ batteries is their high energy density, which means they can store a large amount of energy in a relatively small volume. Additionally, they have a low self-discharge rate, which allows them to retain their charge for up to 20 years when stored at room temperature. However, Li-SOCl₂ batteries have some limitations. They can only be used as a primary battery and cannot be recharged. They also have a relatively high internal resistance, which limits their ability to provide high current output. Finally, they require careful handling due to the risk of thermal runaway if the battery is subjected to overcharge or short-circuiting. This battery used in this research is

depicted in figure 3.3. This type of a battery has the following characteristics: the nominal voltage 3.6 V, capacity 1000 mah.



Figure 3.3: Minamoto Lithium thionyl battery.

3.3 Equipments

3.3.1 Battery tester

Two battery testers were utilized in this Master's thesis work: the Neware BTS4000 series and the Arbin BT2000. These testers were employed to plot the charge-discharge profiles of the batteries. The Arbin tester was chosen for determining the thermodynamic parameters due to its high sensitivity to voltage response. The Neware tester, on the other hand, was utilized for data collection on charge-discharge profiles, which were subsequently employed for AI techniques. Both testers were also employed for galvanostatic measurements, where the appropriate voltage range for the batteries was maintained. The NCR 18650 battery was cycled within a voltage range of 2.7 – 4.2 V, while the lithium thionyl battery was discharged within a voltage range of 3.65 – 2 V.

3.3.2 Thermal chamber

A programmable thermal chamber was constructed from thermally insulating foams and Peltier junctions which is a device that uses the thermoelectric effect to regulate the temperature of a battery or other electronic components. In addition, heat sink and fan was used on the hot side of Peltier to increase heat transfer from the device. The benefits of using a programmable battery chamber constructed from Peltier junctions include precise temperature control, low power consumption, and minimal moving parts. Additionally, the Peltier junctions are generally reliable and can operate for long periods of time with minimal maintenance. The temperature of the battery is measured by UT320 Series Mini Contact Type Thermometers. The thermometer and temperature chamber is shown in figure 3.4.

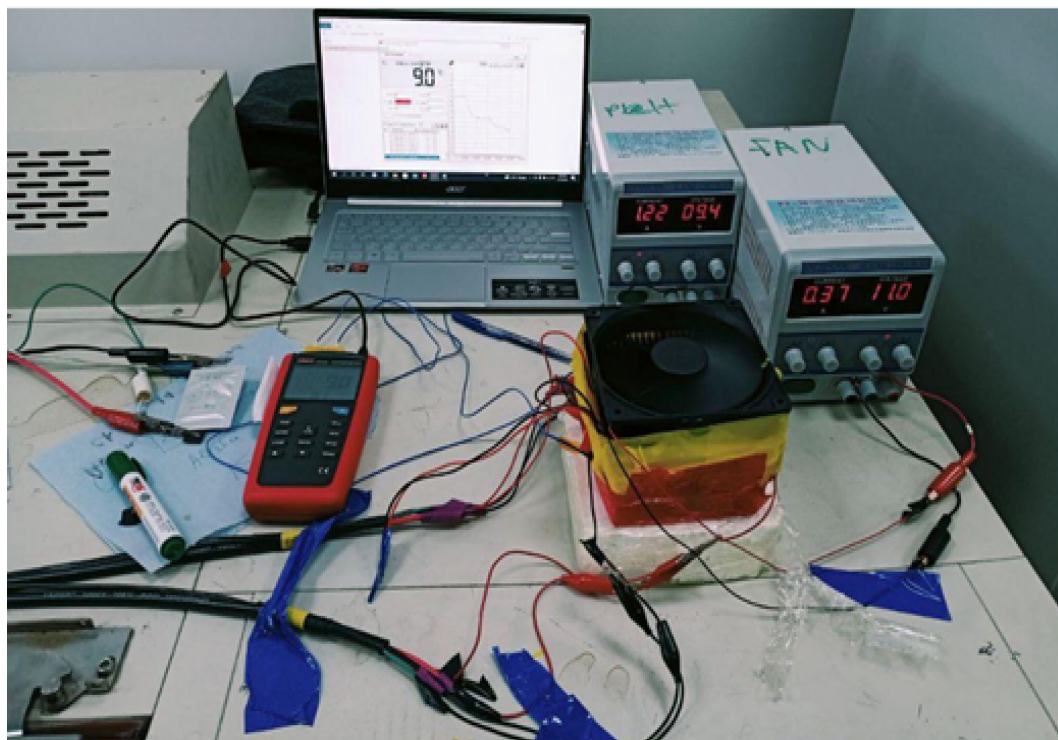


Figure 3.4: Programmable temperature chamber and thermometer.

3.4 Obtaining of the thermodynamics results

To obtain thermodynamics profiles, it was used the following methods: the simple potentiometric method and the fast developed method. The verification of the fast developed method is shown further in the following sections. In the table, the introduced program into the battery tester for simple potentiometric method is shown in table 3.1. The value of $\frac{dE}{dT}$ is obtained at various states of charge. Based on this value, thermodynamics parameters (enthalpy, entropy, Gibb's energy) can be evaluated by the following equations:

$$\Delta S = n * F * \frac{dE}{dT} \quad (7)$$

$$\Delta G = n * F * E \quad (8)$$

$$\Delta H = \Delta G + T \Delta S \quad (9)$$

Where, E – is potential, F – faraday constant (96500 C/mol), n – number of electrons, ΔH – enthalpy, ΔS – entropy, ΔG – Gibb's energy

Table 3.1: The methodology of simple potentiometric method

Step #	Purpose of step	Instruction procedure of NCR 18650
1	The determining the discharge capacity of the battery.	The battery is charge and discharge at 0.05 C-rate and 2.7 - 4.2 V range. Finally, The value of the discharge capacity is extracted.
2	Full charging of the battery	Charging the battery till 4.2 V at 0.05 C – rate.
3	To obtain the value of $\frac{dE}{dT}$	After reaching equilibrium of the battery, the OCV is measured at various temperatures.
4	Discharging till appropriate SOC	The battery is discharged at 0.1 C rate within 1 hour and applied current is calculated by the following formula: $I = 0.1 * \text{cap}$, where cap – is discharge capacity determined in 1 st step.
5	To obtain values of $\frac{dE}{dT}$ at various SOC	To perform that, 2 nd , 3 rd , and 4 th steps are repeated till final SOC.

Table 3.2: The methodology of fast developed method

Step #	Purpose of step	Instruction procedure of NCR 18650
1	The determining the discharge capacity of the battery.	The battery is charge and discharge at 0.05 C-rate and 2.7 - 4.2 V range. Finally, The value of the discharge capacity is extracted.
2	Full charging of the battery	Charging the battery till 4.2 V at 0.05 C – rate.
3	To obtain the value of $\frac{dE}{dT}$	After reaching equilibrium of the battery, the OCV is measured at various temperatures.
4	Discharge the battery SOC decrease by 11%.at 1 A current.	At this stage, the discharge time is calculated to SOC decrease by 11%.
5	Charge the battery SOC increase by 1%.at 0.2 A current.	At this stage, the charge time is calculated to SOC increase by 1%.
6	To obtain values of $\frac{dE}{dT}$ at various SOC	To perform that, 2 nd , 3 rd , and 4 th steps are repeated till final SOC.

