# Lithium-ion Battery State Monitoring Method via Frequency Excitation: Verification in Experiments and Simulations

vorgelegt von M. Sc. Jonghyeon Kim ORCID: 0000-0003-2632-3695

von der Fakultät IV - Elektrotechnik und Informatik der Technischen Universität Berlin zur Erlangung des akademischen Grades

> Doktor der Ingenieurwissenschaften - Dr.-Ing. -

> > genehmigte Dissertation

Promotionsausschuss:

Vorsitzender: Prof. Dr.-Ing. Sibylle Dieckerhoff Gutachter: Prof. Dr.-Ing. Julia Kowal

Gutachter: Prof. Dr. Sangyoung Park

Gutachter: Prof. Dr.-Ing. Young Hyun Lee

Tag der wissenschaftlichen Aussprache: 06. April 2022

Berlin 2022

## Abstract

As rapid industrialization and the use of fossil fuel resources accelerate climate change, such as greenhouse effects, interest in eco-friendly energy is increasing worldwide. Especially, as interest in eco-friendly vehicles and efforts to reduce carbon emission from vehicles with internal combustion engines increase, the demand for secondary batteries is increasing, and among them, lithium-ion batteries (LIBs) are leading the innovation. However, LIBs with high energy have high safety risks as well, requiring improved diagnosis and management technology.

Electrochemical impedance spectroscopy (EIS) is a non-invasive analysis technique that determines the dynamic behavior of an electrochemical system and is used to characterize battery behavior with impedance at a wide frequency range. Therefore, it can be used to measure parameters of battery cells in which the model structure is determined by cell state of charge (SoC), state of health (SoH), temperature, internal defects, etc. However, typical EIS analyzers require high performance applicable to general-purpose measurement, thus they may be an excessive investment to be used in battery monitoring systems and are especially large in mass and volume to be applied to portable devices. Furthermore, they require a long time to measure impedance in a wide frequency range.

This thesis deals with LIB state monitoring methods using frequency excitation. By using the proposed method, the cell SoH and SoC can be monitored by impedance, and an over-discharged cell in a battery pack can be detected by frequency distortion rate. Unlike other studies on battery impedance, the state of the battery is monitored during operation. By applying multi-sine frequency signals, SoH and SoC of operating cells are estimated at the same time and the time required to measure cell impedance at a wide range of frequencies is reduced.

A MATLAB/Simulink model is developed as well to optimize and simulate LIB cell state monitoring algorithms using frequency excitation. The battery cell simulation model saves experimental time as well as cost for experimental devices. This is because simulation results are quickly displayed by simply entering parameters representing the state of the battery cell. Considering the effect of cell SoC, SoH, temperature and C-rate, the proposed model successfully predicts the continuous cell voltage, impedance and distortion rate when multiple frequency signals are applied to DC bias of cell while being discharged.

## Zusammenfassung

Da die rasante Industrialisierung und Nutzung fossiler Brennstoffe den Klimawandel wie den Treibhauseffekt beschleunigen, steigt weltweit das Interesse an umweltfreundlicher Energie. Insbesondere mit dem steigenden Interesse an umweltfreundlichen Fahrzeugen und den Bemühungen, die CO2-Emissionen von Fahrzeugen mit Verbrennungsmotor zu reduzieren, steigt die Nachfrage nach Sekundärbatterien, und unter diesen sind Lithium-Ionen-Batterien (LIBs) führend bei der Innovation. Dennoch können LIBs mit hohen Energien kritische Sicherheitsprobleme aufwerfen, die verbesserte Diagnosetechniken erfordern.

Die elektrochemische Impedanzspektroskopie (EIS) ist eine nicht-invasive Analysetechnik zur Bestimmung des dynamischen Verhaltens elektrochemischer Systeme und wird genutzt, um das Batterieverhalten durch Impedanz über einen weiten Frequenzbereich zu charakterisieren. Daher kann es verwendet werden, um die Parameter einer Batteriezelle zu messen, deren Modellstruktur durch Ladezustand (SoC), Gesundheitszustand (SoH), Zelltemperatur, interne Defekte usw. bestimmt wird. Nichtsdestotrotz sind typische EIS-Analysatoren auf Allzweckmessungen angepasst und haben deshalb einen hohen Leistungsumfang, sodass sie für den Einsatz in Batterieüberwachungssystemen eine Überinvestition darstellen können, und insbesondere sind Masse und Volumen zu groß, um auf tragbare Geräte angewendet zu werden. Außerdem benötigen sie eine lange Zeit für die Impedanzmessung über einen weiten Frequenzbereich.

Diese Dissertation befasst sich mit der Überwachung des Zustands von LIBs durch Frequenzanregung. Die Batteriezellenimpedanz wird gemessen, um SoH und SoC zu überwachen, und die Frequenzverzerrungsrate des Batteriepacks wird gemessen, um eine überladene Zelle zu erkennen. Unter Verwendung von Multi-Sinus-Frequenzsignalen werden SoH und SoC der Betriebszelle gleichzeitig geschätzt, wodurch die Zeit für die Messung der Zellimpedanz über einen weiten Frequenzbereich reduziert wird.

Außerdem wurde ein MATLAB/Simulink-Modell entwickelt, das zur Optimierung und Simulation von frequenzbasierten Algorithmen zur Überwachung des Batteriezustands verwendet werden kann. Das Batteriezellen-Simulationsmodell spart nicht nur Zeit für das Experimentieren, sondern auch die Kosten für den Versuchsaufbau, da die Simulationsergebnisse durch einfache Eingabe von Parametern, die den Zustand der Batteriezellen anzeigen, schnell angezeigt werden. Die Auswirkungen von SoC, SoH, Temperatur und C-Rate der LIB-Zelle werden berücksichtigt, und das vorgeschlagene Modell gibt erfolgreich eine kontinuierliche Spannung, Impedanz und Frequenzverzerrungsrate aus, wenn mehrere Frequenzsignale während der Batterieentladung angelegt werden.

# List of Contents

Abst	tract			
ZusammenfassungV				
List	List of Contents VII			
AcknowledgementsIX				
List	of Abb	oreviati	ons	XI
List	of Figu	ures		XIII
List	of Tab	les		XVII
1	Motivation1			
2 Fundamentals			als	3
	2.1	Fun	damentals of LIB Cells	3
		2.1.1	Operating principles of LIB cells	4
	2.2	Agiı	ng Processes of LIB Cells	6
	2.3	Ove	erview of Battery Cell Management	8
	2.4	Def	inition of Key Terms	10
	2.5	SoH	Estimation Methods of LIB Cells	12
	2.6	SoC	Estimation Methods of LIB Cells	20
3	Experimental			25
	3.1	EIS	Measurement	25
		3.1.1	Cell impedance at different SoHs	25
		3.1.2	Cell impedance at different SoCs	27
		3.1.3	Cell impedance at different temperatures	28
	3.2	Free	quency Excitation	29
		3.2.1	Signals applied to measure the cell impedance	29
		3.2.2	Methods for applying test signals	29
	3.3	Setu	up for the frequency excitation	30
		3.3.1	Measurement system for frequency excitation	30
		3.3.2	Selection of test frequencies	33
		3.3.3	Selection of test amplitude	33
4	SoH E	Estimat	ion of LIB Cells Using Frequency Excitation	35
	4.1	Imp	edance Measurement during Discharge of Cells with Different SoHs	35
		4.1.1	Cell impedance at different SoHs	37
		4.1.2	Measurement time required for SoH estimation	
	4.2	Imp	edance Measurement in Another Type of Cell	41
5	SoC N	Monito	ring of LIB Cells Using Frequency Excitation	43

	5.1	Mu	lti-sine EIS	43
		5.1.1	Selection of test frequencies for estimating cell SoH and SoC	44
	5.2	Con	tinuous cell impedance measured with multiple frequencies	45
		5.2.1	Effect of polarization	46
	5.3	Con	sideration of cell temperature	47
	5.4	Con	sideration of cell SoH	50
	5.5	SoC	Monitoring at Different Initial SoCs	52
6	Mode	eling of	LIB Cells for State Monitoring	55
	6.1	Stat	e of the Art	56
	6.2	A LI	B Cell Simulation Model for Monitoring SoH and SoC via Cell Impedance.	59
		6.2.1	SoC model	59
		6.2.2	LIB cell model	61
		6.2.3	The output of continuous cell impedance at multiple frequencies	67
		6.2.4	Cell temperature model	70
	6.3	Sim	ulation Result and Validation	71
		6.3.1	Simulation of continuous cell impedance	71
		6.3.2	Simulation of cell impedance discharging from different initial SoCs	74
		6.3.3	Simulation results at different diagnostic parameters	77
7	Frequ	uency E	xcitation to the Battery Pack	81
	7.1	Cell	Balancing	83
	7.2	Cau	ses of Cell Imbalance	84
	7.3	Pro	blems Due to Battery Cell Imbalance	85
	7.4	Det	ection of an Over-discharged Cell in a Battery Pack Using THD	86
		7.4.1	THD simulation of a cell during discharge	87
		7.4.2	THD measurement of a cell during over-discharge	90
		7.4.3	THD measurement of the battery pack during over-discharge	92
		7.4.4	THD simulation in different numbers of serial-connected cells	94
8	Conc	lusion a	and Future Work	99
9	References			
10	Appendix			

## Acknowledgements

This thesis originates from my studies at the Electrical Energy Storage Technology (EET) of the Technical University of Berlin.

The studies have been able to be conducted with scholarship funding from the German academic exchange service (DAAD) for a total of four and a half years, and I sincerely appreciate this benevolent support.

First of all, I would like to express my gratitude to Prof. Dr.-Ing. Julia Kowal for giving me the opportunity to start my studies and guiding me all the time. Furthermore, I am very honored and grateful that Prof. Dr.-Ing. Young-hyun Lee and Prof. Dr. Sangyoung Park review this thesis.

In addition, I sincerely thank all my colleagues in the EET. Throughout all my studies, I received a lot of help from them. They have a tremendous passion for their studies and are always full of willingness to help. In particular, I received a lot of help from Dipl.-Ing. Lars Krüger to build a measurement system.

Last but not least, I want to thank my family, especially my wife Sua Kang. They trusted me with all their heart and supported me with all their might, so I was able to do my best in my studies and achieve this achievement.

## **List of Abbreviations**

LIB lithium-ion battery. 1 EV electric vehicles. 1 **COP21** 21st conference of the parties. 1 **ZEV** zero-emission vehicle. 1 ESS energy storage system. 1 **BNEF** Bloomberg new energy finance. 1 BMS battery management system. 1 SoH state of health. 2 **SoC** state of charge. 2 **EIS** electrochemical impedance spectroscopy. 2 **THD** total harmonic distortion 2 LMO lithium manganese oxide spinel. 4 LCO lithium cobalt oxide. 4 NMC nickel manganese cobalt oxide. 4 NCA Lithium nickel cobalt aluminum oxide. 4 LFP lithium iron phosphate. 4 LTO lithium titanium oxide. 4 SEI solid electrolyte interface. 6 DoD depth of discharge. 10 CC constant current. 10 CV constant voltage. 10 EoL end of life. 11 PCM protection circuit module. 12 ECM equivalent circuit model. 14 ICA incremental capacity analysis. 14 **DVA** differential voltage analysis. 14 **OCV** open-circuit voltage. 21 NN neural network. 22 SVM support vector machine. 22 **GA** genetic algorithm. 22 KF Kalman filter. 22 **EKF** extended Kalman filter. 22 **UKF** unscented Kalman filter. 22 SPKF sigma point Kalman filter. 22 **PF** particle filter. 23 RLS recursive least square. 23 **NLO** nonlinear observer 23 PIO proportional integrated observer. 23 **SMO** sliding mode observer. 23 BI bi-linear interpolation. 23 EMF electromotive force. 23 MARS multivariate adaptive regression spline. 23 IR impulse response. 23

SNR signal to noise ratio. 29 DAQ data acquisition. 30 ADC analog to digital converter. 30 DAC digital to analog converter. 30 GUI graphical user interface. 30 RMSE root mean square error. 49 CPE constant phase element. 56 CNLS complex nonlinear least square. 58 EoD End of discharge. 84

# List of Figures

Figure 1.1 Annual LIB demand, announced by Bloomberg New Energy Finance (2021)	2
Figure 2.1 Main components of a LIB cell.	4
Figure 2.2 Voltage and current of the battery cell in the CC-CV charging stage1	4
Figure 2.3 Pulse test to obtain the resistance of the battery cell1	5
Figure 2.4 A representative example of Nyquist plot of LIB cell impedance.	8
Figure 3.1 (a) Nyquist plot and (b) Bode diagram at different cell SoHs	6
Figure 3.2 (a) Nyquist plot and (b) Bode diagram showing impedance at each cell SoC2	7
Figure 3.3 (a) Nyquist plot and (b) Bode diagram at different cell temperatures2	8
Figure 3.4 (a) A block diagram of the measurement system and (b) a photo of the measurement	
system3	1
Figure 3.5 Schematic diagram of the electronic load3	2
Figure 3.6 Lissajous plot of current for potential in a stable pseudo-linear system	4
Figure 4.1 Continuous cell impedance at five different frequencies and cell voltage during cell	
discharge3	5
Figure 4.2 Cell voltage and impedance at 1, 10, 20, 100, and 250 Hz during CC charge	6
Figure 4.3 Mean values of cell impedance at different cell SoHs and fitted line	8
Figure 4.4 Cell charge curve and cell impedances at 1, 10, 20, 100, and 250 Hz	9
Figure 4.5 Increasing cell temperature during 1C discharge	9
Figure 4.6 Nyquist plot showing impedance in different SoHs4	1
<b>Figure 4.7</b> 1 kHz impedance during cell discharge at different SoHs4	2
Figure 4.8 1 Hz, 250 Hz, and 1 kHz impedance in different SoHs4	2
Figure 5.1 A flow chart showing the cell state estimation process4	3
Figure 5.2 Continuous 1 Hz and 1 kHz impedance during discharging of cells with different SoHs4	5
Figure 5.3 Typical discharge curve of a battery cell, showing three different regions of polarization.	
4	6
Figure 5.4 The temperature change of the battery cell during discharging with 1C current4	7
Figure 5.5 Cell impedance at each frequency at 20, 25, 30, and 35 °C. (a) Nyquist plot. (b) Bode	
diagram4	8
Figure 5.6 1 Hz impedance measured at 20, 25, 30 and 35 °C and fitted curve	8
Figure 5.7 1 Hz impedance adjusted to 25 °C4	9
Figure 5.8 Normalized 1 Hz impedance and fitted curve of cells with different SoHs5	0

Figure 5.9 (a) Cell voltage and cell temperature, and (b) 1Hz impedance and 1 kHz impedance while the cell is being discharged
<b>Figure 5.10</b> (a) 1 Hz impedance adjusted to cell temperature and (b) Temperature-adjusted 1 Hz impedance normalized to cell SoH and expected value while the cell is being discharged
Figure 6.1 Overall view of the proposed simulation model59
Figure 6.2 Voltage curves of the LIB cell discharged at different C-rates
Figure 6.3 Cell equivalent circuit used in the model61
Figure 6.4 OCV of the battery cell used for modeling
Figure 6.5 Nyquist plots of measured cell impedance and fitted results
<b>Figure 6.6</b> (a) Input current and (b) output voltage expressed in the time domain, and (c) the output voltage expressed in the frequency domain as a result of the simulation model
<b>Figure 6.7</b> Simulation result of 1, 10, 100, and 1000 Hz impedance in the entire DoD range of the discharged cell
Figure 6.8 Temperature changes of cells discharging at different C-rates
<b>Figure 6.9</b> (a) Simulated and measured 1 Hz impedance of cells discharged at different C-rates (dashed line: measured impedance, solid line: simulated impedance). (b) Percentage errors of the estimated impedance compared to the measured impedance at different C-rates
Figure 6.10 Continuous 250 Hz impedance at each SoH73
<b>Figure 6.11</b> (a) Discharge curve of a cell in which 10 minutes of discharge and 60 minutes of relaxation are repeated. (b) Percentage error of simulated cell voltage compared to the measured voltage
<b>Figure 6.12</b> (a) Output of the cell temperature model when discharging for 10 minutes and relaxation for 60 minutes are repeated. (b) Measured continuous 1 Hz impedance and simulated results. (c) Percent error of simulated 1Hz impedance considering the cell temperature compared to the measured impedance
<b>Figure 6.13</b> (a) Continuous cell impedance from 1 Hz to 100 Hz simulated in the entire DoD range. (b) The increased rate of impedance at each frequency
<b>Figure 6.14</b> (a) Continuous cell impedance in the entire DoD range simulated at different sampling rates. (b) Percentage errors of the simulation results between the sampling rate of 2048 Hz and each sampling rate of 16 Hz to 1024 Hz79
Figure 7.1 (a) Series-connected cells having a uniform voltage and (b) having a non-uniform voltage
<b>Figure 7.2</b> Results of 1 Hz and 250 Hz impedance simulation of a battery pack consisting of series- connected cells
Figure 7.3 Simulated cell voltage, 1 Hz impedance, and THD while the cell is discharged
Figure 7.4 (a) Simulated voltage response and (b) frequency response for 1 second at 50% SoC88
Figure 7.5 (a) Simulated voltage response and (b) frequency response for 1 second at 2% SoC89

Figure 7.6 A photo of a device that connect three LIB cells in series.	90
Figure 7.7 Cell voltage and THD measured until the cell is over-discharged	91
Figure 7.8 Voltage and THD of the battery pack while one cell is over-discharged	92
Figure 7.9 THD of the battery pack and voltages of each cell while one cell is over-discharged	93
Figure 7.10 Battery pack voltage and normal cell voltage while one weak cell reaches EoD	94
Figure 7.11 THD for weak cell voltages in different numbers of series-connected cells.	95
Figure 7.12 THD increased rate in the different number of series-connected cells.	96