3.5 Softwares for processing of result

3.5.1 MATLAB

Matlab (short for "Matrix Laboratory") is a programming language and development environment that is widely used for numerical computation, data analysis, and visualization. Matlab is not an open source programming language. It is used by the license of Nazarbaev University for students. In this research work, Matlab is used for fitting the linear regression model defined by an equation 3.4. According to the article, Manane, Yassine, and Rachid Yazami used the thermodynamics parameters of the battery to evaluate the state of charge of the Li/MnO₂ battery by the following equation [57].

$$\text{SOC} = \alpha + \beta(\text{K} \cdot \text{mol})/\text{J} \Delta\text{S} + \gamma[\text{mol}/\text{kJ}] \Delta\text{H} \quad (10)$$

Where, SOC – is the state of charge, α , β , γ – coefficients of linear regression model, ΔS – entropy, ΔH – enthalpy.

3.5.1 Python 3.10

Python is a versatile programming language that is well-suited for scientific applications, and various scientific computing libraries such as NumPy, SciPy, Pandas, and Scikit-learn which is used in this research work. These libraries offer a comprehensive set of tools for data analysis, numerical computation, machine learning, and scientific visualization.

NumPy is a library designed specifically for numerical arrays and matrices in Python, which facilitates the efficient and easy execution of mathematical operations on arrays. Additionally, NumPy provides tools for linear algebra, Fourier analysis, and random number generation.

SciPy extends the functionality of the library with additional scientific computing tools. These include optimization, signal processing, interpolation, and statistical functions, which can be utilized in research work. For instance, evaluation metrics like R² and RMSD can be assessed with the aid of SciPy in this research work.

Pandas is a data manipulation and analysis library that simplifies the handling of structured data by providing user-friendly data structures and functions. It enables data cleaning, merging, grouping, and aggregation tasks, which are essential to scientific data analysis.

Finally, Scikit-learn is a powerful machine learning library that offers a diverse range of supervised and unsupervised learning algorithms, including classification, regression, clustering, and dimensionality reduction. Moreover, Scikit-learn provides tools for model

selection, evaluation, and preprocessing of data, making it a valuable resource for research work.

Chapter 4 – Results and Discussion

4.1 Thermodynamics parameters of Lithium thionyl battery

First, the optimum C-rate for evaluation of the entropy and discharge capacity of the Li-SOCl₂ battery was determined. Therefore the battery was discharged at various current rates. Charge discharge profile of the battery at various C-rate is depicted in Figure 4.1. As can be observed, on the initial discharge at high currents, there is a dip in the voltage values. This is typical for Li-SOCl₂ battery and discussed in detail elsewhere [61]. By looking at the voltage profiles, 0.005 A discharge current was selected as the optimum value for this research.

By discharging at 0.005 A, various state of charge (as well as state of health for primary battery) of the thionyl battery was achieved. OCV measurements by varying temperature is shown in Figure 4.2. According to dependence of OCV to temperature shown in Figure 4.3, dE/dT of the batteries at various SOC were obtained. Subsequently, thermodynamics profiles of the battery for the two samples were calculated which are depicted in Figures 4.3, 4.4, and 4.5

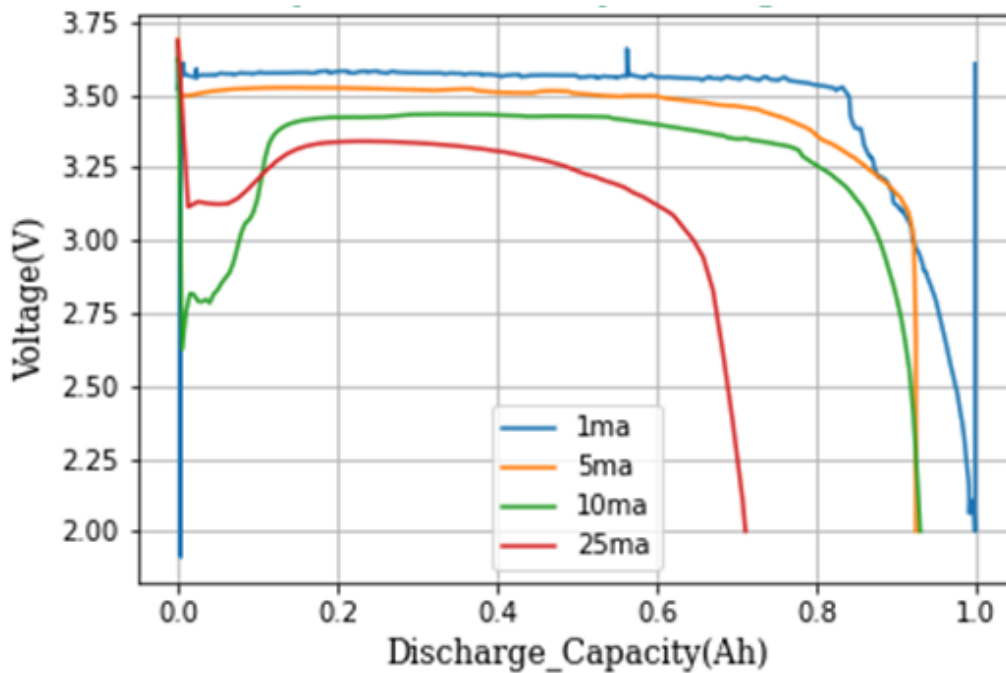


Figure 4.1: Charge discharge profile of LiSOCl₂ battery at various C-rate.

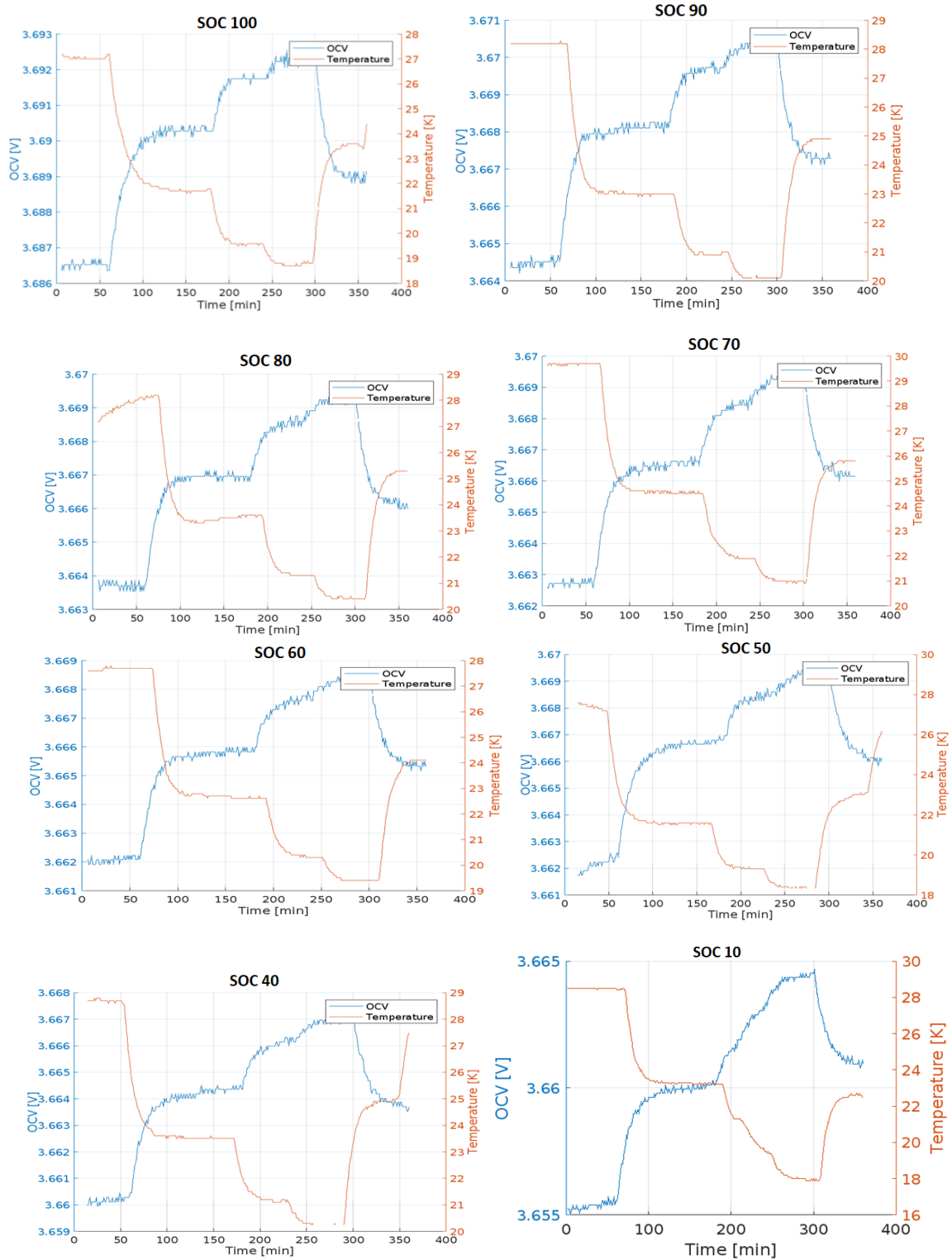


Figure 4.2:OCV measurements of lithium battery by varying the temperature at various SOC

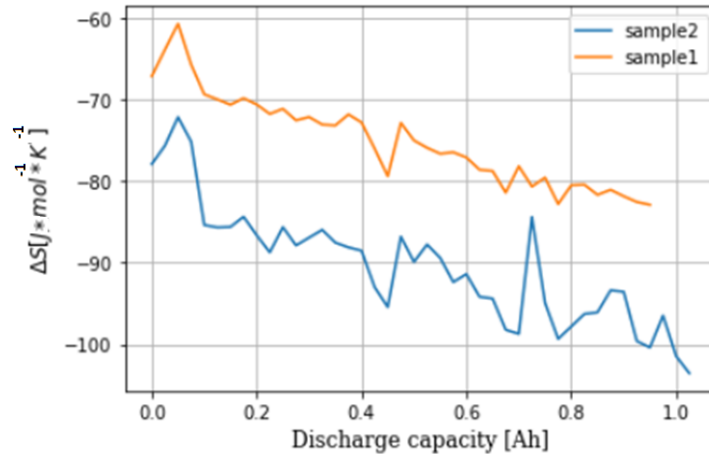


Figure 4.3 Entropy profile of the lithium thionyl battery at various SOC.

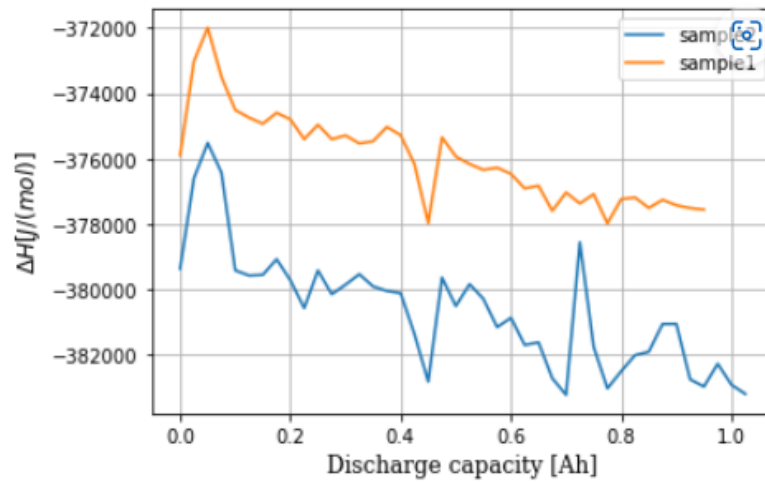


Figure 4.4 Enthalpy profile of the lithium thionyl battery at various SOC.

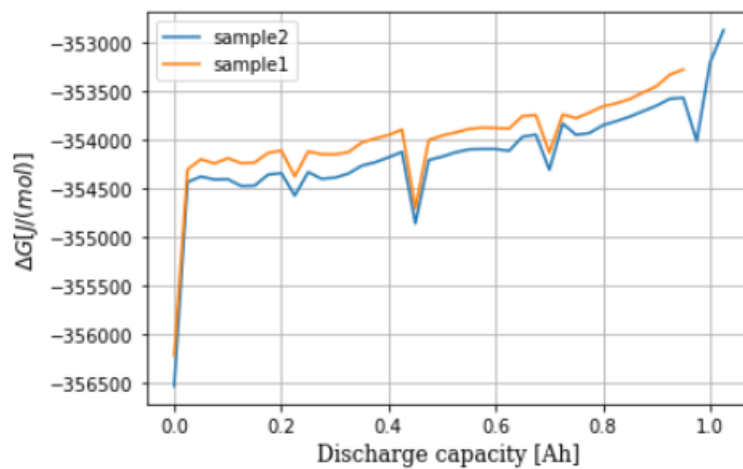


Figure 4.5 Gibb's profile of the lithium thionyl battery at various SOC.

4.1.1 State of health estimation of lithium thionyl battery based on mathematical model.

In the case of primary battery, the state of charge and state of health of the battery are the same thing. because the electrochemical processes in lithium thionyl battery are irreversible. Yazami's universal SOC equation was verified for the Li/ MnO₂ primary battery [57]. Analogical dependence was checked for our the Lithium thionyl battery. However, mathematical model with very low accuracy was obtained. This might be due to the fact that Yazami's SOC estimation equation was verified for the solid state battery. But in the case of Lithium thionyl battery, there is no solid cathode material. Instead, an electrolyte is used as the cathode material. In such cases, it is called a catholite.

Since mathematical inconsistency with universal SOC equation, another approach was proposed. In this case, it was assumed that entropy depends on state of charge of the battery by 6th order polynomial function defined by the following equation:

$$\Delta S = a + a_1 * cap^1 + a_2 * cap^2 + a_3 * cap^3 + \dots a_6 * cap^6 \quad (11)$$

Where, cap – is discharge capacity of the battery, and it is in direct ratio to the SOC of the battery. Based on this proposed mathematical model was obtained fitted graph as depicted in figure 4.8. The value of coefficients and precision of the model are shown in table 4.1.

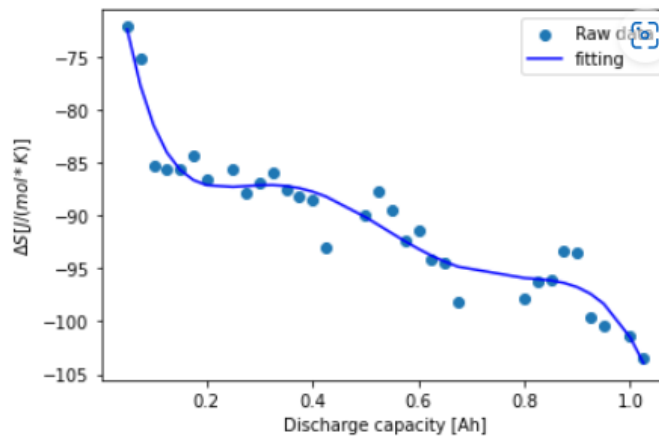


Figure 4.6 Fitted entropy profile of the lithium thionyl battery at various SOC.