# List of Tables

Table 2.1 Equations of major electrode processes in LIB cells.         17
Table 3.1 Measurement conditions for EIS analysis.         25
Table 3.2 Specifications of the Li-ion cell.         25
<b>Table 4.1</b> Experimental conditions for measuring cell impedance during discharge.         35
Table 4.2 Standard deviation of measured cell impedance at five different frequencies.         36
Table 4.3 Experimental conditions for measuring cell impedance during charging.         36
Table 4.4 Standard deviation of measured cell impedance at each frequency during charging.         37
Table 4.5 Experimental conditions for measuring cell impedance at different SoHs.         37
Table 4.6 Experimental conditions for impedance measurements from different initial SoCs.         38
Table 4.7 Measurement time required for moving average to reach 98% confidence level40
Table 4.8 Specifications of another type of LIB cell41
Table 4.9 Conditions for EIS analysis of Bexel cells.         41
Table 4.10 Experimental conditions for measuring cell impedance at different SoHs (cell #7)42
<b>Table 5.1</b> Experimental conditions for measuring cell impedance during discharge.         45
Table 5.2 Parameters for EIS measurement (Galvanostatic)47
Table 5.3 Accuracy of SoC estimation in cells with different SoHs.         51
Table 5.4 Time for SoC estimation in cells of different SoHs to reach 95% and 98% confidence levels.         51
<b>Table 5.5</b> Experimental conditions for SoC estimation of cells that start operating at different SoCs.         52
Table 6.1 Different equivalent elements in ECMs.       57
Table 6.2 Relative capacities of a LIB cell discharged at different C-rates
<b>Table 6.3</b> Fitted element values for each SoC and $\chi^2/N$ representing the fitting error
Table 6.4 Increased rates in impedance at each frequency.         69
<b>Table 6.5</b> Conditions for both simulation and measurement of the impedance of the cell during         discharge.       71
Table 6.6 Average values of each percent error at different C-rates.         72
<b>Table 6.7</b> Average values of percent errors of the estimated impedance relative to the measuredimpedance at different SoHs.73
Table 6.8 Conditions for simulation and measurement of cell impedance discharged from different
initial SoCs74

Table 6.10 Simulation conditions for comparing continuous 1 Hz impedance at different sampling           rates.	3 80
<b>Table 6.11</b> Percent errors of the mean of the impedance simulated at a sampling rate of 2048 Hz           and the mean of the impedance simulated at each different sampling rate.	80
<b>Table 7.1</b> Conditions for simulating 1 Hz and 250 Hz impedance of a battery pack consisting of           series-connected cells.	81
Table 7.2 Conditions for THD simulation of a battery cell that is discharged	87
Table 7.3 Experimental conditions for THD measurement until a cell is over-discharged.	90
Table 7.4 THD values at different cell voltages.	91
Table 7.5 Experimental conditions for measuring THD of a battery pack while one cell is over-           discharged	92
Table 7.6 THDs at different cell voltages of a cell with 70% SoH	93
Table 7.7 Conditions for THD simulation in different numbers of series-connected cells	94
Table 7.8 THD increased rate in the different number of series-connected cells.	97
Table 10.1 Cells used in the measurements and the SoH at the time.	125

### 1 Motivation

The 2019 Nobel Prize in Chemistry was awarded to John B. Goodenough, M. Stanley Whittingham and Akira Yoshino for their contributions to lithium-ion battery (LIB) development. The Nobel Committee of the Royal Swedish Academy of Sciences said the lithium-ion rechargeable battery laid the foundation for wireless electronic devices such as mobile phones and laptops, and has been used to power electric vehicles (EVs) to store energy from renewable sources.

Due to rapid industrialization and the use of fossil fuel resources, climate change such as the greenhouse effect caused by carbon dioxide is accelerating around the world, increasing interest in eco-friendly energy sources. In December 2015, the 21st Conference of the Parties (COP21) was held in Paris, France. At the meeting, representatives of 195 countries agreed that the average global temperature rise would not exceed 2°C by 2100 compared to before industrialization. The Paris Agreement, which took effect in November 2016, replaces the Kyoto Protocol, which was an international commitment to greenhouse gas emissions from 1997 to 2020. The concept that emerged as a global issue in this process is carbon neutral (net zero), which reduces carbon dioxide emissions and increases absorption to zero net emissions. Finland has set a goal of achieving carbon neutrality by 2035, Iceland and Austria by 2040, Sweden by 2045, the European Union, the United Kingdom, Canada, Japan and South Korea by 2050, and China by 2060. In particular, interest in eco-friendly cars is increasing, and efforts are being made to reduce carbon emissions from internal combustion engine vehicles. Norway banned the launch of internal combustion engine vehicles by 2025 and set a goal of selling 100% of EVs. In Europe, a fine of €95 per g/km will be imposed on car manufacturers and dealers for carbon dioxide emissions exceeding their targets. The EU fleet-wide target by 2025 is an average of 81g  $CO_2$ /km. In the United States, greenhouse gas reduction and zero-emission vehicle (ZEV) mandate are being implemented, and tax breaks are provided depending on battery capacity when purchasing EVs. The U.S. also established energy storage system (ESS) obligatory rules and installation grants. China announced a new energy vehicle credit obligation system in 2017. Companies that produce or import more than 30,000 cars a year must either produce or import new energy vehicles (electric, plug-in hybrid, and fuel cell vehicles) or buy from other manufacturers that have exceeded new energy car credits [1].

For the reasons mentioned, technologies using secondary batteries are rapidly developing, such as ESS, which increases the power reserve ratio and enables efficient use of renewable energy, and EVs that reduce emissions of environmental pollutants [2, 3]. Bloomberg New Energy Finance (BNEF) estimates that demand for LIBs will increase about 5 times between 2022 and 2030, mainly due to EVs in 2021 as shown Fig. 1.1.

However, high-energy batteries using electrode materials with low thermal stability have high safety risks [4–6] for battery failure caused by an excessive external force, excessively high/low temperature, overcharge, over-discharge, etc. [7–9]. Therefore, there is an increasing need for the development of battery management system (BMS) technology that responds appropriately to the operation of the battery under various conditions and ensures safety while allowing it to operate for a longer time.



Figure 1.1 Annual LIB demand, announced by Bloomberg New Energy Finance (2021).

This thesis deals with methods of monitoring the state of LIBs using frequency response, which includes methods of monitoring cell state of health (SoH) and state of charge (SoC) as well as a method of detecting an over-discharged cell in a battery pack.

Chapter 2 introduces the components and operating principles of LIB cells and outlines battery management. In addition, not only the major degradation processes of LIB cells but also the state of the arts of cell state estimation methods are introduced.

Chapter 3 presents an overview of the experiments. Electrochemical impedance spectroscopy (EIS) of LIB cells at different SoHs, SoCs, and temperatures is analyzed to select the optimal test frequency for the state estimation. A measurement system for measuring the continuous impedance of a cell during operation as well as considerations for selecting measurement parameters are presented.

Chapter 4 introduces the SoH monitoring method of LIB cells during operation using impedance. The investigations and results presented in this chapter have been published in [10].

Chapter 5 deals with the SoC monitoring method of LIB cells using impedance. A multi-sine frequency signal is used to estimate SoH and SoC simultaneously during cell discharge. To estimate the SoC, the cell temperature and the estimated cell SoH are considered. The investigations and results presented in this chapter have been published in [11].

Chapter 6 presents a LIB cell simulation model that outputs continuous impedance during discharging. This simulation model is developed in the MATLAB/Simulink environment and can be used for the simulation and optimization of a cell state monitoring algorithm using cell impedance, considering cell SoC, SoH, temperature, and C-rate. The investigations and results presented in this chapter have been published in [12].

In Chapter 7, a method of detecting one over-discharged cell by measuring the nonlinearity of the battery pack is introduced. A test frequency is applied to the operating current of the battery pack in which the battery cells are connected in series. Even if each cell voltage is not measured, the presence of one over-discharge cell can be detected with the total harmonic distortion (THD) measured by voltage responses at two terminals of the battery pack. The proposed method is verified through simulation and measurement. The investigations and results presented in this chapter have been published in [13].

Lastly, chapter 8 summarizes the results and presents conclusions, limitations, and future works.

## 2 Fundamentals

This chapter deals with the main components and operating principles of LIB cells. In addition, major degradation processes of LIB cells as well as state estimation methods presented in the literature are introduced.

### 2.1 Fundamentals of LIB Cells

Since early lithium secondary batteries were developed for the purpose of rechargeable lithium primary batteries, lithium metal was used as an anode. Although Lithium metals allow for high capacity, it is transferred to dendrite during the charging process, which can cause ignition or explosion due to an internal short circuit by penetrating a thin polymer separator inside the battery cell. In addition, since dead lithium is produced, lithium metals need to be filled in large quantities. Later, graphite was developed as a new anode for battery cells to replace lithium metal. When graphite is used as an anode, the theoretical capacity is smaller than that of lithium metal, but the operating voltage of the battery cell is not significantly different. Graphite has layered structures that enable intercalation and de-intercalation of lithium-ions. In lithium-ion secondary batteries, lithium participates in reactions in ionic states, not metallic states. Since lithium metals are not used as electrodes, the problems of dead lithium and internal short circuits caused by the growth of lithium dendrite are greatly improved.

The secondary batteries are rechargeable, unlike the primary batteries that cannot be reused after a complete discharge. Therefore, secondary batteries are considered eco-friendly by reducing the consumption of resources to make cells as well as reducing environmental substances caused by chemicals in the disposal process. Lithium secondary batteries, which use lithium-ions as charge carriers within electrodes and electrolytes, exhibit high energy density by maintaining a high average discharge voltage of 3.7 V or higher while being lightweight, making them the leading battery in innovation. In addition, since they hardly show self-discharge and memory effects and have stable performance and long cycle life, they are widely adopted [14, 15] in portable electronic devices [16], EVs [17], spaceships and aircraft power systems [18], renewable energy systems [19], marine current energy systems [20], stationary energy storage [21], etc.

The terms battery and battery cell are often used incorrectly. In this thesis, a battery or battery pack refers to a device composed of galvanic cells connected in series or parallel and the battery cell or cell is used as a term for a single individual galvanic device [22].

#### 2.1.1 Operating principles of LIB cells

LIB cell converts chemical energy into electrical energy through redox reactions at the anode and cathode. The main components of LIB cells are anode, cathode, electrolyte, and separator as Fig. 2.1.



Figure 2.1 Main components of a LIB cell.

#### - Positive electrode (cathode)

The cathode is an electrode that is reductive. Therefore, the positive electrode is cathode when the battery cell is discharged, but it is also technically anode when charged. However, the positive electrode in the battery cell is called cathode regardless of charge or discharge, which has continued in the primary cell field.

LIB cells are applied with different electrode materials depending on their application and each has its own advantages and disadvantages [23, 24]. The most commercially used cathode materials are lithium manganese oxide spinel (LMO) and lithium cobalt oxide (LCO). Subsequently, a cathode composed of lithium nickel manganese cobalt oxide (NMC) belonging to the mixed transition metal oxide is widely used for longer cycle life and higher energy density. However, a major disadvantage of NMC is its high cost due to limited cobalt resources. Lithium nickel cobalt aluminum oxide (NCA) is used for LIB cathode in some applications because it has a relatively high practical specific capacity of 199 mAh/g [24]. However, it is thermally less stable than other cathode materials. Lithium iron phosphate (LFP) is widely used as a cathode material as well [25, 26].

#### - Negative electrode (anode)

The anode is an electrode where oxidation occurs. Therefore, the negative electrode is an anode when the cell is discharged and technically a cathode when the cell is charged. However, the negative electrode in the battery cell is called an anode, regardless of charging or discharging. An anode of a LIB cell is generally composed of copper current collecting foil coated with a carbonaceous active material [27], and graphite is most widely used due to advantages such as low cost, mechanical stability, good electrochemical, and wide availability. The anode material lithium titanium oxide (LTO) is also used for high power purposes [28] along with the cathode material LFP. There are Silicon alloys as anode and nickel enriched NMC as a cathode are thought to be in use in 2030 [23], and LIBs using Si/C composite anode have also been developed [29, 30].

#### - Electrolyte

The electrolyte is an ionic conductor, a medium that transfers internal ion charges between the two electrodes. It is often composed of a liquid solvent containing dissolved chemicals that provide ionic conductivity, and solid polymer electrolytes are also available. Carbonate-based solvents are mainly used as electrolytes for LIB cells [31].

#### - Separator

The current is generated by ionic transport via an electrically insulated separator. The separator is a porous polymer film for an ion conductor and an electronic insulator, which physically isolates positive and negative electrodes. It prevents internal short circuits between two electrodes and prevents cells from becoming useless by rapidly self-discharging. An electrolyte composed of an organic solvent, a conductive salt, and an additive is located in the pores of the active material and the separator [32].

#### - Current collector

The current collector is an electronic conductor attached to or mixed with electrode materials. Current collectors are not involved in the chemical reactions of cells, instead being included to allow electronic connections to materials that are difficult to connect to cell terminals or to reduce the electronic resistance of electrodes. In LIB cells, the negative electrode current collector is usually made of copper foil and the positive electrode current collector is usually made.

#### - LIB cell operation

The operation of a LIB cell is based on intercalation and deintercalation of lithium-ions [33]. During charging, lithium-ions stored in the cathode are oxidized and deintercalated, and the cathode is oxidized. While electrons are released from the positive terminal to the external current path, lithium-ions are transferred from the cathode to the anode through diffusion and migration through the electrolyte. When electrons from an external current path reach an anode active material through a negative terminal, lithium-ions from an electrolyte are intercalated into the active material and reduced to neutral lithium atoms. During discharging, this process is reversed [34]. During discharging of the LIB cell, while the anode is oxidized and electrons are released through an external current path, lithium-ions pass through the electrolyte to reach the cathode and the cathode is reduced. When M is a transition metal mixture used in an oxide, the chemical equation during charging and discharging is represented by Eq. 2.1, and the equation for the anode and the cathode is represented by Eq. 2.2.

$$\mathrm{Li}_{\mathrm{x}}\mathrm{C}_{6} \rightleftharpoons \mathrm{x}\mathrm{Li}^{+} + \mathrm{x}\mathrm{e}^{-} + \mathrm{C}_{6} \tag{2.1}$$

$$\mathrm{Li}_{1-x}\mathrm{MO}_2 + x\mathrm{Li}^+ + x\mathrm{e}^- \rightleftharpoons \mathrm{Li}\mathrm{MO}_2 \tag{2.2}$$

#### 2.2 Aging Processes of LIB Cells

Battery cell performance deteriorates over time due to unwanted chemical reactions and physical changes in active chemicals. Aging of battery cells is usually irreversible and eventually results in cell failure.

The following are representative aging processes of LIB cells:

#### - Corrosion

Corrosion is degradation due to undesirable chemical side reactions in the cell, and in some cases, the product of these reactions itself has corrosion effects on other cell components. This includes the reaction between the solvent and the current collector and the reaction between the solvent and the electrode active/inactive material. LIB cells with graphite negative electrodes are vulnerable to certain corrosion called passivation, and electrochemical corrosion may occur in the aluminum current collector on the positive electrode side due to acidic HF, which increases contact resistance between the current collector and the active material of the cathode [35, 36].

#### - Solid electrolyte interface (SEI) formation

The formation of SEI is the most prominent aging process in the anode, which reduces the electrolyte at the electrode-electrolyte interface during the initial cycle [17, 22, 23].

In most LIB cells, the solvent in the electrolyte is not chemically stable at a high voltage, and thus reacts with graphite particles to form a passive layer called SEI on the surface of the particles. The formation of this layer has the advantage of protecting graphite from further reactions and significantly slowing the passivation process, but also has the disadvantage of permanently losing cell capacity because lithium consumed by SEI growth cannot return to the previous properties that enabled cycling [37, 38]. Afterward, the SEI slowly grows, and when the pores of the electrode and the separator penetrate, the active area accessible to the electrode is reduced [39], so that the capacity of the battery cell is reduced and the internal resistance is increased. At high temperatures, additional SEI is formed in graphite exposed by the decomposition reaction of the SEI layer. When the cell is charged at a high C-rate, the solvent is distilled with lithium to cause an SEI reaction inside the graphite particles, in which case the expansion pressure of the generated gas is applied to the graphite particles to crack or exfoliate along the grain boundaries, and more graphite is exposed to the solvent to form more SEI [40, 41]. Electrolytes, solvents, and conductive salts cause SEI to have different stability, structure, and conversion [31].

#### - Lithium plating

Among the aging effects at an anode, lithium plating significantly reduces the remaining cell capacity, degrades cell performance, and causes an internal short circuit due to dendritic growth or an external short circuit due to an exothermic reaction between the electrolyte and plated lithium [39, 42]. When a positive potential falls below 0 V as compared to Li/Li+ during charging of a LIB cell, lithium is plated on the surface of an anode particle, and as lithium is plated, the positive potential is lower, and thus

lithium plating is a self-accelerated aging effect. In particular, lithium plating is formed during cell operation at a high charging rate, a high SoC, and a low external temperature [43–45], and when the plated lithium loses electrical contact with the anode and is separated into the electrolyte, it reacts with the electrolyte to form an SEI component, resulting in irreversible capacity loss.

#### - Crystal formation

In chemical redox cells, a material removed from the electrode during discharging does not return to an original position during charging, but instead forms a crystal structure on the surface of the electrode, which reduces the effective surface area of the electrode to increase resistance and degrade the ability to transfer high power. As an example of crystal growth in a LIB cell, when lithium metal is deposited on particles of a negative electrode due to overcurrent or charging at a low temperature, lithium dendrite grows on the surface of the electrode, which may penetrate a separator to accelerate self-discharge and cause a short circuit.