Table 4.1: The coefficients of the mathematical model

Coefficient label	Sample 1, R ² = 0.97	Sample 2, R ² = 0.96
a	-55,642	-55,642

a1	-436,286	-436,28
a2	2277,76	2277,761
a3	-5644,84	-5644,82
a4	6895,76	-5644,82
a5	-3977,48	-3977,459
a6	839,212	839,204

According to the literature analysis, there is no state of charge estimation models for lithium thionyl battery. However, one of the research investigations of this battery indicated the entropy profile change at various state of charge. They propose idea to select the entropy as feature of state of charge estimation method. But it was not proposed any models [65].

Another study of entropy profile of NCM cathode battery suggest to configurational entropy model which considere information about the distributional variability of Li atoms in the host structure. In a very simplified ideal solid solution model with Li atoms moving freely between a given number of empty sites, without changing interactions (among each other and with the host lattice), the molar entropy change is given by [67]:

$$\Delta S = -R * (SOC * \ln(SOC) + (1 - SOC) * \ln(1 - SOC)) \quad (12)$$

But the equation is not corresponded entropy profile of lithium thionyl battery. Because in this equation, the ideal distribution of the lithium atoms in cathode material is considered. Due to this fact, It can be suggested the lithium ions in lithium thionyl battery is not ideally distributed [66].

4.2 Thermodynamics parameters of NCR 18650 Battery

This part investigated the entropymetry of the NCR18650 Panasonic battery at various cycle numbers. The battery's charge-discharge profile at a 0.05 C rate is presented in Figure 4.8, and Figure 4.9 illustrates the discharge capacity of the battery at each cycle number. It was found that both samples exhibited a comparable capacity degradation pattern. To determine the entropy profiles of the battery at each cycle number, the fast entropy estimation method was utilized. However, before using this method, its validity was confirmed by comparing it with the simple potentiometric method.

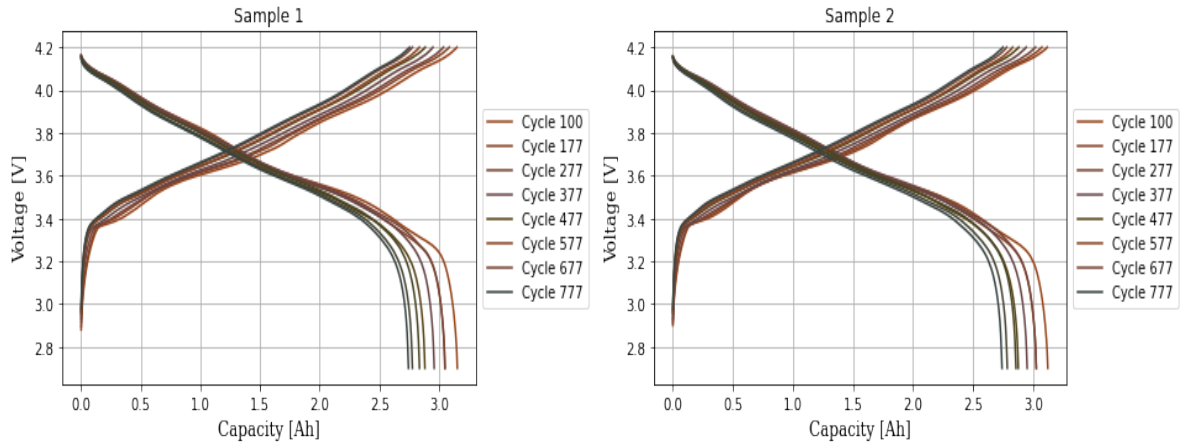


Figure 4.7 Charge discharge profile of the battery at various cycles

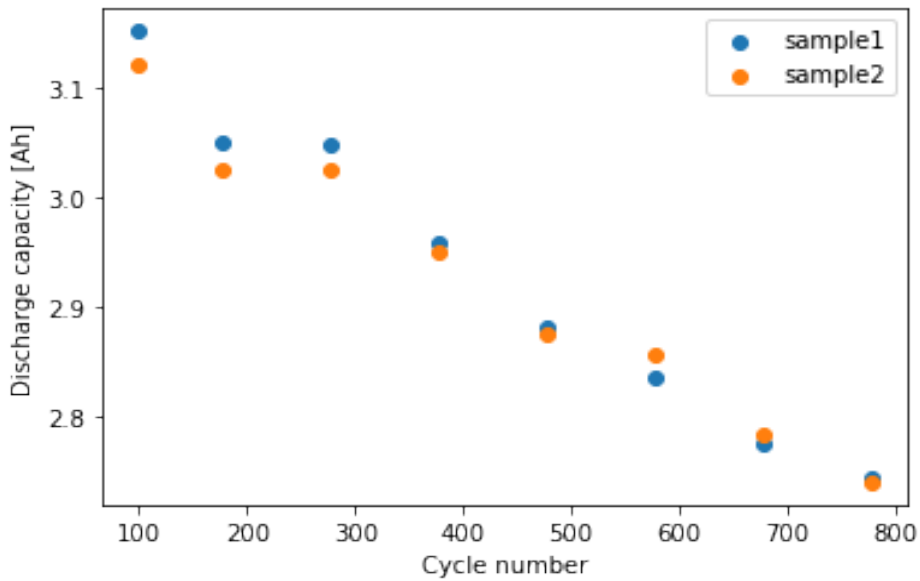


Figure 4.8. Dependence of the discharge capacity to cycle number of the battery at 1.5 C-rate

According to the research study, degradation of the capacity of battery illustrated in Figure 4.9 can be described by three phase degradation of the battery. The first phase degradation curve of capacity retention with cycle number which corresponds to degradation at following diapason: 100 – 300 cycles. The first phase is sharp decrease of capacity, the second is a steady deterioration which is in the following diapason: 300 -800 cycles. At high cycle number of battery for a lot of studies, it is noticed the third which is a dramatic decrease in capacity[45]. But in our case, third phase cannot be noted because, cycling of the battery should be continued till approximately 2000 cycles.

4.2.1 Entropymetry based on simple potentiometric method

To begin with, a straightforward potentiometric method was used to compute the entropy of the battery. The battery's open circuit voltage (OCV) was measured at various

states of charge while adjusting temperatures, as illustrated in Figure 4.10. The OCV was linearly correlated to temperature, and the resulting correlation was graphed in Figure 4.11. The slope of this linear correlation, which corresponds to the potential gradient to temperature (dE/dT) in equation 1, was determined. Using this slope, the entropy of the battery at the corresponding state of charge was calculated. Finally, Figure 4.12 illustrates the relationship between the entropy and state of charge (SOC) of the battery.

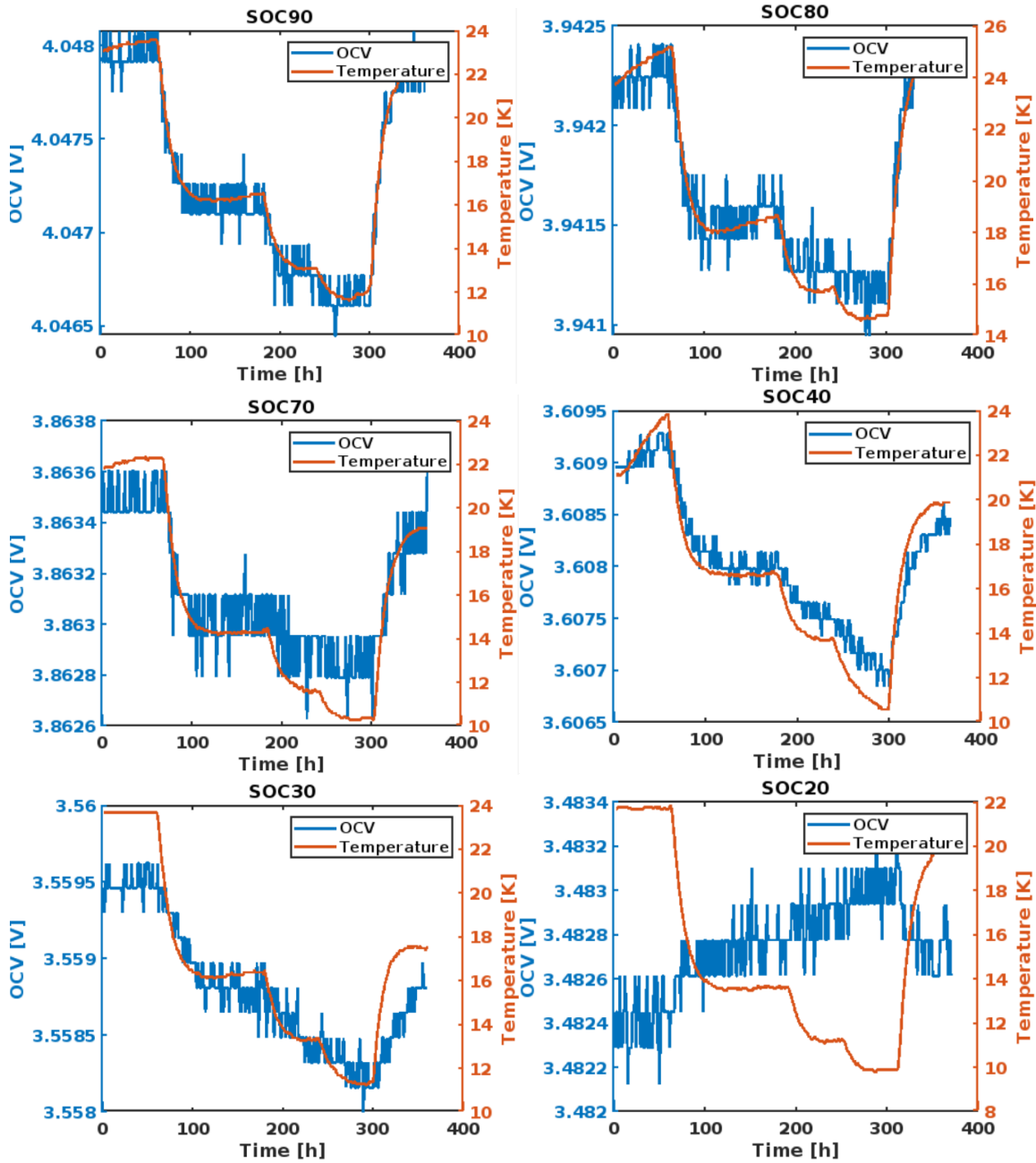


Figure 4.9. Open circuit voltage dependence to relaxation time with simple entropy computation method.

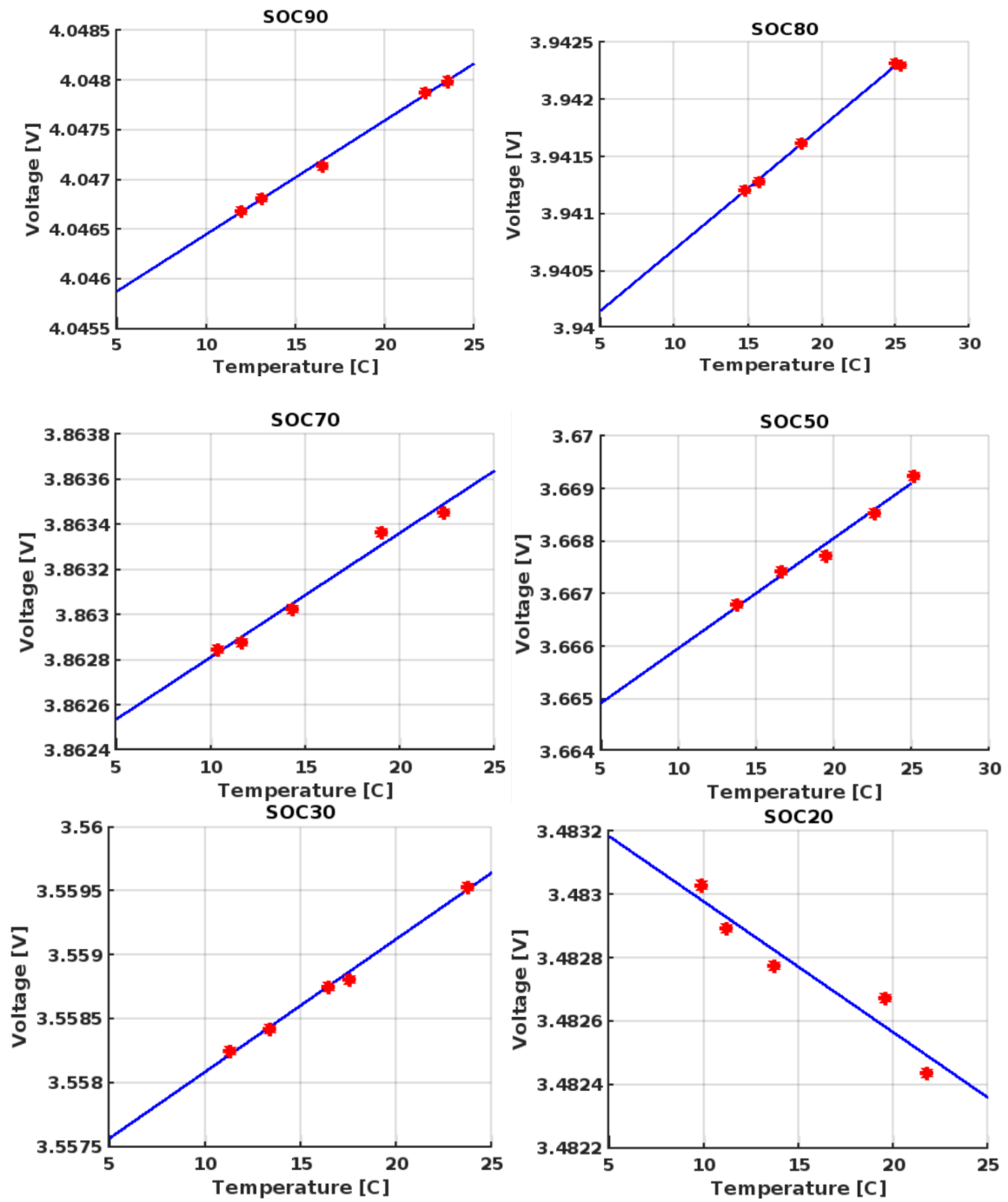


Figure 4.10. Open circuit voltage dependence to temperature with simple entropy computation method.