#### - Volume change

Charging and discharging of the intercalation-based electrode causes a volume change of less than 10% of graphite, which stresses the electrode and causes cracks in the active material and the SEI, particularly at high rates [46]. The electrolyte leaked from cracks reacts with the active material to form an additional SEI layer, which consumes cyclable lithium [40, 47–50]. In addition, changes in volume during cycling weaken electrical contact between active material particles and cause delamination of the current collector, increasing the internal resistance of the cell [50, 51].

- Gas evolution

Some chemicals in the LIB cell evolve gas when charged and return to the previous aqueous state when discharged, but if gas leaks due to cracks in the cell enclosure, the cell capacity is lost and the cell may be ruptured or exploded due to an increase in pressure in the sealed cell.

#### - Aging from porous separators

The porous separator of LIB cells is electrochemically inactive but can affect the performance of cells. Aging studies have shown that deposits due to electrolyte decomposition can block pores in the separator, increasing impedance and reducing the accessible active surface area of the electrodes [39, 52]. Mechanical stress can change the porosity and tortuosity of the separator, and mechanical compression and viscoelastic creep can block pores, interfere with ionic pathways, and increase impedance at high frequencies [53, 54].

#### 2.3 Overview of Battery Cell Management

This thesis deals with the method of monitoring the battery cell state using cell impedance. Therefore, it is necessary to distinguish three terms; battery cell diagnosis, monitoring, and management so that they are not misused.

#### - Battery diagnosis

Battery diagnosis is to determine the state of the battery. For example, batteries can be diagnosed in laboratory environments for accelerated aging tests or performance tests in the development of new materials. In most cases, the target battery must be disconnected from the application system and connected to a separate diagnostic device.

#### - Battery monitoring

Battery monitoring is the continuous observation of the battery state during operation. The battery monitoring system reports battery state data to the user or management system and stores it for later analysis. In most cases, due to limitations in weight, volume, and cost, measuring devices such as in a laboratory environment are not applicable. In addition, continuous changes in operating current, temperature, SoC, etc. make it difficult to estimate the battery state during operation.

#### - Battery management

The purpose of the BMS is to operate LIB cells in optimal conditions within acceptable electrical parameters to maximize cell life. The BMS maintains the optimal battery operating range in response to the state information received as a result of battery monitoring and diagnosis. In order to prevent overcharge and over-discharge of the battery cells, the cut-off voltage should be determined at different temperatures and unnecessary electrical loads should be terminated. These active responses are not performed in battery monitoring and diagnostic systems and are processed in a BMS that has received diagnostic information from them. As a result, the increased discharge range increases the available energy, which reduces the size of the battery pack and simplifies the design. This not only reduces the required number of cells, pack design and manufacturing costs, but also reduces the weight of the battery pack, as well as ensures stability and user safety.

The main purpose of the BMS can be summarized as follows:

• It protects the user safety of battery-powered systems. The BMS must detect and respond to unsafe operating conditions.

• It protects cells in battery packs from damage in cases of abuse or failure.

• It extends battery life during normal operation. BMS sets a limit on the power that can be consumed or absorbed to prevent cells in the battery pack from being overcharged or over-discharged. In addition, the thermal management system should be controlled to ensure that the battery pack remains within the appropriate temperature range.

• It maintains the battery pack in a state where the functional design requirements are met. For example, it does not allow the battery pack to discharge beyond the limits that can provide rated discharge power.

#### 2.4 Definition of Key Terms

SoC and SoH of the battery cell may be defined differently depending on the battery application system, and therefore, it is required to clarify the key terms before discussing cell state estimation.

#### - Definition of C-rate

C-rate refers to the rate at which the battery is discharged in relation to the maximum capacity, and 1C rate refers to the discharge current that discharges the entire battery within 1 hour. The relationship shown in Eq. 2.3 is given between the cell maximum capacity  $C_{max}$  and the operating current *i*.

$$h = C_{max} / i$$
 (2.3)

where h is the time (hour) taken to completely discharge the battery cell, i is the current at which the cell operates, and  $C_{max}$  refers to the maximum capacity of the battery in the present state (Ah). Here, the reciprocal of the h value is defined as the C-rate.

#### - Definition of SoC

The SoC of a battery cell generally means the residual capacity ( $C_{residual}$ ) of the cell in proportion to the maximum capacity ( $C_{max}$ ) as a percentage, and in this thesis, the cell SoC is defined by Eq. 2.4. SoC =  $C_{residual} / C_{max} \times 100$  (%) (2.4)

0% SoC means that the cell is completely discharged, and 100% SoC means that the cell is completely charged. The depth of discharge (DoD) has the opposite definition of SoC. In other words, 80% SoC cells have the same meaning as 20% DoD cells.

The steps to set up the cell SoC in this thesis are as follows:

1) Full charge of the battery cell. Following the constant current (CC) charging procedure at 1C, a constant current (CV) charging procedure is performed at 4.2V, which is the upper limit cut-off voltage designated by the cell manufacturer. Charging ends when the charging current falls below C/10.

2) The cell is discharged at 1C to a low cut-off voltage, and the actual maximum cell capacity  $C_{max}$  is obtained at this stage.

3) Cell is set to target SoC. After the first step is performed again for full charge of the cell, a specific amount of charge of the cell is consumed until the target SoC is reached.

Different cell relaxation times can cause errors [55, 56], so the relaxation of the same 90 minutes is strictly observed at the end of each step. Each cell is given the same 90 minutes of relaxation time after the target SoC is set before it is used for the measurement.

#### - Definition of SoH

The battery cycle life represents the number of complete charge and discharge cycles achievable. The cell SoH can be expressed as a ratio of the maximum available capacity of the present condition and the nominal capacity as shown as Eq. 2.5.

SoH(%) = 
$$\frac{Q_{\text{max}}}{Q_{\text{n}}} \times 100 \ (\%)$$
 (2.5)

where  $\boldsymbol{Q}_{max}$  is the maximum available capacity of the present condition, and  $\boldsymbol{Q}_n$  is the nominal capacity.

Battery end of life (EoL) is reached when capacity or power is no longer sufficient for the target application. In many cases, when the battery SoH reaches 80%, it is considered to have reached the EoL [57–60].

#### 2.5 SoH Estimation Methods of LIB Cells

One of the major problems with electrochemical energy storage devices is the loss of performance and eventual loss of function due to the aging process. Batteries end their lives much earlier than all other parts of the system, contributing to the cost of replacement and maintenance, which can significantly exceed the initial investment. Moreover, many aging processes of LIB cells have a nature of self-acceleration, and the presence of one degraded cell inside the battery pack leads to the aging of other cells [17]. In addition, energy storage devices using LIB cells are safety-critical in many applications [4]. Generally, the larger the battery size, the greater the electrical energy stored in the battery, which can lead to fatal safety issues, requiring a higher level of safety assurance. For example, EVs often have thousands of LIB cells connected in series and parallel depending on their required voltage and capacity. Therefore, protection circuits such as protection circuit modules (PCM) and BMSs that guarantee safety and durability should be used.

Battery cells can fail during service or even during standby for a number of reasons. Failure in battery cell management includes overcharging, over-discharging, the use of overcurrent, and operation at temperatures that are too high or too low. Cells also fail due to physical abuse such as dropping, crushing, puncture, impact, immersion in fluids, freezing, contact with fire, etc. Cells do not need to survive all these extremes. However, management is required to ensure that the cell itself does not increase the risk or safety concerns in these situations.

In most cases, even if it appears to be a sudden battery failure, the battery cell has already been degraded and this degradation could have been detected in advance by the monitoring system. Applying appropriate operating strategies through monitoring and management can slow down the aging process of battery cells. Moreover, if the latest degradation state of the battery cell is identified as SoH estimation, it is possible to more accurately estimate the cell SoC, available energy, and available power. Estimated battery cell SoH can be used to determine when to replace the cell, to evaluate residual value for the second life of battery cells, and prevent unnecessary replacement or sudden failure.

The battery capacity that reflects the energy capacity of a battery cell and the internal resistance that reflects power capacity are the most widely used SoH indicators [61, 62]. As mentioned earlier, among the internal aging mechanisms of LIB cells, the loss of cyclable lithium, decomposition of active materials, and structural changes are the main causes of capacity loss [63–65], and the increase in resistance is mainly due to the growth of the SEI layer. It is recommended that the battery is replaced when the capacity is reduced to 80% of the initial rated capacity [66].

SoH estimation is an essential technology required for BMS and has been researched with various approaches, but it takes a lot of time for cycling cells and for characteristic tests, and it is difficult due to various parameters, such as temperature and charge/discharge rate, which affect the battery aging process. Various measurement methods are performed in the laboratory to analyze battery aging behavior. Some measurement methods are useful for studies that provide a theoretical basis for aging mechanisms, although they cannot be used for on-board SoH estimation due to specific experimental devices required or differences between actual operation and laboratory environment.

The following are the methods used to estimate the LIB cell SOH:

#### - Destructive method

The destructive method is a method for observing cell aging mechanisms from a micromechanism perspective to know cell SoH [67], and devices such as Raman spectroscopy [68], X-ray diffraction [69], and scanning electron microscope [70] are used to observe changes in microstructure during aging. However, the battery cell must be decomposed for measurement, which causes permanent damage, thus these methods are suitable for use in laboratories as post-mortem examination methods of battery cells.

#### - Ultrasonic inspection method

Ultrasonic inspection is a non-destructive technique that can detect every minor defect inside the material for quality inspection and product maintenance. Ultrasonic technology detects aging and internal defects without disassembling battery cells [71], and is used for rail inspection [72] and composite material inspection [73] as well. Although estimating cell SoH with measured waveforms still requires more research, in some areas, it is possible to compare signal characteristics through machine learning methods [72, 73].

#### - Capacity or energy level measurement

The battery cell capacity means the amount of energy stored in a fully charged battery, and if it is measured accurately, the cell SoH can be determined. There are capacity testers which accurately measure the amount of energy of a battery cell, but the battery cell capacity could be calibrated only in a specific environment, like laboratories, because it is difficult to measure the energy under appropriate conditions while operating in actual battery applications.

#### - Cycle number counting

This is a simple method of determining the cell SoH by counting the number of charging and discharging cycles, and is commonly used in small electronics such as laptops and nanosatellites [74]. If the total available cycle number of the cell is known in advance through the manufacturer and from the cycle number experienced by the cell is counted, the battery SoH can be determined. Since the number of complete discharges must be counted, conversion coefficients obtained through experimental tests are used to convert charging and discharging at different depths into full charging and discharging.

#### - Ampere hour counting method

If the amount of charge transferred within the battery cell during full charge-discharge is accurately calculated, the remaining capacity can be calculated, and the cell SoH can be determined [75]. However, there are limitations to using the ampere-hour counting method. Long-term current

monitoring and memorization using high-precision current sensors are required to reduce cumulative errors and obtain accurate remaining capacity. In most experiments, the battery cell capacity is measured as being fully charged and discharged with a constant current at the controlled temperature, but in most battery applications, an error occurs because these conditions are not satisfied. Many studies use the ampere-hour counting method to verify the accuracy of their cell capacity estimation method [76] which is also mainly used for SoC and capacity estimation using equivalent circuit models (ECM).

#### - Charging curve method

The charging curve can be used to characterize the battery SoH because it varies depending on the battery degradation process. In most cases, the CC-CV mode is used to charge the battery, which is shown in Fig. 2.2. The cell SoH can be obtained during CC charging, and capacity loss may be estimated with parameters obtained from the current curve of CV charging [77]. However, this method depends on the charging mode and cannot be used for fast charging, and since the cell temperature must be considered, the estimation accuracy decreases unless it is 25°C [78, 79].



Figure 2.2 Voltage and current of the battery cell in the CC-CV charging stage.

#### - ICA and DVA methods

Since there is not much information that can be obtained directly through the cell voltage curve, incremental capacity analysis (ICA), an electrochemical characterization and analysis technique, is used [78, 79]. The IC curve is calculated by charging or discharging cells at a very low current rate to integrate the capacity at a small voltage interval (dQ/dV), which converts the voltage plateaus of two-phase transition into a recognizable IC peak. Another method is differential voltage (dV/dQ) analysis (DVA) [80]. The distance between the two peaks of the DV curve represents the amount of electrical particles in the two-phase transition. Therefore, the DV curve facilitates quantitative analysis of cell capacity fading [81]. ICs and DV peaks in different aging states reveal specific shapes, amplitudes, and positions, thus they can be indicators representing cell SoH [82]. They are used with machine learning methods as well [80]. Very low current rates, such as C/25, should be used to identify the cell aging mechanism in ICA and DVA, thus it is very difficult to accurately measure these small signals in actual on-board applications, and accuracy is lowered when larger currents such as C/3 [60, 81] and C/2 [83] are used.

Since obtaining IC or DV curves generally requires numerical derivation that results in high computational effort in microcontrollers, the point counting method [81] and improved center least square method [84] are used, and a method using Gaussian filters is proposed to obtain noise-removed smoothing curves [83].

- Measurement of cell resistance

As mentioned above, the aging processes of LIB cells result in undesirable results such as reduced capacity, increased self-discharge, and increased internal resistance. Since an increase in the internal resistance of LIB cells is caused by unwanted side effects and structural degradation, cell SoH can be estimated by equivalent series resistance. Measuring the latest available capacity to know the SoH of a cell requires at least one cycle and takes a long time, whereas estimating the SoH from the cell resistance or impedance requires measuring the voltage response to the current signal only for a short time. Various techniques have been widely studied to measure resistance, representing the SoH of a battery cell. The total internal resistance of a LIB cell includes ohmic resistance and polarization resistance, and under normal operating conditions, ohmic resistance mostly contributes to voltage drops that depend linearly on operating current and thus can be calculated according to Ohm's law. Pulse tests are mainly used to obtain ohmic resistance and can be obtained as shown in Eq. 2.6 [85].

$$R_{O} = \frac{\Delta V_{P}}{\Delta I_{P}}$$
(2.6)

where,  $\Delta V_P$  is the pulse voltage, and  $\Delta I_P$  is the applied current pulse.

Fig. 2.3 shows an example of obtaining battery resistance through a pulse test.  $R_{CT}$  is attributed to charge transfer resistance [61] and  $R_P$  to polarization resistance [86].



Figure 2.3 Pulse test to obtain the resistance of the battery cell.

Because LIB cells are complex electrochemical devices, ohmic resistance is affected by many variables and operating conditions, such as temperature and aging state [61].

#### - EIS analysis method

EIS is a non-invasive analysis technique that determines the dynamic behavior of an electrochemical system [87–89] and can be used to characterize battery impedance behavior in a wide range of frequencies from several mHz to several kHz to obtain a characteristic impedance spectrum [90–94]. Therefore, it can be used to measure battery cell parameters in which a model structure is determined by cell SoC, SoH, aging, temperature, internal defects, etc [95–97].

Galvanostatic or potentiostatic mode is used for EIS analysis, i.e., system response is measured by the amplitude and phase (real and imaginary parts) when a sinusoidal voltage or current signal is applied to an electrochemical cell. In general, a galvanostatic mode is preferred because an overcurrent may easily occur in the potentiostatic mode due to very low battery cell impedance [98].

If the current i of the battery cell is given by Eq. 2.7, and the voltage e is measured as Eq. 2.8, the cell impedance Z can be obtained as Eq. 2.9.

$$i = I_{dc} + \Delta I_{f} \cdot \sin(2\pi ft)$$
(2.7)

$$e = E_{dc} + \Delta E_{f} \cdot \sin \left(2\pi f t + \phi_{f}\right)$$
(2.8)

$$Z_{f} = \frac{\Delta E_{f}}{\Delta I_{f}} \cdot e^{j\phi_{f}} = |Z_{f}| \cdot e^{j\phi_{f}} = Z_{f}' + j \cdot Z_{f}''$$
(2.9)

where  $I_{dc}$  indicates direct current (DC) bias,  $\Delta I_f$  indicates the amplitude of the test frequency f,  $E_{dc}$  indicates the offset voltage,  $\Delta E_f$  indicates the amplitude of the output voltage, and  $\phi_f$  refers to the phase difference.

As shown in Eq. 2.9, the electrochemical impedance of a battery cell is a frequency-dependent complex number characterized by its modulus  $|Z_f|$  and phase angle  $e^{j\phi}$ . Another expression is given as the real and imaginary parts of the complex impedance.

Table 2.1 shows equations of major electrode processes in LIB cells, except for non-faradaic processes including charging or discharging of equivalent capacitors in the interphase of an electrode. EIS can isolate most of these processes [99] because the electrochemical loss process occurs at a wide range of frequencies, and each process has its own time constant [100].

Table 2.1 Equations of major electrode processes in LIB cells.		
Electrode process	Governing equation	
Charge transfer	$j_{fd,i} = j_{0,i} \left[ exp\left(\frac{\alpha F}{RT}\eta_i\right) - exp\left(\frac{-(1-\alpha)F}{RT}\eta_i\right) \right]$	(2.10)
Solid-phase diffusion	$\frac{\delta c_{s,i}(r_i, t)}{\delta t} = \frac{D_{s,i}}{r_i^2} \frac{\delta}{\delta r_i} (r_i^2 \frac{\delta c_{s,i}(r_i, t)}{\delta r_i})$	(2.11)
Liquid-phase diffusion	$\varepsilon_{e,i} \frac{\delta c_{e,i}(x,t)}{\delta t} = \frac{\delta}{\delta x} \left( D_{e,i} \frac{\delta c_{e,i}(x,t)}{\delta x} \right) + \frac{1 - t_{+}}{F} j_{tot,i}(x,t)$	(2.12)
Solid-phase conduction	$\frac{\delta}{\delta x} \left( \sigma_{s,i} \frac{\delta}{\delta x} \varphi_{s,i}(x,t) \right) = j_{fd,i}$	(2.13)
Liquid-phase conduction	$\frac{2RT\kappa_{e,i}(1-t_{+})}{F}\frac{\delta^{2}\ln\varphi_{e,i}(x,t)}{\delta x^{2}} - \kappa_{e,i}\frac{\delta^{2}\varphi_{e,i}(x,t)}{\delta x^{2}} = j_{tot,i}(x,t)$	(2.14)

 Table 2.1 Equations of major electrode processes in LIB cells.

where, F: Faradaic constant ( $C \cdot mol^{-1}$ ), R: Gas constant ( $J \cdot mol^{-1} \cdot K^{-1}$ ), T: Temperature (K), i: Domain of negative electrode/positive electrode/or separator,  $\alpha$ : Transfer coefficient of electrochemical reaction (1),  $\eta_i$ : Over potential (V),  $j_{0,1}$ : Exchange current density ( $A \cdot m^{-2}$ ),  $j_{fd,i}$ : Faradaic current density ( $A \cdot m^{-2}$ ),  $j_{tot,i}$ : Total current density ( $A \cdot m^{-2}$ ), t: Time (s),  $r_i$ : Radial coordinate of solid spherical particles (m), x: Coordinate in the thickness direction of electrodes (m),  $\epsilon_{e,i}$ : Effective volume factor of liquid phase,  $c_{s,i}$ : Concentration of lithium ions in solid phase (mol  $\cdot m^{-3}$ ),  $c_{e,i}$ : Solid-phase diffusion coefficient ( $m^2 \cdot s^{-1}$ ),  $D_{e,i}$ : Effective liquid-phase diffusion coefficient ( $m^2 \cdot s^{-1}$ ) and  $\varphi_{s,i}$ : Potential in solid phase (V). Fig. 2.4 is an example of a Nyquist plot showing the real part of the battery cell impedance on the horizontal axis and the negative imaginary part on the vertical axis [101].



Figure 2.4 A representative example of Nyquist plot of LIB cell impedance.

Different sections of the cell impedance spectrum are related to different cell processes because the movement of charged particles and the time constant of the reaction in processes are different [102]. The influence of mass transfer, whose time constant is slow, is dominant at impedance at low frequencies ( $\leq$ 1 Hz), while the influence of charge transfer with a faster time constant is dominant at impedance at a mid-high frequency.

At low frequencies drawn in red, impedance is determined by solid and liquid phase diffusion processes such as Eq. 2.11 and Eq. 2.12, and is shown as a line with an angle of ca. 45° on the horizontal axis.

In the medium-high frequency range drawn by a yellow line, impedance in the charge transfer process predominates, which is expressed by Eq. 2.10.

In the high-frequency range drawn in green, it is affected by the impedance of the SEI film. And at a frequency where the imaginary part of impedance becomes 0, the phase changes of the inductive effect and the capacitive effect compensate for each other, indicating the pure ohmic behavior of the cell. It mainly consists of the resistance of the electrolyte, the resistance of the current collector and the resistance of the active mass, and the contact resistance between the current collector and the active mass [103]. The resistance of the electrolyte depends on the conductivity, i.e., the concentration of the conductive salt that changes with cell aging [104, 105], thus it can be used to measure electrolyte decomposition related to cell aging. The impedance of the solid phase and liquid phase conduction process related to ohmic resistance is expressed by Eq. 2.13 and Eq. 2.14.
Induction impedance in the super-high frequency range drawn in blue represents inductance mainly from the geometric design of cells and electrodes, such as wires and collectors [106]. The position of the tab connecting the current collector foil to the external electrode affects the inductance of the cell, for example, the longer the spiral winding of the jelly roll between the two tabs, the higher the cell inductance [107]. Since the impedance is related to the corresponding processes, the changes in these processes directly affect the impedance.

Note that the shape of the Nyquist plot in Fig. 2.4 depends on the inherent characteristics of each battery cell.

Despite these advantages of EIS, typical EIS analyzers are mainly used in laboratories to measure the impedance of electrochemical systems for general purposes [4, 108]. Since high performance applicable to general-purpose measurement is required, it may be an excessive investment to be used in a battery monitoring system, and in particular, has a large mass and volume to be applied to portable devices. Moreover, EIS measurements take a long time to measure impedance over a wide frequency range, and analyze only the impedance of the target system and cannot determine the SoH and SoC of the battery cell without an estimation algorithm.

#### 2.6 SoC Estimation Methods of LIB Cells

The battery SoC is often described as a fuel gauge on a vehicle dashboard reporting values between empty (0%) and full (100%). On petrol vehicles, the fuel tank has sensors that can accurately measure the amount of gasoline remaining, but there are no sensors that can directly measure the SoC of the battery. Therefore, SoC should be estimated indirectly with measured cell current, voltage, temperature, etc. Scientifically, the standard unit for battery capacity is Coulomb. A coulomb is a unit of charge equal to one-ampere second (As). This explains how long the battery can produce a constant current. However, battery capacity is more commonly described as ampere-hour (Ah) or milliamperehour (mAh).

It is important for the BMS and the battery system itself as it allows the estimation of SoC-dependent battery parameters. Accurate SoC values are required as input values for energy and power calculation as well as cell balancing strategies. Knowing cell SoC is useful to users as well because it allows them to know the estimated operating time of the power system or the remaining driving range of the EV.

Overcharge, which occurs when a charge current flows in even after reaching the upper limit cut-off voltage of LIB cell, is one of the most important safety issues and is caused by inaccurate SoC estimation of BMS or a malfunction of battery cell charger. When a LIB cell is overcharged, internal resistance increases, binder and electrolyte decomposition, insoluble products are formed, blocked electrode pores and gas are sequentially generated [109] and when the internal pressure exceeds the limit value, structural deformation, rupture, and internal short circuit may occur [110, 111]. The heat generated by the side reaction and the internal short circuit may accelerate the battery failure mechanism through natural positive feedback to cause thermal runaway, hence causing ignition or explosion of the battery [8, 112, 113], and when lithium metal and moisture in the air react after cell rupture, combustible gases may ignite [8, 114]. When a LIB cell is over-discharged, the active lithium and cathode materials are lost [115] thereby reducing the battery capacity [116, 117], changing the SEI on the surface of the cathode to increase the impedance [117], and generating gas due to the decomposition of the SEI [118]. LIB applications implemented with higher energy and higher power capabilities require higher SoC estimation accuracy. Accuracy requirements of 3% to 5% are often required for EVs, meanwhile higher accuracy is required for aerospace or defense applications.

Accurate battery cell SoC estimation has the following advantages:

- It increases the battery cell cycle life by preventing overcharge and over-discharge that may cause permanent damage.

- If the reliability of SoC estimation is low, the battery cell must be operated conservatively for safe operation, thus accurate SoC estimation enables more aggressive cell operation.

- It improves the reliability of the application system as it shows reliable estimation results for various cell usage profiles.

- If accurate SoC estimation is possible, the battery pack design does not need to be over-engineered to manufacture a smaller and lighter battery pack and reduce battery pack prices and battery maintenance costs.

Nonetheless, there are factors that make it challenging to monitor cell SoC accurately. Although LIB cells have very high Coulombic efficiency, the discharge capacity is different from the charging capacity. In addition, the cell voltage is affected not only by SoC but also by polarization and hysteresis and depends on the cell temperature and charge/discharge rate. Especially, care should be taken for cell voltages that are cut-off early at high currents. Since the cell available capacity depends on the cell temperature and the discharge rate, the capacity dependence on the C-rate should be considered. The higher the discharge rate, not only the greater the cell temperature, but also the voltage drop due to ohmic resistance, polarization, and hysteresis. If a cell is discharged at a constant current until the cut-off voltage is reached, the current causes an additional voltage drop, resulting in a lower apparent capacity at a higher discharge rate. However, when residual energy is discharged after the cell is relaxed, a capacity similar to that measured at other C-rates may be obtained.

Methods for LIB cell SoC estimation can be classified as follows:

#### - Methods based on open-circuit voltage (OCV)

OCV, which is the cell voltage when an electrode is stabilized without the flow of current for a sufficient time, is used to represent the thermodynamic state of cell electrode energy. Since the cell voltage is related to the temperature and the surface concentration of electrode particles and the average particle concentration, OCV that reflects Gibbs free energy in thermodynamic equilibrium can be measured when the electrode reaches equilibrium and there is no voltage deviation depending on the position inside the electrode. OCV shows a strong dependence on SoC, but it is unrealistic to be used for real-time state estimation of battery cells, in particular, for battery applications where sufficient relaxation time cannot exist, because it generally requires a few hours of relaxation to reach electrochemical equilibrium [119]. In addition, LIB cells have a flat OCV curve compared to lead-acid battery cells, making it difficult to estimate SoC [120], and cell temperature and SoH are factors that cause errors when estimating SoC using OCV.

#### - Methods based on ampere-hour counting

In the SoC estimation method based on ampere-hour counting, the accumulated amount of charge and discharge current for the discharge capacity is defined as  $\Delta$ SoC and calculated with the initial SoC set. As only the data of the accumulated current for SoC estimation are used, the required hardware and software performance is relatively low, but there becomes a problem if the SoC of a battery cell entirely depends on the initial SoC. Since only  $\Delta$ SoC is calculated, if the initial SOC is incorrectly set or the total capacity or Coulomb efficiency of the cell is not accurately identified, estimation error increases. Self-discharge current, leakage current to electronic circuits that measure cell performance, and measurement errors in voltage, current, and temperature contribute to the increase in SoC estimation errors [75] as well. These errors are integrated and intensified as the battery cell operation, thus if there is no feedback mechanism for error correction, the estimation result of this method is accurate for a short time only if the initial conditions are well known. Periodic capacity calibration including complete discharge of the cell must be performed to accurately know the maximum capacity in the present state of the battery cell, but this results in cell degradation [121]. The cell SoC estimation with ampere counting is expressed by Eq. 2.15.

$$SoC_{k} = SoC_{0} - \int_{t_{0}}^{t_{k}} \eta I_{L}(t) dt/Q$$
(2.15)

where  $SoC_k$  and  $SoC_0$  represent the SoC at discrete-time  $t_k$  and  $t_0$  respectively.  $t_0$  represents the initial value,  $t_k = t_0 + k \times \Delta t$ ,  $\Delta t$  represents the sampling interval,  $\eta$  represents the coulomb efficiency,  $I_L(t)$  represents the load current of the battery and Q represents the maximum available capacity in the present state. As the battery capacity is influenced by the operation profile and the aging state, it is not a constant in the SoC calculation, and thus the maximum available capacity is used here.

#### - SoC estimation method based on heuristic data

The heuristic-based SoC estimation methods are based on experimental data and use statistical rules or patterns found in data obtained through various cell charging/discharging experiments. These methods include fuzzy logic [122–127], neural networks (NNs) [128, 129], support vector machines (SVMs) [130–132], genetic algorithms (GAs) [133, 134], and implementing learning techniques using large amounts of experimental data under various conditions can yield reliable estimation results, but it takes a lot of time to get the necessary experimental data properly.

#### - SoC estimation method based on the adaptive filter algorithm

Kalman Filter (KF) is an intelligent tool for estimating the dynamic state of a battery, a well-designed method of filtering parameters from uncertain and inaccurate observations, and is commonly used in many applications such as automobile, radar tracking, aerospace technology, and navigator tracking. KFs can be used for cell SoC estimation despite high computational costs [135, 136]. KFs have the property of self-calibration that help withstand high current changes, and they can accurately estimate even under the influence of external obstacles, such as noise controlled by Gaussian distribution. However, KFs cannot be used directly to predict the state of nonlinear systems and require very complex mathematical calculations.

Unlike KFs, which cannot handle nonlinear characteristics of battery models, extended Kalman filters (EKFs) can be used in nonlinear applications such as LIBs [137–139]. EKFs correct the estimated parameters of SoC by linearizing the battery model using partial derivatives and first-order Taylor series expansion. However, the first-order Taylor series lacks accuracy due to linearization errors if the system is severely nonlinear [140].

The unscented Kalman filter (UKF) applies discrete-time filtering algorithms and unscented transformations to solve filtering problems, and the posterior mean and covariance of the third-order Taylor series can also be accurately covered by the UKF [141–143]. In general, LIBs have very nonlinear characteristics, and the property of noise is unknown. This algorithm has the advantage that noise does not need to be Gaussian and it is not necessary to calculate a Jacobian matrix, moreover, the accuracy of UKF is superior to that of EKF because it accurately predicts the system state up to the third order of nonlinear systems, but this method is less robust due to uncertainty in modeling and disturbances in the system.

The Sigma Point Kalman Filter (SPKF) is another alternative method for evaluating the state of nonlinear systems, achieving higher accuracy than EKF in the mean and covariance where a limited number of functions are used [144, 145]. This algorithm selects a set of sigma points similar to the

mean and covariance values in the model, has the same computational complexity as EKF without considering the Jacobi matrix, and has the advantage that derivatives and original functions do not need to be calculated.

In addition, H $\infty$  filters [146, 147], particle filters (PF) [148, 149], recursive least squares (RLS) [150, 151], etc. are used for LIB cell SoC estimation.

#### - Cell SoC estimation method using nonlinear observers (NLOs).

As nonlinear observers [152, 153], proportional integrated observer (PIO) [154], sliding mode observer (SMO) [155, 156], bi-linear interpolation (BI) [157], and Luenberger observer [158] can be used to estimate battery cell SoC.

#### - SoC estimation method based on ECM

The SoC of the battery cell can be estimated through the ECM obtained through EIS [86, 159]. However, as stated in Section 2.5, for EIS analysis, battery cells must be separated from the operating load and generally take a long time to measure impedance in a wide frequency range. In addition, the use of a typical EIS analyzer in battery monitoring systems can be an excessive investment, especially mass and volume are too large for use in portable devices.

Unlike the methods using commercialized EIS analyzers, the proposed method in this thesis can be used to estimate the SoC of the cell during operation measuring cell impedance. There is an increasing interest in using cell impedance to monitor battery conditions [160, 161]. Although there are literature that estimates cell SoC with the impedance of an operating cell, physical models and non-linear differential equations that increase the complexity of the operation are required [162], and in some cases, the effect of temperature on impedance is not applied [163].

#### - Other SoC estimation methods

Other methods for battery cell SoC estimation include a battery electromotive force (EMF) [164, 165] method, multivariate adaptive regression spline (MARS) [166], impulse response (IR) [157], etc.

# **3** Experimental

This chapter presents an overview of the measurement system for impedance measurement experiments of LIB cells. Measurement conditions for EIS analysis in different states of LIB cells are shown, and considerations are presented in selecting parameters to measure impedance by applying frequencies to operating current. In addition, a measurement system configured for continuous impedance measurement of operating battery cells is introduced.

## **3.1 EIS Measurement**

## 3.1.1 Cell impedance at different SoHs

An EIS analyzer (IM6ex of Zahner-Elektrik GmbH & CoKG) is used to measure cell impedance in different cell states, and the temperature is adjusted to 25°C in the temperature chamber MK53 of BINDER GmbH.

Table 3.1 shows conditions for the EIS measurement, and Table 3.2 shows the specifications of the battery cell used. The appendix chapter of this thesis summarizes which cells are used for which measurements.

Item	Description	
EIS method	Galvanostatic	
Min. frequency	200 mHz	
Max. frequency	2 kHz	
DC bias	0 A	
AC amplitude	100 mA	
SoC	100 %	
Chamber temperature	25 °C	

#### **Table 3.1** Measurement conditions for EIS analysis.

Table 3.2 Specifications of the Li-ion cell.

Item	Description
Anode	Based on intercalation graphite
Cathode	Based on lithiated metal oxide <sup>1</sup>
Product name	Samsung ICR 18650-26F
Battery system	Li-ion (LCO)
Nominal voltage	3.7 V
Rated capacity	2.6 Ah

Fig. 3.1 (a) shows the cell impedance when the cell SoH is 100 (cell #1), 90% (cell #2), and 80% (cell #3), as a Nyquist plot. Cell SoH is obtained as shown in Eq. 2.5 through cycling repetition and cell capacity measurement. Fig. 3.1 (b) is a Bode diagram showing the absolute value of cell impedance at different frequencies.



Figure 3.1 (a) Nyquist plot and (b) Bode diagram at different cell SoHs.

As the cell deteriorates and the SoH decreases, the impedance of the cell increases, and the lower the frequency, the greater the difference in impedance at each SoH, especially at a frequency lower than ca. 10 Hz.

## 3.1.2 Cell impedance at different SoCs

Battery cell impedance depends not only on SoH but also on SoC. Fig. 3.2 (a) is a Nyquist plot showing cell impedance at different SoCs, and Fig. 3.2 (b) is a Bode diagram showing the absolute value of cell impedance. Cell SoH is 100 % in this measurement (cell #1).



**Figure 3.2** (a) A Nyquist plot and (b) a Bode diagram showing impedance at each cell SoC. In the Nyquist plot, the '+' marker represents 1 Hz impedance, the 'o' marker represents 250 Hz impedance, and the 'x' marker represents 1 kHz impedance.

The cell impedance becomes higher as SoC is lower, and in particular, the difference in impedance at each SoC becomes larger when the frequency is lower than ca. 10Hz.

## 3.1.3 Cell impedance at different temperatures

Cell impedance is affected by cell temperature as well. Fig. 3.3 (a) is a Nyquist plot that compares cell impedance at different temperatures, and Fig. 3.3 (b) is a Bode diagram showing the absolute value of frequency. The cell temperature of each measurement is regulated to 25°C, and cell SoH is 90% (cell #1).



Figure 3.3 (a) Nyquist plot and (b) Bode diagram at different cell temperatures.

The cell impedance becomes lower at a higher cell temperature, and the difference in cell impedance at each cell temperature becomes larger as the frequency is lower. This is especially noticeable when the frequency is less than ca. 10 Hz.

In summary, cell impedance is higher at lower SoHs, lower SoCs, and lower temperatures, and this tendency is particularly noticeable as it is lower than 10 Hz.