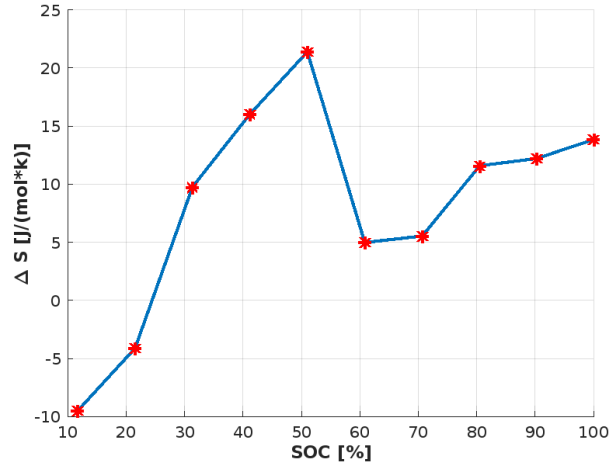


Figure 4.11. Entropy profile of the battery at various state of charge (SOC)

It can be noticed from Figure 4.12 that entropy changes significantly upon different SOC. This behavior is nonlinear and its shape is similar to large anisotropic unit volume changes happening in $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC) type battery [64]. Upon delithiation of cathode NMC, lattice parameter of c-axis is increased up until 4 V, and then suddenly drops upon further delithiation, while lattice parameter of a-axis is steadily decreasing. Figure 4.12 depicts the same behavior since cathode delithiation indicates increase in the state of charge. Since entropy is related to degree of randomness, microscopic changes happening inside of a cell can be observed by noninvasive technique such as entropymetry. This nonlinear behavior is reported for the first time to the best of our knowledge.

4.2.2. Entropymetry based on fast potentiometric method

Figure 4.13 displays the open circuit voltage (OCV) of the battery as measured at various states of charge while adjusting temperatures. It can be observed that the OCV doesn't reach full relaxation even when a positive adjustment is applied to achieve the appropriate state of charge. To analyze the results, the OCV data at the second temperature was linearly extrapolated until the OCV was measured at the final temperature. The extrapolated OCV value at the second temperature is labeled as E_2 , while the OCV value at the final temperature is labeled as E_1 . Using these values, the entropy of the battery was estimated using the following equation:

$$\Delta S = n * F * \frac{E_2 - E_1}{T_2 - T_1} \quad (13)$$

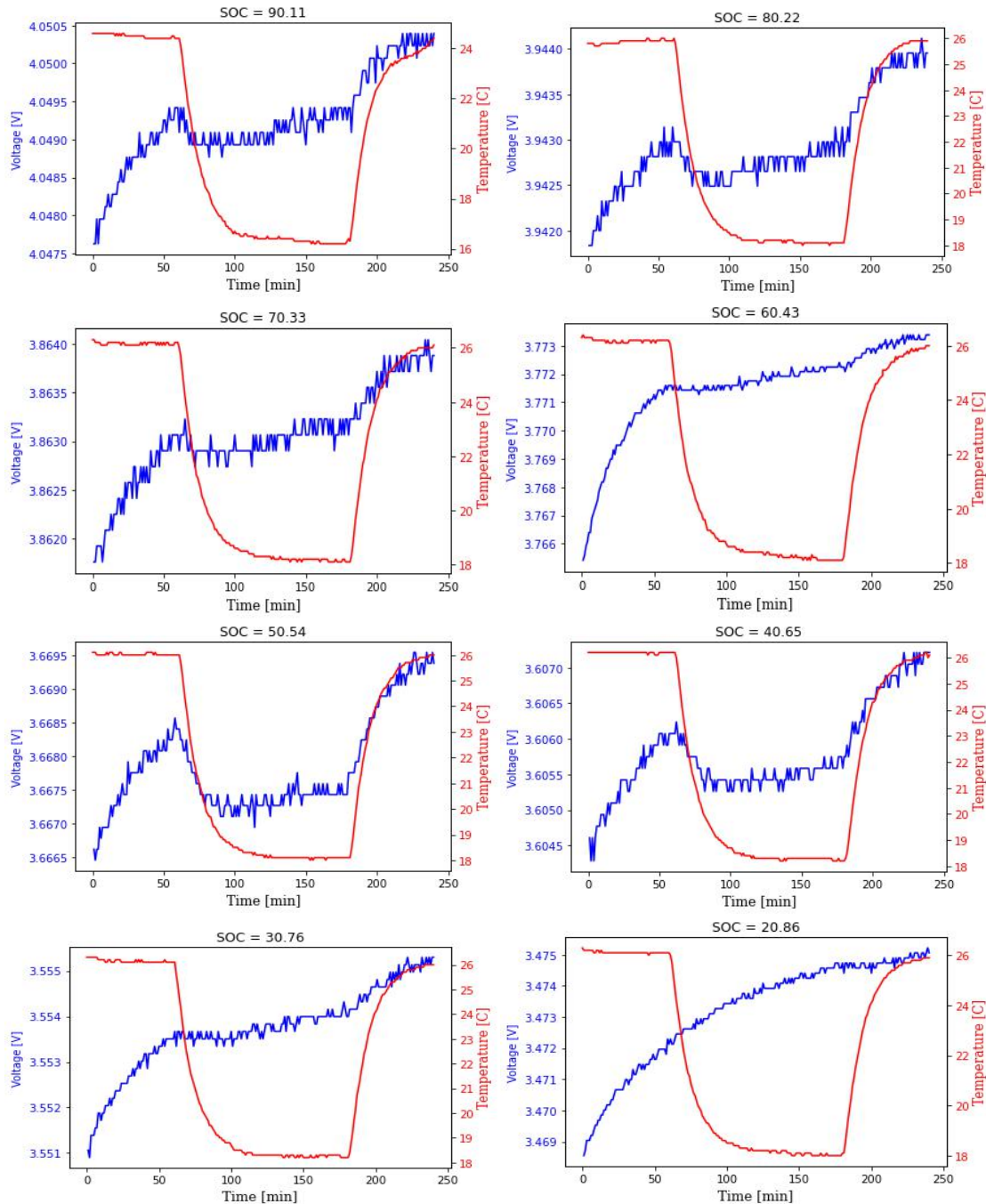


Figure 4.12. Open circuit voltage dependence to relaxation time at developed fast entropy computation method.

The entropy values obtained using the fast potentiometric method were verified by comparing them with the results obtained through the simple potentiometric method, as illustrated in Figure 4.14. It can be seen that the two methods give same entropy profile with R^2 value of 0.9994, while the fast potentiometric methods is much quicker.

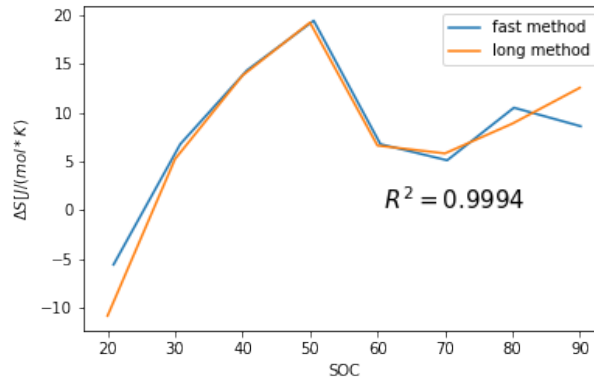


Figure 4.13. Verification of the fast entropy estimation method by comparison with the long entropy estimation method. The R^2 of the fast entropy estimation method is 0.9994.