## **3.2 Frequency Excitation**

#### 3.2.1 Signals applied to measure the cell impedance

Various signals can be used to measure cell impedance, and can be divided into two categories, depending on whether they contain only a single frequency or multiple frequencies. A single frequency measurement method is advantageous in the signal-to-noise ratio (SNR) of a response signal, but it takes a long time to measure battery impedance in a wide frequency range and is suitable for cases where precision is more important than speed. In the meanwhile, some applications use signals containing multiple frequencies or harmonics to quickly measure the cell impedance, but the magnitude of harmonics decreases as the order increases, causing lower SNR at higher frequencies [167]. A single frequency measurement method is studied with DC bias [167–171], or without DC bias [172]. Methods using multiple frequencies or harmonics include sum-of-sines signals [173, 174], square signals, triangular signals and sawtooth signals [170, 171], pseudo-random binary signals [175–179], step signals [167, 180–185], chirp signal [186], white noise [187], and dynamic signals [188].

In order to consider the effect of biased or large disturbances on impedance, it is recommended to check whether impedance is independent of dynamic disturbances with Kramers-Kronig transformation [189]. Different sizes of disturbances, DC deflection or relaxation time, have a significant influence on the obtained impedance [55, 61, 190]. In pseudo-random binary and chirp signals, spectral leakage during signal processing increases the error [173]. In addition, during the long period of signal or dynamic driving cycle, the battery SoC and temperature continue to change, resulting in greater measurement errors. Therefore, in addition to considering measurement accuracy and speed, the type of test signal must be carefully selected in order for the measured impedance to have meaning.

#### 3.2.2 Methods for applying test signals

Various signal application methods can be used to measure cell impedance. A DC-DC converter [160, 167, 191], a frequency-applied charger [169, 170], a half-bridge DC-DC converter [168], a phase-shifted full-bridge converter [171], a dual-active-bridge converter [172, 192], a switching inductor balancing circuit [193], and a switching capacitor balancing circuit [194] are used in literature. NXP [195] and Panasonic [196] provide a single board solution for measuring impedance in each battery cell, but these systems apply weaker signals to battery cells due to their power capability. Battery cells or modules having high capacity generally have very low impedance, so such a single-chip solution may not provide a sufficient SNR to ensure measurement accuracy of impedance.

## 3.3 Setup for the frequency excitation

#### 3.3.1 Measurement system for frequency excitation

A measurement system is configured to compare continuous battery cell impedance by applying a test frequency to the charge and discharge currents with different cell SoHs. Fig. 3.4 (a) shows a block diagram of the measurement system, and Fig. 3.4 (b) shows a photo of the measurement system.

The voltage signal output port of USB-6212 which is the National Instrument's data acquisition (DAQ) module is connected to the electronic load to apply the test frequency to the cell operating current. The analog input of the DAQ module has 16-bit analog-to-digital converter (ADC) resolution, the maximum sampling rate is 400 kS/s, and the input range is  $\pm$  10 V. The analog output has 16-bit digital-to-analog converter (DAC) resolution, and the output range is  $\pm$  10 V and the maximum update rate is 250 kS/s. In addition to generating test frequency signals, the DAQ module is used to collect cell voltage, current, and temperature data as well.

Experiments are controlled by adjusting measurement parameters through a graphical user interface (GUI) developed using the LabVIEW of the National Instruments.

LIB cells are tested inside the temperature chamber of Binder GmbH. NXP's silicon temperature sensor KTY81-110 is attached to the center of the cell surface. Cell temperature is measured every second through the DAQ module.

Fig. 3.5 shows a schematic diagram of the electronic load designed by Dipl.-Ing. Lars Krüger for the experiment.



(b)

Figure 3.4 (a) A block diagram of the measurement system and (b) a photo of the measurement system.



Figure 3.5 Schematic diagram of the electronic load.

### 3.3.2 Selection of test frequencies

This subsection covers a general description of frequency selection, and specific frequency selection for SoH and SoC monitoring is covered later in Subsection 5.1.1.

#### - The use of lower frequencies

The influence of mass transfer with a slow time constant is dominant at low-frequency impedance as shown in Section 2.5. The higher the temperature and the higher the lithium-ion concentration (the higher the cell SoC), the faster the mass transfer rate, resulting in a lower cell impedance [197]. Therefore, the impedance at lower frequencies may be more suitable for cell SoC estimation, which has a greater impact. However, since the frequency is the reciprocal of the period, the lower the frequency, the longer time required for cell impedance measurement. For example, if 1 mHz is used for impedance measurement, it takes about 17 minutes to collect signals in a period. This not only lengthens the time required to estimate the cell state but also increases the measurement time.

#### - The use of higher frequencies

The impedance at high frequencies is dominated by charge transfer with a fast time constant rather than mass transfer. In the case of the cells used in this thesis, the imaginary part of the impedance becomes 0 at ca. 1 kHz, which indicates the ohmic resistance of the cell, and since most cell degradation causes an increase in the ohmic resistance, the impedance at this frequency can be used for cell SoH estimation [36, 50, 198, 199]. However, there are also considerations to use higher frequencies. Theoretically, signals can be measured when the Nyquist-Shannon criteria are met, but in practice, the noise and non-ideal properties of analog filters require oversampling, which requires faster hardware sampling rates. In addition, since cell impedance is generally lower at higher frequencies, larger test amplitudes may need to be used to overcome SNR problems.

#### 3.3.3 Selection of test amplitude

The amplitude of the test frequency should be selected in consideration of the trade-off between the measurement accuracy and the investment cost for battery management according to the application of the battery cell. Although the test amplitude suitable for impedance measurement should be small enough not to violate the pseudo-linear conditions of the electrochemical battery system, it should be large enough to obtain a stable SNR. Cell impedance cannot be measured if the amplitude of the voltage output from the individual frequency is less than the system noise. Because a current-voltage curve of a LIB cell is governed by nonlinear Butler-Volmer kinetics, the amplitude of a test signal should be small enough to satisfy pseudo linearity of the cell output voltage, and in general, a voltage response amplitude of 5 to 10 mV is recommended [200]. Fig. 3.6 shows pseudo-linearity observed at a small amplitude. In particular, when multiple frequency signals are applied, a lower amplitude should be used for each frequency because the amplitude of each frequency contributes to the total amplitude.

However, if the amplitude of each signal is too small, the problem is caused due to the finite resolution of the hardware that acquires or generates the test signal.



Figure 3.6 Lissajous plot of current for potential in a stable pseudo-linear system.

# **4** SoH Estimation of LIB Cells Using Frequency Excitation

In this chapter, frequency excitation is used to estimate SoH of LIB cells. Continuous impedance is measured while cells with different SoHs are discharged or charged. The measurement time required to estimate the cell SoH and the corresponding accuracy are shown. The investigations and results presented in this chapter have been published in [10].

## 4.1 Impedance Measurement during Discharge of Cells with Different SoHs

The continuous impedance of a LIB cell is measured during charging and discharging using the measurement system described in Chapter 3. Table 4.1 shows the experimental conditions, and Fig. 4.1 shows the continuous cell impedance during discharge. Cell impedance at five frequencies of 1, 10, 20, 100, and 250 Hz is compared here. Note that, these five frequencies are not applied at the same time, and the impedance at each frequency is measured individually.



Figure 4.1 Continuous cell impedance at five different frequencies and cell voltage during cell discharge.

 Table 4.1 Experimental conditions for measuring cell impedance during discharge.

Parameter	Value
Discharge range	From 4.2 V to 2.8 V
DC bias	2.6 A (1 C)
Amplitude	260 mA (0.1 C)
Test frequency	1, 10, 20, 100, 250 Hz
Cell SoH	100 % (cell #4)
Initial temperature	22 °C

At 10, 20, 100, and 250 Hz, the higher the frequency, the lower the cell impedance. The impedance change due to the cell DoD change is most noticeable at the lowest frequency of 1 Hz.

Table 4.2 shows the standard deviation of cell impedance at each frequency to compare how much the impedance measured at each moment deviates from the average impedance.

Fig. 4.2 shows the cell impedance and cell voltage while the cell is being charged according to the conditions in Table 4.3.

Table 4.2 Standard deviation of measured cen impedance at five different nequencies.		
Frequency (Hz)	Standard deviation (m $\Omega$ )	
1	2.6320 (5.47 %)	
10	0.7728 (1.56 %)	
20	0.6896 (1.41 %)	
100	0.5966 (1.29 %)	
250	0.5368 (1.29 %)	

Table 4.2 Standard deviation of measured cell impedance at five different frequencies

 Table 4.3 Experimental conditions for measuring cell impedance during charging.

Parameter	Value
Charge range	From 2.8 V to 4.2 V
DC bias	2.6 A (1 C)
Amplitude	260 mA (0.1 C)
Test frequency	1, 10, 20, 100, 250 Hz
Cell SoH	100% (cell #4)
Initial temperature	22°C



Figure 4.2 Cell voltage and impedance at 1, 10, 20, 100, and 250 Hz during CC charge.

In Fig. 4.2, a change in cell impedance during charging is greater than that during discharging, and at 10, 20, 100, and 250 Hz, the higher the frequency the lower the cell impedance.

Table 4.4 shows the standard deviations of impedance at each frequency during charging.

Frequency (Hz)	Standard deviation (m $\Omega$ )
1	3.6633 (7.29 %)
10	2.6548 (5.22 %)
20	2.3084 (4.61 %)
100	1.6674 (3.52 %)
250	1.1875 (2.81 %)

 Table 4.4 Standard deviation of measured cell impedance at each frequency during charging.

The impedance deviation during charging is larger than that during discharging, and the higher the frequency, the lower the standard deviation of impedance (i.e., the lower the frequency, the less affected by DoD).

#### 4.1.1 Cell impedance at different SoHs

As shown earlier, the effect of cell SoC and cell temperature on cell impedance decreases as the frequency increases. This subsection compares the cell average impedance at 250 Hz while the cell is gradually deteriorating.

The experimental conditions are shown in Table 4.5. Fig. 4.3 shows the average of 250 Hz cell impedance measured at different SoHs, the relationship between cell SoH and cell impedance is fitted as shown in Eq. 4.1 through linear regression and is drawn as a dotted line. Here,  $R^2$  is 0.993.

ParameterValueDischarge rangeFrom 4.2 V to 2.8 VDC bias2.6 A (1 C)Amplitude260 mA (0.1 C)Test frequency250 HzCell SoH100% to 73% (cell #4)Temperature22 °C

 Table 4.5 Experimental conditions for measuring cell impedance at different SoHs.

As the cell degrades, the cell 250 Hz impedance increases linearly, which can be used for cell SoH  $(y_{SoH})$  estimation.

$$y_{SoH} = ax + b \tag{4.1}$$

where *a* = -0.1064 and *b* = 54.8584.

4.1 Impedance Measurement during Discharge of Cells with Different SoHs



Figure 4.3 Mean values of cell impedance at different cell SoHs (circle) and fitted line (dotted line).

### 4.1.2 Measurement time required for SoH estimation

Battery cell SoH estimations from different initial SoCs are simulated in this subsection. The battery cell is discharged for 10 minutes and then has a relaxation time of 60 minutes. Discharge and relaxation of the cell are repeated until the cell voltage reaches 2.8V.

Cell impedance of 1 Hz and 250 Hz are compared here. The experimental conditions are shown in Table 4.6, and the results are shown in Fig. 4.4.

Parameter	Value
DC bias	2.6 A (1C)
Test frequency	1, 250 Hz
Amplitude	260 mA (0.1 C)
Relaxation time	60 minutes (each)
Discharge time	10 minutes (each)
Cell SoH	73% (cell #4)
Temperature	22 °C

 Table 4.6 Experimental conditions for impedance measurements from different initial SoCs.



Figure 4.4 Cell charge curve and cell impedances at 1, 10, 20, 100, and 250 Hz.

During relaxation, the cell voltage rises, and when the discharge starts again, the recovered voltage drops rapidly. The 1Hz impedance changes more than the 250Hz impedance during relaxation and discharge.

The factors that greatly change the cell 1Hz impedance are cell SoC and cell temperature. As DoD increases, impedance increases. 1 Hz impedance, which increased at the start of measurement after each relaxation, gradually decreases during discharge because the cell temperature decreases during the relaxation and increases during discharge. This change in impedance reduces the accuracy of SoH estimation and makes the time required for SoH estimation longer in situations when the cell SoC and cell temperature are unknown.

Fig. 4.5 shows the temperature change of the battery cell discharged at 1C.



Figure 4.5 Increasing cell temperature during 1C discharge.

A moving average is used to reduce the noise of the measured impedance. The effect of the time required for the moving average on the error of the measured cell impedance is compared at different frequencies.

	Measurement time (sec)	
Frequency (HZ)	Discharge	Charge
1	1408	1052
10	242	833
20	240	792
100	66	718
250	4	623

Table 4.7 shows the measurement time required to reach a 98% confidence level.

 Table 4.7 Measurement time required for moving average to reach 98% confidence level.

The higher the frequency, the shorter the required measurement time, and it takes longer to measure while charging than to measure while discharging. The measurement time represents the time required for the measured cell impedance to reach the target value.

As mentioned above, the measurement time is not only affected by noise, but also by changes in cell impedance due to SoC and temperature changes. When cell impedance is measured at 250 Hz for 4 seconds during discharging, the confidence level reaches 98% and ca. 10 minutes is required during charging.

## 4.2 Impedance Measurement in Another Type of Cell

Samsung's LCO cells are used in the experiments in the previous sections. In this section, cell impedance at different SoHs in the other type of LIB cell is compared. The NMC cell of the Bexel is used (cell #7), and the specifications of the cell used are shown in Table 4.8.

Item	Description
Product name	Bexel INR 18650-2600 SP01
Battery system	Li-ion (NMC)
Rated capacity	2.6 Ah (0.2 C)
Nominal voltage	3.7 V

Fig. 4.6 shows the impedance of the cell at different SoHs measured using Ametek's EIS analyzer. Table 4.9 shows the conditions used for EIS measurement. The temperature chamber is not used in this measurement.

Table 4.9 Conditions for EIS analysis of Bexel cells.

Item	Description
EIS method	Galvanostatic
Min. frequency	200 mHz
Max. frequency	2 kHz
DC bias	0 A
AC amplitude	100 mA
SoC	100 %



Figure 4.6 Nyquist plot showing impedance in different SoHs.

Fig. 4.7 shows the continuous 1 kHz impedance of the cell during discharge at different SoHs, and Table 4.10 shows the measurement conditions.

Parameter	Value
Discharge range	From 4.2 V to 2.75 V
DC bias	2.6 A (1 C)
Amplitude	40 mA (each)
Test frequency	1 Hz, 250 Hz and 1 kHz
Cell SoH	100% to 70%

Table 4.10 Experimental conditions for measuring cell impedance at different SoHs (cell #7).



Figure 4.7 1 kHz impedance during cell discharge at different SoHs.

The continuous impedance of the discharging cell is higher as the cell SoH is lower.

Fig. 4.8 shows the impedance at 1 Hz, 250 Hz, and 1 kHz of the cell being discharged.



Figure 4.8 1 Hz, 250 Hz, and 1 kHz impedance in different SoHs.

The lower the frequency or cell SoH, the higher the impedance. Using the same method as the LCO type cells, the continuous impedance of operating cells of NMC type cells could be used to estimate cell SoH. Please note that Bexel's NMC cell is used only in this section. Measurements in all other sections of this thesis are made with Samsung's LCO cells with specifications shown in Table 3.2.

# **5** SoC Monitoring of LIB Cells Using Frequency Excitation

In this chapter, the frequency is used to estimate the SOC of the lithium-ion battery cell. For accurate SOC estimation, the cell SOH estimated in Chapter 3 is considered along with the cell temperature. By applying two frequencies simultaneously, the cell SOH and SOC can be monitored simultaneously. The measurement time required to estimate the cell SOC and the resulting accuracy are shown. The investigations and results presented in this chapter have been published in [11].

# 5.1 Multi-sine EIS

In general, EIS analyzers have a disadvantage in that it takes a long time to measure impedance in a wide frequency range because a single sine signal is applied by the so-called step sine method or frequency sweep method. This drawback can be overcome by multi-sine EIS, which is already used in fields such as biomedical applications [201, 202], material characterization [203], and battery measurements [91, 95], while measuring multiple frequencies at the same time.

In general, multi-sine EIS requires the cells to be separated from the application circuit to measure impedance, such as a single-sine EIS, but in this thesis, cells are not separated from the circuit for cell state monitoring and continuous impedance is measured by applying a test signal including multiple frequencies to the cell operating current. As a multi-sine signal is applied to the cell operating current, the cell SoH and SoC are monitored simultaneously with the impedance measured at each frequency.

The measurement system described in Chapter 3 is used to measure cell impedance, and the overall process of cell state estimation is shown in Fig. 5.1 as a flow chart.



Figure 5.1 A flow chart showing the cell state estimation process.

Cell 1Hz impedance is adjusted and normalized for proper use for SoC monitoring because it depends on the cell SoH and temperature as well as the cell SoC.

#### 5.1.1 Selection of test frequencies for estimating cell SoH and SoC

In Chapter 4, it is shown that cells with low SoH have high impedance. In addition, impedance changes at different SoCs and different temperatures are greater at lower frequencies. When the frequency is high enough, the impedance is relatively constant even with SoC or temperature changes.

Therefore, impedance at a higher frequency is used for the SoH estimation of a cell, and impedance at a lower frequency should be used in consideration of SoH and temperature for the SoC estimation of a cell. Subsection 3.3.2 describes the limitation of the use of test frequencies that are too low or too high in terms of the measurement system. However, also from the perspective of the battery operation process, the use of impedance at lower or higher frequencies is not always better for SoH and SoC estimation.

To be specific, the impedance at the high frequency in Fig. 2.4 is suitable to use for cell SoH estimation, and the impedance at the mid-high and low frequencies is suitable for SoC estimation.

#### - Frequency Selection for SoH Estimation

As described in Section 2.2, the SoH in the LIB cell is closely related to the SEI film and the ohmic resistance. The impedance of the SEI film in the LIB cell affects the impedance at high frequency and Ohmic resistance is related to impedance at ca. 1 kHz in which the imaginary part of the impedance becomes 0.

For the cell SoH estimation, the impedance in the high frequency range is used in this thesis, especially 250 Hz or 1 kHz. However, they are used as examples, and the frequency for SoH estimation is not limited to these frequencies. The appropriate frequency to be used depends on the system requirements of the battery application.

#### - Frequency selection for SoC estimation

The 1 Hz frequency is used for SoC estimation. Again, the appropriate test frequency is dependent on the system requirement and is not limited to the use of 1 Hz frequency impedance. For the used cell, 1 Hz is located between the low frequency range and the mid-high frequency range.

Impedance in the low frequency range (< 1 Hz) is affected by temperature and SoC. Mass transfer (including diffusion) becomes faster as the temperature is higher and the Li-ion concentration is higher (=SoC is higher = DoD is lower). Faster transfer speed can be interpreted as lower impedance. On the other hand, this transfer becomes slower as the temperature is lower and the Li-ion concentration is lower (=SoC is lower = DoD is higher). And it results in a higher impedance.

Impedance in the mid-high frequency range, where the effect of charge transfer is dominant, is also affected by SoC. Impedance in cathodes consisting of layered structures with active materials is not significantly affected by SoC. However, in the anode composed of graphite, the reduction reaction increases as SoC increases, and the conductivity increases due to the combination of lithium-ion and graphite, and the impedance decreases [204].

## 5.2 Continuous cell impedance measured with multiple frequencies

A multi-frequency test signal is applied as the sum of the two frequencies so that the impedance at both frequencies is measured simultaneously. Amplitude of 65 mA is used at each of 1 Hz and 1 kHz, and a total amplitude of 130 mA is used. This ensures that the output voltage amplitude is less than 10 mV so that the measurement does not violate pseudo-linearity. Table 5.1 shows the experimental conditions.

Parameter	Description
Chamber temperature	25 °C
Depth of discharge	From 0 to 100 %
DC bias	2600 mA (1 C)
Test frequency	1 Hz, 1 kHz
Amplitude	65 mA (each)
Cell SoH	From 100 to 80 % (cell #5)
Measurement interval	Every second

**Table 5.1** Experimental conditions for measuring cell impedance during discharge.

Fig. 5.2 shows continuous 1 Hz and 1 kHz impedance during discharging of cells with different SoHs.



Figure 5.2 Continuous 1 Hz and 1 kHz impedance during discharging of cells with different SoHs (Solid line: 1 Hz impedance, dotted line: 1 kHz impedance).

The lower the cell SoH, the higher the overall cell impedance. And during cell discharge, the 1 Hz impedance changes significantly while the 1 kHz impedance is relatively constant. The increased rate of the highest impedance from the lowest impedance at 1 kHz frequency is 3.74%. At the same time, the increased rate of the highest impedance from the lowest impedance between DoD 5% and 95% at a frequency of 1 Hz is 10.16%. The smaller increased rate of 1 kHz impedance means that it is less dependent on cell SoC and is suitable for SoH estimation of cells with unknown cell SoC. In contrast, at 1 Hz impedance, the increased rate is higher. This means that 1 Hz impedance is more suitable for cell SoC estimation.

#### 5.2.1 Effect of polarization

If the full range of DoD is considered in Fig 5.2, the increased rate of 1 Hz impedance becomes much higher, but only between 5% and 95% of DoD should be considered. This is because the 1Hz impedance at the beginning and end of the cell discharge cannot be accurately measured and thus cannot be used for cell SoC estimation.

The cell discharge process causes overpotential, which is a voltage loss due to polarization, which occurs when the electrode potential in equilibrium is excessive or insufficient. The charge transfer rate of each reaction process of the battery cell is not the same, and a specific process having a relatively slow rate limits the rate at the overall reaction of the cell. The cell voltage is measured below the equilibrium potential when the cell is discharged and the current flows between two terminals, and the difference between the voltage and the equilibrium voltage, which indicates the degree of polarization, is called an overpotential. During the discharge process of LIB cells, polarization can be classified into three categories; activation polarization, concentration polarization, and ohmic polarization. Fig. 5.3 shows these three polarization regions in the discharge curve [199].



Figure 5.3 Typical discharge curve of a battery cell, showing three different regions of polarization.

Ohmic polarization is also called ohmic loss, and at this region, the discharge curve has a linear slope, enabling the most accurate cell impedance measurement. Since the ohmic loss is proportional to the current density, the voltage drop increases in proportion to the internal resistance of the cell. Meanwhile, the cell output voltage of the activation and concentration polarization regions has nonlinearity. Activation polarization has a dominant effect on the voltage drop at the beginning of cell discharge due to various inherent delay factors in the dynamics of electrochemical reactions, such as work function, in which ions must overcome in the junction between electrodes and electrolytes. In the concentration polarization region, a voltage drop is revealed due to a decrease in the mass transfer rate at which ions move across the electrolyte from one electrode to another when the cell charge is low. These two polarizations, based on processes with relatively slow transfer rates in battery cells, are more evident at impedance at lower frequencies. Therefore, in Fig 5.2, the effects of activation and concentration polarization at 1 Hz frequency are more pronounced than 1 kHz.

## 5.3 Consideration of cell temperature

Changes in the temperature of battery cells during discharge are affected by discharge rate, discharge time, relaxation time, and ambient temperature [205]. Fig. 5.4 shows the cell temperature rise while the cell is discharged at 25°C.



Figure 5.4 The temperature change of the battery cell during discharging with 1C current.

The battery cell impedance measured at different temperatures of 20, 25, 30, and 35°C is shown in Fig. 5.5 with a Nyquist plot and a bode diagram. The measurement conditions are shown in Table 5.2.

Table 5.2 Parameters for EIS measurement (	Galvanostatic).
--	-----------------

Parameter	Description	
Cell temperature	20, 25, 30, 35 °C	
SoH	80 % (cell #5)	
SoC	50 %	
DC bias	0 mA	
Frequency range	0.2 to 2 kHz	
AC amplitude	100 mA	



Figure 5.5 Cell impedance at each frequency at 20, 25, 30, and 35 °C. (a) Nyquist plot (O: 1 Hz, X: 1 kHz). (b) Bode diagram.

The higher the cell temperature, the lower the cell impedance, and 1Hz impedance is more affected by temperature than 1kHz impedance.

Fig. 5.6 shows a curve that fits the impedance of 1 Hz at each temperature into a quadratic equation.



Figure 5.6 1 Hz impedance measured at 20, 25, 30 and 35 °C (dotted line) and fitted curve (solid line).

The fitted quadratic equation has an  $R^2$  of 1.00 and a root-mean-square error (RMSE) of 0.19 mOhm and is expressed by Eq. 5.1.

$$Z(T)_{\text{fitted}} = -0.03717 \cdot T^2 - 3.217 \cdot T + 133.3$$
(5.1)

where T is the cell temperature and  $Z(T)_{fitted}$  is the impedance obtained through the equation at the cell temperature T.

The 1Hz impedance measured at various cell temperatures is adjusted to the impedance at 25°C using Eq. 5.2.

$$Z(T)_{adjusted} = Z(T)_{measured} - (Z(T)_{fitted} - Z(25)_{fitted})$$
(5.2)

where  $Z(T)_{adjusted}$  is the adjusted impedance to 25 °C and  $Z(T)_{measured}$  is the measured impedance at temperature T.

The temperature-adjusted result using Eq. 5.2 for the 1Hz impedance in Fig. 5.2 is shown in Fig. 5.7.



Figure 5.7 1 Hz impedance adjusted to 25 °C.

Temperature-adjusted 1Hz impedance increases as the cell discharges. The cell temperature increases with the discharge time as Fig. 5.4, and the cell impedance decreases with increasing cell temperature as Fig. 5.5. Fig. 5.7 shows 1 Hz impedance adjusted to 25°C, which is a lower temperature than the actual cell temperature, thus it shows a higher impedance than the 1 Hz impedance in Fig. 5.2.

### 5.4 Consideration of cell SoH

Cell SoH obtained by Eq. 4.1 is used for temperature-adjusted 1 Hz impedance normalization.

The measured cell 1Hz impedance ( $Z_{measured}$ ) is normalized to  $Z_{norm}$  by Eq. 5.3.

$$Z_{\text{norm}} = (Z_{\text{measured}} - Z_{\text{min}}) / (Z_{\text{max}} - Z_{\text{min}}) \times 100$$
(5.3)

where  $Z_{max}$  and  $Z_{min}$  represent the maximum and minimum values of the impedance between DoD 10% and 90% and can be obtained by Eq. 5.4 and Eq. 5.5 respectively.

$$Z_{\text{max}} = -0.00593 \cdot \text{SoH}^2 + 0.79922 \text{ SoH} + 63.09$$
(5.4)

$$Z_{\min} = -0.2969 \cdot \text{SoH} + 103.1 \tag{5.5}$$

In Eq. 5.4,  $R^2$  is 1.00 and RMSE is 0.12 m $\Omega$ , and in Eq. 5.5,  $R^2$  is 1.00 and RMSE is 0.26 m $\Omega$ .

The result of applying Eq. 5.3 to the 1 Hz impedance in Fig. 5.7 is shown in Fig. 5.8.

Due to the cell nonlinear response mentioned in Subsection 5.2.1, SoC estimation using 1 Hz impedance is made between 10% and 90% of DoD.



Figure 5.8 Normalized 1 Hz impedance and fitted curve of cells with different SoHs.

The average of the normalized impedance at each SoH is fitted with a cubic equation and plotted as a curve in Fig. 5.8. This fitted curve is expressed by Eq. 5.6 and has an  $R^2$  of 1.00 and an RMSE of 1.51.

$$Z_{norm} = -0.00014 \cdot SoC^3 + 0.032 \cdot SoC^2 - 0.85 \cdot SoC + 7.58$$
(5.6)

Table 5.3 shows each  $R^2$  and RMSE when Eq. 5.6 is applied to cells with different SoHs.

5 SoC Monitoring of LIB Cells Using Frequency Excitation

Table 5.3 Accuracy of SoC estimation in cells with different SoHs.			
SoH	R <sup>2</sup>	RMSE	
100 %	0.99	2.42	
95 %	0.99	2.66	
90 %	0.99	2.02	
85 %	0.99	2.51	
80 %	0.98	3.85	
Average	0.99	2.69	

Table 5.4 shows the time for the estimated SoC to reach 95% and 98% confidence levels, respectively.

Table 5.4 Time for Soc estimation in cells of different Sons to reach 95% and 98% confidence levels.		
SoH	95% confidence level	98% confidence level
100 %	179 sec	187 sec
95 %	290 sec	291 sec
90 %	219 sec	225 sec
85 %	229 sec	384 sec
80 %	249 sec	249 sec
Average	233.2 sec	267.2 sec

Table 5.4 Time for SoC estimation in cells of different SoHs to reach 95% and 98% confidence levels.

As a result, it takes 233.2 seconds to reach the 95% confidence level and 267.2 seconds to reach the 98% confidence level to estimate the SoC of cells of different SoHs.

# 5.5 SoC Monitoring at Different Initial SoCs

Battery cells are not always operated in 100% SoC, thus this subsection emulates impedance measurements during cell discharge at different initial SoCs.

Discharge for 10 minutes and relaxation for 60 minutes are repeated until the cell is completely discharged, and measurements after each relaxation indicate cells that are discharged at different initial SoCs. Cell impedance is measured every second while the cell is discharged. The experimental conditions are shown in Table 5.5.

Table 5.5 Experimental conditions for SoC estimation of cells that start operating at different SoCs.		
Parameter	Description	
SoH	80 % (cell #5)	
Chamber temperature	25 °C	
Discharge time	10 min (each)	
Relaxation time	60 min (each)	
Depth of discharge	From 0 to 100 %	
DC bias	2.6 A (1 C)	
Test frequency	1, 1000 Hz	
Amplitude	65 mA (each)	

Fig. 5.9 (a) shows the cell voltage and cell temperature for the cell DoD, and Fig. 5.9 (b) shows the 1 Hz and 1 kHz impedances.



Figure 5.9 (a) Cell voltage (solid line) and cell temperature (dotted line), and (b) 1Hz impedance (solid line) and 1 kHz impedance (dotted line) while the cell is being discharged

In Fig. 5.9 (a), the cell voltage drops while discharging, and temporarily recovers when relaxed. The cell temperature increases during discharge of the cell and decreases during relaxation. Fig. 5.9 (b) shows that cell 1Hz impedance is more affected by SoC and temperature than 1kHz impedance.

The DoD range in which the 1Hz impedance cannot be accurately measured is indicated as a gray area, each for ca. 267 seconds, and the range from 95% DoD is added. However, it should be noted that in most cell operations in which the cell is not completely discharged, this range in which the cell impedance cannot be accurately measured appears only once at the start of the cell discharge. The reason why five or six gray ranges are shown in Fig. 5.9 (b) is that the cell impedance when discharged at five different initial SoCs is shown as one figure.

The 1 Hz impedance in Fig. 5.9 (b) after being adjusted to a temperature of 25 °C is shown in Fig. 5.10 (a). The result of normalizing the temperature-adjusted 1 Hz impedance to cell SoH is indicated by a dotted line in Fig. 5.10 (b). Eq. 5.6 is used to normalize the temperature adjustment impedance for cell SoH. The solid line in Fig. 5.10 (b) is the result of Eq. 5.6, and when compared to the dotted line,  $R^2$  is 0.99, and RMSE is 3.07 m $\Omega$ . Cell impedance in the gray range is excluded for the calculation of  $R^2$  and RMSE.



Figure 5.10 (a) 1 Hz impedance adjusted to cell temperature and (b) Temperature-adjusted 1 Hz impedance normalized to cell SoH (dotted line) and expected value (solid line) while the cell is being discharged.
# 6 Modeling of LIB Cells for State Monitoring

The purpose of this chapter is to propose a LIB cell model for simulation and optimization of cell state monitoring algorithms using frequency excitation. As shown so far, the battery cell impedance can be used to estimate the cell SoH and SoC.

However, it takes a long time for the cells in each state to be prepared and for the cell voltage reaction to be measured during charging and discharging under each condition. E.g., charging, discharging, and relaxation for one cell test can take several hours, and it can take several weeks to set the cell to the target SoH. Accurate cell simulation models significantly reduce experimental costs. In addition to the cost of purchasing experimental devices and cells, the time cost for setting each cell state can be saved. Results of cell state estimation algorithms under different conditions can be simulated and compared within a short time before being measured by experiments. This is because simulation results are quickly displayed simply by entering parameters representing the state of the battery cell into the model.

There are factors that make it difficult to make accurate battery cell models. As described in Chapter 2, the degradation mechanism of LIB cells is dependent on the operating profile and is complicated and difficult to understand clearly. The physical state of the battery cell depends on various parameters such as electrolyte concentration, conductivity, and crystal structure of the electrode material, and most of these parameters depend on the geometric position of the device. Moreover, chemical additives are used in most cell manufacturing, but information on these additives is often not disclosed to BMS engineers. Nevertheless, it is not necessary that every mechanism of the battery cell be fully modeled to obtain useful simulation results. A mechanism that does not affect the simulation results does not need to be modeled, and a model representing the battery behavior required for the target application is sufficient. Because in most electrochemical systems, model parameters vary nonlinearly depending on cell temperature, SoH, SoC, cell potential, current rate, etc., parameterization becomes one of the main challenges to create a simulation model [29, 78, 79, 93].

Section 6.1 presents the state of the art of LIB cell modeling methods in the literature, and Section 6.2 shows the proposed MATLAB/Simulink model and explains considerations for selecting model parameters as well as details of each simulation block. Each element value of the ECM is determined by EIS measured in different cell SoCs. In Section 6.3, the model is verified as a simulation result under various conditions compared to the measurement. The developed model outputs continuous cell impedance considering cell SoC, SoH, temperature, and C-rate through voltage prediction of a cell while being discharged.

The investigations and results presented in this chapter have been published in [12].

## 6.1 State of the Art

Increasing the complexity of the model to obtain accuracy increases computational effort and increases computational time. Therefore, an appropriate modeling method for the target application should be selected. Battery models presented in the literature can be classified into physics-based electrochemical models, electrical ECMs, and data-driven models.

### - Physics-based electrochemical models [206-208].

Because the electrochemical model of the battery is structurally based on the electrochemical processes and reactions inside the cell, the physical and chemical processes inside the battery cell can be explained in more detail than other models. Specifically, the electrochemical model can be used to describe macroscopic quantities such as cell current and voltage and local distribution, as well as cell concentration, potential, current, and temperature on the microscopic scale [209, 210]. The application of these models requires parameters including the electrode thickness, the initial salt concentration of electrolyte, the total heat capacity, etc., and since the calculation includes nonlinear differential equations, the longest time for simulation is required.

As an alternative to the physics-based modeling method, a gray box model represented by an electrically equivalent circuit model and a black box model including an empirical model are used.

### - Data-driven models

The data-driven model belongs to the black-box model, which does not require an understanding of the reaction mechanisms and characteristics inside the battery cell, so it is advantageous for estimating systems that are unknown, highly uncertain, cannot be modeled by empirical equations, or are not suitable for analysis [211]. Fuzzy logic controllers [212], SVM [213], GA [214], and NN algorithms [215], etc. are used in black-box models, and estimation accuracy depends heavily on training datasets and training methods.