After verifying the fast potentiometric method, the entropy profiles of the battery were obtained for various cycle numbers, as depicted in Figure 4.15. The figure indicates a rapid change in entropy in the 40-60% state of charge (SOC) range, which we believe corresponds to a significant phase transition previously identified through differential capacity analysis of the charge-discharge profile at the 3.3-3.7 V region. As the battery degrades, the amplitude of the peaks in the entropy profile decreases, which is consistent with Hye J.'s findings in the case of a LiCoO_2 battery. This behavior is attributed to the high ordering of the structure as battery degradation increases, leading to a decrease in entropy due to an increase in the ordering of the microstructure of the material [58].

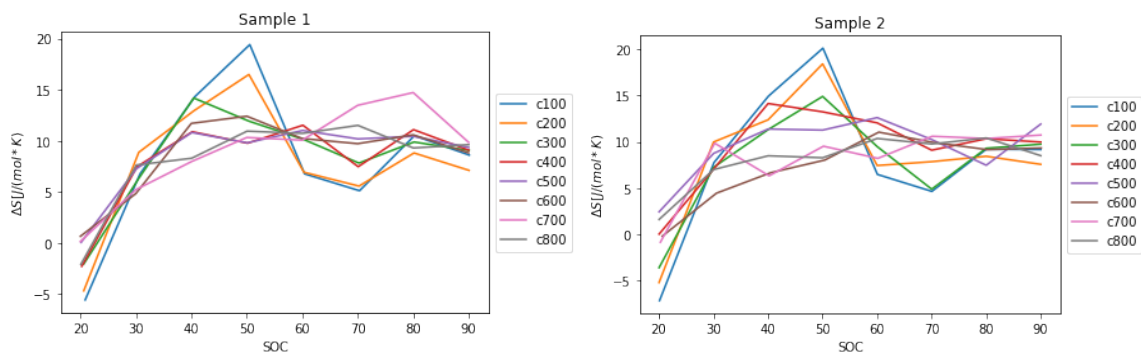


Figure 4.14. Entropy profile of two samples of NCR18650 PANASONIC battery at various cycles of the battery. The battery is cycled at 1.5 C rate.

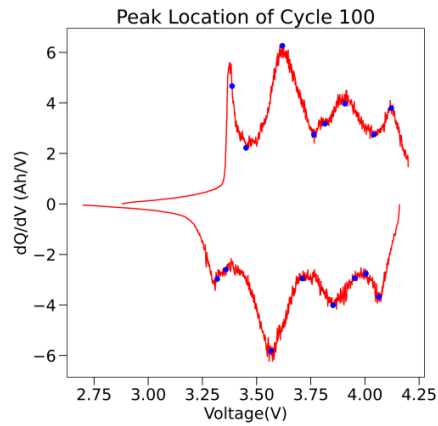


Figure 4.15. Differential capacity of the NCR18650 battery at 100 cycle.

SOC estimation based on entropymetry

It seems that the data collected for a process involving NCR 18650 Panasonic batteries at various states of health were used to establish a relationship between the state of charge (SOC) and the thermodynamic parameters of enthalpy and entropy. The relationship between SOC and these thermodynamic parameters were established using Equation 3. A linear regression model was created using the data collected, and a 3D model of the linear regression is depicted in Figure 4.16.

Tables 4.2 and 4.3 present the coefficients of the linear regression for different states of health of the battery. It can be noticed that the coefficient of determination (R-squared) of the model at various states of health is higher than 0.99, indicating that the linear regression model provides a very good fit to the data. However, correlation between the coefficients and SOH was not found. This might be attributed to the fact that better interpretation of universal SOC equation should be improved.

It is worth noting that entropy (ΔS) and enthalpy (ΔH) are thermodynamic parameters that are commonly used to describe the energy changes that occur during a process. Enthalpy is a measure of the heat energy that is absorbed or released during a process, while entropy is a measure of the disorder or randomness of the system.

Based on the high accuracy of the SOC linear regression model illustrated in tables 4.2 and 4.3, it can be concluded that SOC can be estimated with high precision at various state of health of the battery.

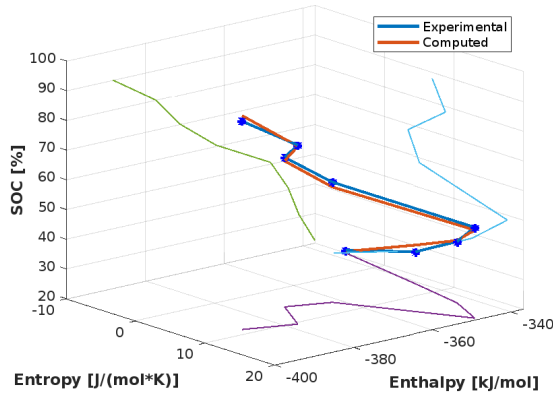


Figure 4.16. 3D representation of linear regression model of state of charge of the battery at cycle 100

Table 4.2. Linear regression coefficients at various state of health of the battery – sample 1

Cycle, 1.5C	SOH [%]	α [%]	β [mol * K/J]	γ [K/kJ]	R^2
100	96,33425	-388,579	0,612008	-1,22409	0,996572
177	93,20128	-403,533	0,639442	-1,26342	0,9968
277	93,1519	-392,211	0,66367	-1,23001	0,997524
377	90,42072	-397,364	0,655986	-1,2434	0,997705
477	88,03792	-404,842	0,758827	-1,26192	0,998679
577	86,65717	-407,797	0,69992	-1,26934	0,999051
677	84,84225	-396,911	0,801159	-1,23537	0,999787
777	83,83708	-416,094	0,632264	-1,29259	0,998612

Table 4.3. Linear regression coefficients at various State of health of the battery – sample 2

Cycle, 1.5C	SOH [%]	α [%]	β [mol * K/J]	γ [K/kJ]	R^2
100	0,960624	-391,332	0,560365	-1,23251	0,996264
177	0,931343	-404,212	0,611583	-1,26406	0,997052
277	0,931084	-393,864	0,587583	-1,23549	0,997247
377	0,907876	-399,38	0,645262	-1,24738	0,998313
477	0,885132	-410,296	0,613458	-1,27856	0,997649
577	0,87916	-393,294	0,851047	-1,22893	0,998979
677	0,856921	-417,066	0,587966	-1,29834	0,997822
777	0,843349	-415,521	0,881287	-1,28644	0,999113

4.3 Data-driven method

The artificial intelligence techniques can be applied in two ways: machine learning method or deep learning method. Due to simplicity and limited data in this research work, it was preferred to use machine learning method since deep learning method needs more data than machine learning method. In order to build the data-driven model based on machine learning method, charge discharge profile data of 8 samples of NCR 18650 cylindrical battery was collected at 1.5 C-rate which is depicted in Figure 4.17.