### - Electrical ECMs

ECM is widely applied to BMS and automotive energy management systems [216–220]. ECM belongs to the gray box model, which can reduce complexity compared to the physics-based electrochemical model. ECM provides fast and accurate simulations suitable for system dynamic and frequency response estimation, even if the internal electrochemical state of the battery cell cannot be clearly explained. Linear passive elements including internal ohmic resistance, polarization resistance, polarization capacitance, inductance, normal elements, etc. of the battery cell are used here [221].

ECM has a variety of models depending on the balance between the required accuracy and calculation time. Depending on the shape of the measured cell impedance spectrum, serial ohmic resistance, Warburg diffusion elements, and several RC elements can be included [222–224], and if the standard RC network is not suitable for simulating battery characteristics over the entire frequency range, a constant phase element (CPE) can be used instead of the capacitor of the RC network [225–227].

Impedance spectrum	Equivalent element	Impedance expression
0 -Z'' Z'		$z = j\omega L$
0 -Z'' Z'		$z = \frac{j\omega RL}{R + j\omega L}$
$0 \qquad \qquad$		$z = \frac{R}{1 + j\omega RC}$
$0 \qquad \qquad$	$\xrightarrow{CPE}_{R}$	$z = \frac{R}{1 + (j\omega)^{P} RQ}$ $z = \frac{R}{1 + (j\omega Q)^{n} R}$
$0 \qquad \qquad$		$z = \frac{R_W}{(j\omega)^{0.5}}$
0 -Z'' Z'	$-W_{S}$	$z = R_W \frac{\tanh\left[(j\omega T_W)^{P_W}\right]}{(j\omega T_W)^{P_W}}$
$0 \qquad \qquad$	$-\frac{d}{W_0}$	$z = R_W \frac{\coth\left[(j\omega T_W)^{P_W}\right]}{(j\omega T_W)^{P_W}}$

);ffc مادر Table -

#### 6.1 State of the Art

When these circuit elements are considered comprehensively, they exhibit characteristics similar to those of the battery cell operating process, but individual physical characteristics cannot be explained in detail. Therefore, parameter values cannot be measured by laboratory test methods separating specific physical characteristics, but instead, the values of each element can be fitted so that predictions in the model are similar to those measured through an optimization process called system identification.

The measured complex impedance data is used to fit the equivalent circuit, which represents the physical process that occurs in the system through complex nonlinear least squares (CNLS) regression, and the fit accuracy is used to determine whether the impedance model and fit parameters are suitable for the purpose.

# 6.2 A LIB Cell Simulation Model for Monitoring SoH and SoC via Cell Impedance

Fig. 6.1 shows the overall appearance of the Matlab/Simulink model. The input current (Current<sub>in</sub>) is a signal obtained by adding two frequency signals (Test Freq. 1, Test Freq. 2) to the DC offset, and the SoC model provides a real-time SoC to the cell model. The initial SoC is given as  $SoC_{init}$ , and the real-time SoC is output as  $SoC_{out}$ . The SoC correction model is used to consider the rate-capacity effect. The cell model receives a real-time SoC and current and outputs a real-time cell voltage ( $V_{cell}$ ). The output voltage  $V_{cell}$  is Fourier transformed to calculate the cell impedance at each test frequency, and cell impedance calculations take into account cell SoH and cell temperature. The details of each subsystem are described in the following subsections.



Figure 6.1 Overall view of the proposed simulation model.

#### 6.2.1 SoC model

The cell SoC is represented by Eq. 6.1 in this model. The output of this subsystem is a real-time SoC (SoC<sub>out</sub>).

$$SoC_{out} = SoC_{init} - \int \frac{Current_{in} \times 100}{Q \times 3600} dt$$
(6.1)

The cell SoC is calculated based on the available cell capacity depending on the operating current in consideration of the rate-capacity effect [228, 229]. Fig. 6.2 shows the voltage curves of the LIB cell discharged at different C-rates. The same type of cell is used for modeling as in the experiments above (cell #6 which has 95 % SoH).



Figure 6.2 Voltage curves of the LIB cell discharged at different C-rates.

Table 6.2 shows the relative capacity of the cells discharged at different C-rates. The higher the C-rate, the less the total amount of energy (Wh) that can be released from the cell. While the available capacity of the cell at 0.125 C is 100%, the available relative capacity at 1.5 C is 92%. It is implemented in the SoC correction model using a 2D lookup table that receives  $SoC_k$  and  $Current_{in}$  as inputs. The SoC output corrected by the discharge current is expressed as  $SoC_c$ .

C-rate	Relative capacity	
1.5	0.92	
1	0.92	
0.5	0.94	
0.25	0.97	
0.125	1	

Table 6.2 Relative capacities of a LIB cell discharged at different C-rates.

#### 6.2.2 LIB cell model

The impedance between frequency 1Hz and 1 kHz is considered especially for estimating the SoC and SoH of battery cells used in the model. The equivalent circuit in Fig. 6.3 is used considering the accuracy of fit and complexity of the model in the corresponding frequency range.



Figure 6.3 Cell equivalent circuit used in the model.

The ECM adopted in this model consists of a DC voltage source, an inductor, a series resistor, and four RC parallel networks. The DC voltage source is used to represent the OCV of the cell, the series resistor (R0) is used to represent the internal DC resistance, and the RC parallel network (R1, C1, R2, C2, R3, C3, R4 and C4) is used to characterize the transient response of voltage. L, which represents the inductive behavior of the cell, increases the accuracy of the impedance fit at frequencies above ca. 1 kHz.

In the ECM represented by Fig. 6.3, the cell output voltage ( $V_{cell}$ ) is calculated by Eq. 6.2.

$$V_{cell} = OCV - V_L - V_{R0} - \sum_{n=1}^{4} V_{Pn}$$
 (6.2)

where  $V_L$  is the inductor voltage,  $V_{R0}$  is the series resistance voltage, and  $V_{Pn}$  is the n-th RC parallel network voltage.

#### - Measurement of the battery cell OCV

OCV is the voltage of the battery cell at equilibrium. And the value of OCV depends on the SoC. For this model, cell OCV is measured through the following procedure:

1) CC charge: The cell is charged with a 1C current until an upper limit cut-off voltage (4.2 V) is reached.

2) CV charge: When the cell reaches a voltage of 4.2 V, the charging current is reduced to maintain the voltage. Charging is terminated when the current becomes 1/10 C.

3) 90 minutes of relaxation is given to the cell. Cell relaxation is performed with disconnection from the load. This step completes setting cell SoC to 100%.

4) 1C discharge for 5 minutes and the relaxation for 10 minutes are repeated.

5) When the cell voltage reaches a lower limit cut-off voltage (2.8 V), the discharge is terminated and a final relaxation time of 10 minutes is given. At this step, the SoC of the cell becomes 0%.

6) Cell OCV should not be changed depending on the relaxation time. Cell OCV should be collected after sufficient relaxation time. The cell voltage after each 10-minute relaxation is collected as an OCV voltage. In Fig. 6.4, the measured OCV is shown as a black dot marker.

This series of procedures is performed in the temperature chamber set at 25°C.

6.2 A LIB Cell Simulation Model for Monitoring SoH and SoC via Cell Impedance



Figure 6.4 OCV of the battery cell used for modeling.

Cell OCV is applied to the model as a lookup table that receives  $SoC_c$  as input.

#### - System identification and prediction of cell voltage

The elements of the equivalent circuit in Fig. 6.3 depend on the cell SoC. The cell impedance measured at different SoCs in Fig. 3.2 is fitted to each element of the cell equivalent circuit. For the fitting of equivalent circuit elements, an algorithm to find the minimum  $\chi^2$  value is used.  $\chi^2$  calculates the distance between measured and simulated data, defined as Eq. 6.3.

$$\chi^{2} = \sum_{i=1}^{n} |Z_{\text{meas}}(i) - Z_{\text{simul}}(f_{i}, \text{element})|^{2}$$

$$= \sum \left\{ \frac{\left( \text{Re}(Z_{\text{simul}}) - \text{Re}(Z_{\text{meas}}) \right)^{2}}{\left( \text{Re}(Z_{\text{meas}}) \right)^{2}} + \frac{\left( \text{Im}(Z_{\text{simul}}) - \text{Im}(Z_{\text{meas}}) \right)^{2}}{\left( \text{Im}(Z_{\text{meas}}) \right)^{2}} \right\}$$
(6.3)

where,  $Z_{meas}(i)$  is the measured impedance at the  $f_i$  frequency,  $Z_{simul}$  is a function of the chosen model,  $f_i$  is the frequency i, and element is the model element.

A lower  $\chi^2$  indicates a higher fit accuracy and thus this should be minimized.  $\chi^2/N$  with N points is the normalized expression of  $\chi^2$ , whose value is independent of the number of points and represents the error. Table 6.3 shows the fitted equivalent circuit element values and the error  $\chi^2/N$  in each SoC. Fig. 6.5 shows the measured cell impedance and fitted results for each SoC as a Nyquist plot.

SoC (%)	$\chi^2/N$	L (H)	R0 (Ω)	R1 (Ω)	C1 (F)	R2 (Ω)	C2 (F)	R3 (Ω)	C3 (F)	R4 (Ω)	C4 (F)
100	1.77	3.41	3.82	1.81	1.75	5.53	5.38	5.23	7.82	3.01	2.16
	E-03	E-07	E-02	E-03	E+01	E-03	E-01	E-03	E-02	E-03	E+02
90	1.98	3.38	3.83	2.24	1.67	5.12	6.10	4.98	8.36	4.30	1.55
	E-03	E-07	E-02	E-03	E+01	E-03	E-01	E-03	E-02	E-03	E+02
80	2.12	3.36	3.85	2.32	1.57	5.06	6.22	5.02	8.33	4.41	1.48
	E-03	E-07	E-02	E-03	E+01	E-03	E-01	E-03	E-02	E-03	E+02
70	2.06	3.33	3.88	2.17	1.57	5.23	5.92	5.03	8.09	3.69	1.88
	E-03	E-07	E-02	E-03	E+01	E-03	E-01	E-03	E-02	E-03	E+02
60	2.05	3.27	3.95	1.81	1.67	5.70	5.47	5.19	7.78	2.20	3.24
	E-03	E-07	E-02	E-03	E+01	E-03	E-01	E-03	E-02	E-03	E+02
50	2.37	3.25	4.03	3.17	8.79	6.58	4.80	5.38	7.00	3.02	2.05
	E-03	E-07	E-02	E-03	E+00	E-03	E-01	E-03	E-02	E-03	E+02
40	2.32	3.20	4.07	4.25	7.03	6.96	4.82	5.62	6.80	3.93	1.54
	E-03	E-07	E-02	E-03	E+00	E-03	E-01	E-03	E-02	E-03	E+02
30	3.02	3.48	4.07	6.30	5.42	7.59	4.27	5.72	5.75	5.76	9.97
	E-03	E-07	E-02	E-03	E+00	E-03	E-01	E-03	E-02	E-03	E+01
20	2.41	3.05	4.14	9.32	4.39	7.39	4.80	5.99	6.52	1.11	4.73
	E-03	E-07	E-02	E-03	E+00	E-03	E-01	E-03	E-02	E-02	E+01
10	2.37	3.01	4.16	1.12	4.01	7.64	4.75	6.10	6.46	1.59	3.32
	E-03	E-07	E-02	E-02	E+00	E-03	E-01	E-03	E-02	E-02	E+01
0	2.45	2.99	4.19	1.35	3.51	8.50	4.46	6.16	6.26	2.81	1.98
	E-03	E-07	E-02	E-02	E+00	E-03	E-01	E-03	E-02	E-02	E+01

Table 6.3 Fitted element values for each SoC and  $\chi^2/N$  representing the fitting error.





Figure 6.5 Nyquist plots of measured cell impedance and fitted results.

The fitted equivalent circuit element values in each SoC are respectively applied to the cell model as a lookup table.

The series inductor voltage ( $V_L$ ) is expressed as Eq. 6.4 when the s-domain is used.

$$V_{\rm L} = L \frac{\rm di}{\rm dt} = \rm sLI \tag{6.4}$$

The series resistance voltage ( $V_{R0}$ ) of the equivalent circuit is expressed by Eq. 6.5.

$$V_{R0} = I \times R0 \tag{6.5}$$

By using s-domain, the voltage of n-th RC parallel network  $(V_{Pn})$  can be expressed as Eq. 6.6.

$$V_{\rm Pn} = \left(\frac{1}{s}\right) \left[\frac{I}{C} - \frac{V}{RC}\right] \tag{6.6}$$

When Eq. 6.4, Eq. 6.5, and Eq. 6.6 are used with the measured OCV, the cell voltage ( $V_{Cell}$ ) can be calculated by Eq. 6.2.

### 6.2.3 The output of continuous cell impedance at multiple frequencies

The cell voltage output ( $V_{Cell}$ ) from the cell model is Fourier transformed in a callback function called StopFcn to obtain the amplitude of the output voltage at each test frequency.

If amplitudes at frequencies up to 1 kHz are to be measured, a sampling rate of at least 2 kHz should be used to satisfy the Nyquist-Shannon sampling theory. And the number of data for the Fourier transform must be the n-th power of 2. In the simulation, a sampling rate of 2048 Hz is used, which samples 2048 (2<sup>11</sup>) voltage data every second. The sample time of each test frequency generation model is set to 1/sampling rate. The step size in the model solver should also be an expression related to the sampling rate. 1/sampling rate is used for the max step size.

Fig. 6.6 (a) shows the input current (Current<sub>in</sub>) for 1 second, and Fig. 6.6 (b) shows the output voltage for 1 second (Voltage<sub>out</sub>). If the voltage data in the time domain of Fig. 6.6 (b) is Fourier transformed, it can be expressed in the frequency domain as shown in Fig. 6.6 (c).



Figure 6.6 (a) Input current and (b) output voltage expressed in the time domain, and (c) the output voltage expressed in the frequency domain as a result of the simulation model.

The output voltage amplitudes at 1 Hz and 250 Hz obtained in Fig. 6.6 (c) are used to calculate the impedance at each frequency by Eq. 2.9.

Fig. 6.7 shows the impedance simulation results at four different frequencies of the cell during discharge. While the cell is discharged, the lower the frequency, the more impedance changes. Table 6.4 shows the increased rate in impedance as cell DoD increases. The increased rate of cell impedance at 10 Hz, 100 Hz, and 1 kHz is calculated over the entire DoD range, but at 1 Hz, it is calculated in the 1% to 96% DoD range. This is to exclude impedance that is not properly measured as explained in Subsection 5.2.1.



Figure 6.7 Simulation result of 1, 10, 100, and 1000 Hz impedance in the entire DoD range of the discharged cell.

Frequency	Increased rate
1 Hz	113.15 %
10 Hz	107.29 %
100 Hz	104.73 %
1 kHz	104.32 %

Table 6.4 Increased rates in impedance at each frequency.

#### 6.2.4 Cell temperature model

At lower frequencies, impedance is more affected by cell temperature and cell SoC. Fig. 6.8 shows the temperature change of the battery cells discharged at each different C-rate in a temperature chamber set to 25°C. Cell temperature is related to discharge current and discharge time. The temperature model is implemented as a 2D lookup table that receives the discharge current and discharge time as inputs, as shown in Fig. 6.1.



Figure 6.8 Temperature changes of cells discharging at different C-rates.

The equation between cell temperature and cell impedance can be obtained from the empirical relationship through EIS measurement, which can be used to estimate impedance changes due to temperature changes. The output of the temperature model  $T_{cell}$  is used to adjust the impedance considering the temperature. The 1Hz impedance is adjusted to the cell temperature with Eq. 5.2.

# 6.3 Simulation Result and Validation

This section shows the simulation results of the developed battery cell model. The accuracy of the simulation results is shown in comparison with the measurement results.

### 6.3.1 Simulation of continuous cell impedance

### - 1Hz impedance during discharge

Table 6.5 shows the parameters used for measurements and simulations. The 1 Hz impedance of a cell discharging at different C-rates is shown in Fig. 6.9 (a). The measured impedance is represented by dotted lines and the simulation results by solid lines. Fig. 6.9 (b) shows the percentage error between the measured impedance and the simulation results.

**Table 6.5** Conditions for both simulation and measurement of the impedance of the cell during discharge.

Parameter	Description
DC offset	1.5 C, 1 C, 0.5 C, 0.25 C and 0.125 C
Cell SoC	From 100% to 0 %
Cell SoH	95 % (cell #6)
Test frequency	1 Hz, 250 Hz
Amplitude	50 mA (each)



(b)

Figure 6.9 (a) Simulated and measured 1 Hz impedance of cells discharged at different C-rates (dashed line: measured impedance, solid line: simulated impedance). (b) Percentage errors of the estimated impedance compared to the measured impedance at different C-rates.

Table 6.6 shows the mean of percentage errors at each C-rate.

C-rate	Percent error (%)
1.5	2.28
1	2.36
0.5	1.32
0.25	0.76
0.125	0.56
Total	1.46

Table 6.6 Average values of each percent error at different C-rates.

#### - 250 Hz impedance at each cell SoH

When cell impedance is used for cell SoH estimation, it is recommended to use a higher frequency to be less influenced by SoC. Eq 4.1 for impedance adjustment according to SoH is applied to 250 Hz impedance in the simulation model.

The result is shown in Fig. 6.10, and the percentage errors compared to those measured in cells at each SoH are shown in Table 6.7.



Figure 6.10 Continuous 250 Hz impedance at each SoH (dashed line: measured impedance, solid line: simulated impedance).

Table 6.7 Average values of percent errors of the estimated impedance relative to the measured impedance	at
different SoHs.	