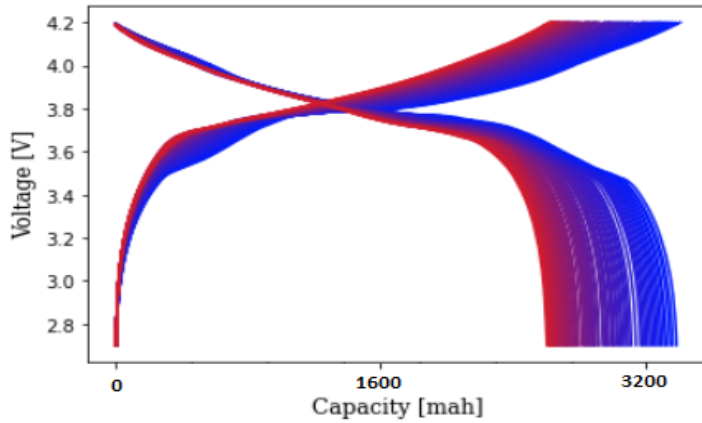


Figure 4.17. Charge discharge profile of the battery at high C – rate.

The first step in creating the machine learning method is feature generation. As the initial data: current, time of charging, capacity, voltage were used. According to the review paper [58], the feature generation method which is the appropriate in our case was selected. In addition to the initial data, the new feature which is obtained based on area under the voltage value in charge discharge profile was extracted.

After feature generation, the new generated data is divided into the following portions: 75 % of data for learning set, 12,5 % of data for validation test, and 12,5 % of data for test set. To efficiently select the right algorithm, the following machine learning algorithm was applied: Gaussian process (GPR), Recurrent neural network (RNN), Gated recurrent unit, and Long-short term memory. The algorithm was selected based on the coefficient of determination R^2 . Overall, the workflow process selecting the best algorithm is illustrated in figure 4.17. According to results illustrated in Table 4.3, Long-short term memory was chosen as the best algorithm for estimation the state of health of the battery.

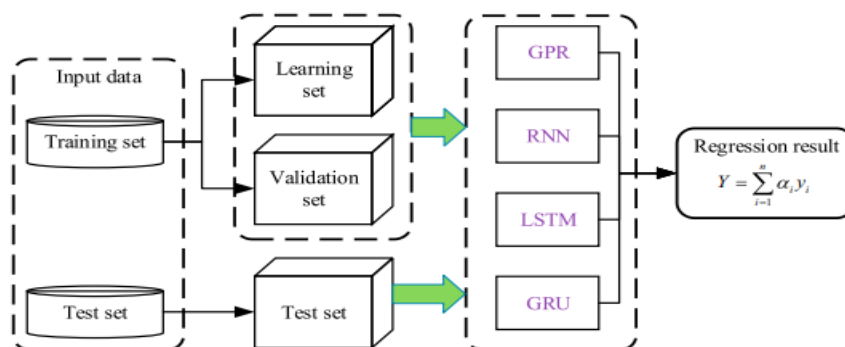


Figure 14. The fusion of multiple ML models

Figure 4.18. The process workflow of training of the data and selecting the best algorithm.

Table 4.4. The precision of each machine learning algorithm

Nº	Algorithm	R ²
1	GPR	0,7886
2	RNN	0,8419
3	LSTM	0,9215
4	GRU	0,8744

Brief description of the algorithms, it is discussed below:

1. Gaussian Process Regression (GPR): GPR is a type of supervised learning algorithm used for regression tasks. It works by modeling the data as a Gaussian process, which is a collection of random variables, any finite number of which have a joint Gaussian distribution. GPR is particularly useful for problems where there are few data points and a high degree of uncertainty. According to the article [51], Gaussian process regression for forecasting battery state of health based on the cycling number history of the battery. They verified their model with 92 % precision on lithium ion battery of different model. They noticed that, this model is not universal for various battery.

2. Recurrent Neural Networks (RNN): RNNs are a type of neural network that can process sequential data by maintaining a state or memory of previous inputs. This allows them to capture dependencies and patterns in the sequence, making them well-suited for tasks such as natural language processing, speech recognition, and time-series analysis.

3. Long Short-Term Memory (LSTM): LSTM is a type of RNN architecture that addresses the problem of vanishing gradients, which can occur when training deep neural networks. LSTMs use a memory cell, which can store information for long periods of time, and gates, which control the flow of information into and out of the cell. This allows them to remember information over longer time periods, making them well-suited for tasks such as speech recognition and language translation.

4. Gated Recurrent Unit (GRU): GRU is another type of RNN architecture that is similar to LSTM but has fewer parameters. Like LSTM, GRU uses gates to control the flow of information, but it combines the forget and input gates into a single "update gate." This simplifies the architecture and can make it faster to train, while still allowing it to capture dependencies in sequential data. GRU is often used in applications such as speech recognition and machine translation.

Chapter 5 – Conclusion

Thermodynamics profile of the lithium thionyl battery was obtained for two samples. The voltage of the lithium thionyl battery is almost constant at various SOH, but thermodynamics profile showed that entropy is altering while discharging of the battery. Universal SOC law model (Eq. 10) showed fitting with low precision. Therefore, mathematical model in which entropy depends on state of charge of the battery by 6th order polynomial function was suggested. The proposed model showed R^2 higher than 0.95 for both samples. In addition constant coefficients of proposed mathematical model to use in estimation of state of health of the battery were determined.

The research work introduces a novel method for estimating entropy quickly by adjusting positive charging for secondary batteries, which was verified by comparing it to a simple potentiometric method. This method was used to obtain the entropy profile of the cylindrical NCR18650 battery at different states of health. The results show a rapid change in ΔS in the 40-60% SOC region, which corresponds to a significant phase transition region. This phase transition region was further confirmed using differential capacity analysis with the DiffCapAnalyzer package [60]. In addition, accurate coefficients of the linear regression model of Eq. 11 were obtained at various states of health of the battery. These findings can be useful for the development of battery management systems.

Moreover, the charge discharge profile of 8 samples of NCR 18650 was collected for AI technique. Based on the charge discharge profile data, new features by area envelope feature generation method was obtained. Consequently, the SOH estimation of battery was tested by various algorithms: Gaussian process (GPR), recurrent neural network (RNN), Gated recurrent unit, and Long-short term memory. Finally, Long-short term memory was selected as the best algorithm of state of health estimation.

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Entropy Measurements of Li-Ion Battery Cells with Li- and Mn- Rich Layered Transition Metal Oxides via Linear Temperature Variation."



Appendix – A (Review paper)

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Review Article

State of Health Estimation Methods for Lithium-Ion Batteries

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Contemporary lithium-ion batteries (LIBs) are one of the main components of energy storage systems that need effective management to extend service life and increase reliability and safety. Their characteristics depend highly on internal and external conditions (ageing, temperature, and chemistry). Currently, the state of batteries is determined using two parameters: the state of charge (SOC) and the state of health (SOH). Applying these two parameters makes it possible to calculate the expected battery life and a battery's performance. There are many methods for estimating the SOH of batteries, including experimental, model-based, and machine learning methods. By comparing model-based estimations with experimental techniques, it can be concluded that the use of experimental methods is not applicable for commercial cases. The electrochemical model-based SOH estimation method clearly explains processes in the battery with the help of multidifferential equations. The machine learning method is based on creating a program trained to predict the battery's state of health with the help of past ageing data. In this review paper, we analyze the research available in the literature in this direction. It is found that all methods used to assess the SOH of an LIB play an essential role, and each method has its pros and cons.

Appendix – B (conference)



Appendix – C (