SoH (%)	Percent error (%)
100	0.43
95	0.33
90	0.75
85	0.55
80	0.45
75	0.35
Average	0.48

### 6.3.2 Simulation of cell impedance discharging from different initial SoCs

In the preceding subsections, the simulation results are represented until the fully charged cell is completely discharged. However, the cell does not always discharge to 100% SoC. Here, simulation results when cells are discharged at different initial SoCs are compared with measurement results. The experimental conditions are shown in Table 6.8. The cell is discharged for 10 minutes after a relaxation of 60 minutes. Then, 10 minutes of cell discharge and 60 minutes of cell relaxation are repeated until the cell is completely discharged. The cell impedance is measured every second while the cell is discharged.

Parameter	Description
Test frequency	1 Hz
Amplitude	50 mA
DC bias	2.6 A (1 C)
Depth of discharge	From 0 to 100 %
Discharge time	10 min. (each)
Relaxation time	60 min. (each)
Cell SoH	95 % (cell #6)
Initial temperature	25 °C

Table 6.8 Conditions for simulation and measurement of cell impedance discharged from different initial SoCs.

Fig. 6.11 (a) shows the measured cell voltage (dotted line) and the model output voltage (solid line), and Fig. 6.11 (b) shows the percentage error between the measured voltage and the simulation result. The average of percent errors in the total DoD range is 0.42%.



(b)

Figure 6.11 (a) Discharge curve of a cell in which 10 minutes of discharge and 60 minutes of relaxation are repeated (dashed line: measured voltage, solid line: simulated voltage). (b) Percentage error of simulated cell voltage compared to the measured voltage.

Fig. 6.12 (a) shows the output of the cell temperature model. The cell temperature rises every 10 minutes of discharge, and after every 60 minutes of relaxation, the cell temperature drops to 25 °C. Fig. 6.12 (b) shows the measured 1 Hz impedance (blue dotted line), simulated 1 Hz impedance (red solid line), and simulated 1 Hz cell impedance after being adjusted to temperature (green solid line). Fig. 6.12 (c) shows the percentage error between the measured 1Hz impedance and the simulated 1Hz impedance adjusted to the temperature. The average percent error in the overall DoD is 2.59%, and the average percent error in DoD 0% to 95% is 1.16%.



**Figure 6.12** (a) Output of the cell temperature model when discharging for 10 minutes and relaxation for 60 minutes are repeated. (b) Measured continuous 1 Hz impedance and simulated results (red line: before adjusting to temperature; green line: after adjusting to temperature). (c) Percent error of simulated 1Hz impedance considering the cell temperature compared to the measured impedance.

### 6.3.3 Simulation results at different diagnostic parameters

As mentioned earlier, one of the advantages of this simulation model is that it shortens the time required for experiments. As examples of this model being used, the following subsections compare simulation results of continuous cell impedance at different diagnostic parameters.

### - Simulation of continuous cell impedance from 1 to 100 Hz

Fig. 6.13 (a) shows the cell impedance from 1 Hz to 100 Hz of cells discharging from DoD 0% to 100%. Fig. 6.13 (b) shows the increased rate of impedance in the range between 1% and 95% of DoD at each frequency. The impedance at each frequency is simulated at 1 Hz intervals. The simulation conditions are shown in Table 6.9.

Table 6.9 Simulation conditions for comparing centimpedance from 1 Hz to 100 Hz.			
Parameter	Description		
Test frequency	1 Hz to 100 Hz		
Depth of discharge	From 0 to 100 %		
Cell SoH	95 % (cell #6)		
DC bias	1.3 A (0.5 C)		
Sampling rate	2048 Hz		
Amplitude	50 mA (each)		

Table 6.9 Simulation conditions for comparing cell impedance from 1 Hz to 100 Hz.



(b)

Figure 6.13 (a) Continuous cell impedance from 1 Hz to 100 Hz simulated in the entire DoD range. (b) The increased rate of impedance at each frequency.

Both Fig. 6.13 (a) and Fig. 6.13 (b) show that the higher the frequency, the fewer impedance changes due to DoD changes. For this simulation to be measured as an experiment, it would take ca. 550 hours (ca. 23 days), assuming that the required time for temperature setting is excluded and cell SoH is not changed even in charging/discharging cycles (ca. 120 minutes for CC-CV charging + 90 minutes for relaxation + ca. 120 minutes for 0.5C discharge) \*100 times).

- Simulation of continuous cell impedance at different sampling rates

Fig. 6.14 (a) shows the simulation results of cell impedance during discharge at different sampling rates. Fig. 6.14 (b) shows the percentage error of simulation results at sampling rate 2048 Hz and from 16 Hz to 1024 Hz. Table 6.10 shows the simulation conditions.



(b)

Figure 6.14 (a) Continuous cell impedance in the entire DoD range simulated at different sampling rates. (b) Percentage errors of the simulation results between the sampling rate of 2048 Hz and each sampling rate of 16 Hz to 1024 Hz.

Parameter	Description
Sampling rate	16 Hz to 2048 Hz
Test frequency	1 Hz
Depth of discharge	From 0 to 100 %
Cell SoH	95 % (cell #6)
DC bias	1.3 A (0.5 C)
Amplitude	50 mA (each)

Table 6.10 Simulation conditions for comparing continuous 1 Hz impedance at different sampling rates.

Fig. 6.14 (a) shows that the lower the sampling rate, the lower the output impedance. This does not mean that the cell impedance actually decreased, but that the measurement error increased. In Fourier transformations, the lower sampling rate results in fewer samples collected in one cycle of signals in the time domain, resulting in a greater error due to the failure of the signal to restore properly in the frequency domain. Table 6.11 shows the average of the percent errors at each sampling rate in Fig. 6.14 (b).

**Table 6.11** Percent errors of the mean of the impedance simulated at a sampling rate of 2048 Hz and the mean of the impedance simulated at each different sampling rate.

Sampling rate	Percent error
16 Hz	1.63 %
32 Hz	0.48 %
64 Hz	0.16 %
128 Hz	0.06 %
256 Hz	0.026 %
512 Hz	0.01 %
1024 Hz	0.00 %

As shown in Table 6.11, when a sampling rate of 16 Hz is used, an average error of 1.63% occurs compared to when 2048 Hz is used. Meanwhile, the simulation result when a sampling rate of 1024 Hz is used do not reveal the difference from when 2048 Hz is used. Such information can be used to select diagnostic parameters and hardware performance for optimized cell monitoring.

# 7 Frequency Excitation to the Battery Pack

Up to Chapter 6, the impedance of single LIB cells is measured to estimate the state. However, in most applications, cells are connected in series to reach the required voltage level and connected in parallel to provide sufficient capacity and used as a battery pack or module. However, it is more likely to fail in a battery pack connected to multiple cells than in a single battery cell. The probability of failure of the battery pack of n cells exceeds n times the probability of failure of a single cell.

While parallel-connected battery cells always have the same voltage, the serial-connected cells experience a non-uniform load even if the same current flows, such that a voltage deviation occurs between the cells shown as Fig. 7.1. In this case, even if the battery pack voltage is in a normal range, some cells may be over-discharged or overcharged, which may cause a fatal failure, such as thermal runaway [230, 231], from an unstable state in the battery pack [232]. Thus, management of serial-connected battery packs is particularly important, and this chapter deals with battery packs in which cells are series-connected. I.e., The battery diagnostic device using the frequency response may be attached to a bundle of battery cells connected in series or attached to each cell.



Figure 7.1 (a) Series-connected cells having a uniform voltage and (b) having a non-uniform voltage

Fig. 7.2 shows the results of simulating the impedance of a battery pack consisting of seriesconnected cells. Table 7.1 shows the simulation conditions.

Darameter	Description
cells.	
Table 7.1 Conditions for simulating 1 Hz and 250 Hz imped	dance of a battery pack consisting of series-connected

Parameter	Description
DC offset	2.6 A (1 C)
Cell SoC	From 100% to 0 %
Test frequency	1 Hz, 250 Hz
Amplitude	260 mA (each)



Figure 7.2 Results of 1 Hz and 250 Hz impedance simulation of a battery pack consisting of series-connected cells.

According to the simulation result in Fig. 7.2, it is shown that the impedance of a battery pack in which cells are connected in series is the sum of the impedance of each cell. Depending on the degradation state or amount of charge of each cell, the impedance of the battery pack will change, and it seems that it can be used for SoH and SoC estimation as covered in Chapters 4 and Chapter 5. However, this is a simulation in an ideal situation where all the chemical properties of the connected cells remain the same, and the impedance in the actual battery pack is not as simple as this simulation result.

This chapter deals with a study on the frequency response when frequencies are applied to battery packs in which battery cells are connected in series. In particular, it is considered that the voltages of the cells in series-connected battery packs are not properly balanced. I.e., it is not enough to simply consider the relationship between the impedance and the SoH or SoC of the battery pack, and different states of the connected cells should be considered.

The investigations and results presented in this chapter have been published in [13].

### 7.1 Cell Balancing

Since not all battery cells are manufactured identically, individual cells do not contribute equally to the system. Even if each cell is made of the same chemistry with the same physical size, shape, and weight, it has different capacities, different self-discharge rates, different internal resistance, different SOHs, etc [233–235]. Therefore, cell balancing must be carried out during the charging or discharging of the battery pack [236]. Otherwise, the cells in the battery pack are charged and discharged at different rates, and the difference in individual cell voltages increases over time [237–240], and as a result, energy loss and heat generation increase [241, 242], charging amount decreases, energy efficiency decreases, and performance degradation accelerates [243], and the battery pack cannot operate efficiently [244]. When the cells are overcharged or over-discharged, the pack capacity is lost over time, the cycle life of the battery pack is reduced, and a safety risk may be caused [245, 246]. Eventually, if one cell with an error in the battery pack is not replaced immediately, fatal consequences may occur. However, even if a cell with an error in the battery pack is replaced, the same problem occurs because the new cell has different chemical properties from the cells already used.

The cell balancing system minimizes cell-to-cell voltage and SoC deviation [246, 247]. As a result, voltage stress of individual cells is reduced [247, 248], overall reliability and safety of individual cells are increased [240, 241, 249, 250], the effect of cell aging due to capacity loss is minimized [251–253], and battery life is extended [244, 254–257]. Additionally, cell balancing not only maximizes the energy transferred to the cell during the charging process but also maximizes the energy emitted from the cell during the discharging process [238, 258–261].

## 7.2 Causes of Cell Imbalance

The cells in a battery pack have different chemical reactions due to different manufacturing processes, internal resistance, self-discharge rate, degradation and temperature for each cell [213, 262, 263]. Factors affecting cell imbalance can be divided into intrinsic and extrinsic factors [264, 265]. Intrinsic factors are related to the manufacturing process, including differences in capacity, impedance, amount of active material, self-discharge rate, etc [266]. Extrinsic factors include the connection method of cells, charge/discharge current, heat dissipation, etc [267]. Temperature deviation of cells in the battery pack affects cell characteristics, including self-discharge rate, and causes performance deviation [268]. And the external circuit connected for cell management exacerbates the imbalance of each cell by consuming different power.

Cell SoC imbalance is an important issue for BMS to solve [269]. Even if cells are produced of the same type by the same manufacturer, there is uncertainty in the battery parameter, and the accuracy of SoC estimation varies from cell to cell [270]. In addition, in SoC estimation performed based on a battery model, an SoC estimation error occurs due to model uncertainty that cannot represent a physical system under various operating conditions without error [271, 272].

Cell capacity imbalance is an important issue to be solved as well. The battery cell capacity varies due to factors such as average cell discharge current, discharge time, internal cell temperature, end of discharge (EoD) voltage value, self-discharge, aging, etc [273]. Manufacturers generally guarantee a difference in cell capacity of  $\pm 5\%$  [238], and serial-connected cells are often imbalanced. An imbalance in battery cells connected in parallel is caused by a difference in the net current of each cell, which is caused by a deviation in the internal resistance of the cell, which is a factor in different discharge and aging performance [274, 275].

# 7.3 Problems Due to Battery Cell Imbalance

If one weak cell is overcharged or over-discharged due to the voltage difference of the cells connected in series, it causes the battery to fail or shorten the cycle life, reduce the available capacity due to the early termination of charging and discharging, and cause the safety problem of explosion [260, 276, 277]. In order to extend the cycle life of the battery pack, each cell needs to be utilized to maintain the SoC balance [278].

Cell balancing prevents the risk caused by an excessive increase in cell voltage. LIBs have very high electrical energy, which can pose a serious safety risk due to cell imbalance [245, 276]. If the cell voltage exceeds the limit, the cathode is decomposed and heat is generated, and a short circuit is caused by the deposition of metallic lithium on the anode surface [279]. As a result, active components react with each other and with electrolytes, resulting in fire and explosion [280, 281]. When one cell is damaged, degradation accelerates sequentially to other cells in the pack due to imbalance.

The cell with the lowest or highest SoC limits overall battery performance. When the battery cell is over-discharged, irreversible chemical reactions reduce the available cell capacity and cause the cell to explode [282, 283]. To prevent over-discharge, the BMS terminates the discharge of the battery pack even if one cell reaches a low voltage threshold, and thus the available capacity is reduced [276, 280, 284, 285]. Due to the early cut-off of the battery discharge, there is residual energy that cannot be used in the battery pack.

Similar problems occur during the charging process as well [284]. If one cell has less capacity than the other cells serially connected in the pack, an imbalance occurs even if all cells have the same initial SoC [286]. BMS terminates the charging process when one cell with the highest SoC reaches the upper limit of the voltage, which wastes the energy and capacity remaining in the other cell.

Therefore, in order to effectively utilize the battery pack, it is desirable to reduce the imbalance of each cell during charging and discharging.

#### 7.4 Detection of an Over-discharged Cell in a Battery Pack Using THD

THD is also called the distortion factor, which is defined as the ratio of the sum of the powers of every harmonic component to the power of the fundamental frequency. When the sinusoidal frequency  $\omega$  signal passes through a nonlinear device,  $n\omega$  components, which are multiples of input frequencies called harmonics, occur. THD can be used to indicate the degree of nonlinearity of the system by representing the proportion of components at the added harmonic frequency to the component at the input frequency. To clarify, THD used in this thesis refers to THD+N, which is more commonly used in devices. THD+N means adding noise to THD and is represented by Eq. 7.1.

THD + N = 
$$\frac{\sqrt{\sum V_n^2 + \sum Noise^2}}{\sqrt{V_1^2}} \times 100 \ (\%)$$
 (7.1)

where  $V_n$  is the RMS value of the n-th harmonic voltage and  $V_1$  is the RMS value of the fundamental component.

THD analysis is a non-invasive method that uses frequency responses for system analysis and has the advantage of being able to measure behavior due to the nonlinear dynamics of the LIB, which is not possible for EIS analysis. As described in Section 2.5, better performance and safe operation of the LIB requires an understanding of electrochemical and physical processes, and EIS is a well-known non-destructive measurement technique used for this purpose. However, despite the non-linear processes involved in the operation of LIB cells, a type of electrochemical cell, EIS cannot analyze them because EIS analysis is only possible in linear systems and requires pseudo-linearity of electrochemical systems.

Among the nonlinear dynamic analysis methods applied to various research fields, THD is commonly used in acoustic studies for noise detection [287]. THD can be applied as a quality criterion for linearity evaluation and is also used to detect nonlinearity that reduces the reliability of EIS measurements [288, 289]. In reference [290–295], nonlinear analysis using THD is used for the electrochemical characterization of fuel cells. In addition, in reference [296], harmonic impedance is applied to characterize the electrode material and electrochemical reaction of the redox system. In addition, in reference [297], distortion of the current response to the sinusoidal excitation voltage is measured to estimate the SoC of the lead-acid battery.

As shown in Fig. 5.2, cell 1Hz impedance cannot be measured at the beginning of the cell discharge and at the deep DoD. The reason is that cell impedance can only be obtained from linear systems. As shown in Fig. 5.3, even if the battery cell is discharged with a constant current, the cell voltage is nonlinearly lowered due to activation polarization and concentration polarization. In these areas, the occurrence of un-inputted harmonic and noise components reduces the output voltage component at the input frequency of 1 Hz, resulting in a higher THD. At the beginning of the cell discharge and when the DoD is discharged beyond a certain limit, the cell does not exhibit a linear voltage output, resulting in an increased THD. I.e., over-discharge of the battery cell can be detected with THD, which indicates distortion of the response due to system nonlinearity.

As mentioned in the previous section, over-discharging of LIB cells reduces the available capacity by irreversible chemical reactions, resulting in serious safety risks such as explosions. Even if only one

over-discharged cell exists in the battery pack, it accelerates the decomposition of other cells. Nevertheless, if only the battery pack voltage is measured, the presence of one over-discharge cell cannot be detected because it cannot be distinguished whether the voltage of each cell is uniformly lowered or only the voltage of one cell is exceptionally over-discharged. When the voltage of every cell in the battery pack needs to be measured in order to detect one over-discharged cell, complexity and cost increase according to the number of cells to be measured. However, when the THD of the battery pack is measured, the presence of one over-discharged cell can be detected through a voltage response at only two terminals of the battery pack even if the voltage of every cell is not measured.

### 7.4.1 THD simulation of a cell during discharge

A simulation model developed in Chapter 6 is used for THD simulation of a battery cell. Table 7.2 shows the simulation conditions and Fig. 7.3 shows the simulated cell voltage, 1 Hz impedance, and THD while the cell is fully discharged.

Parameter	Description	
Test frequency	1 Hz	
Initial SoC	100 %	
SoH	100 %	
DC bias	2.6 A (1 C)	
Sampling rate	1024 Hz	
Amplitude	26 mA	
Lower cut-off voltage	2.8 V	

**Table 7.2** Conditions for THD simulation of a battery cell that is discharged.



Figure 7.3 Simulated cell voltage, 1 Hz impedance, and THD while the cell is discharged.

As shown in Fig. 7.3, at the beginning and end of the discharge, the 1 Hz impedance cannot be correctly estimated and shows a low value, while the THD, which indicates the degree of distortion of the input signal, increases.

Fig. 7.4 and Fig. 7.5 show simulated voltage and frequency responses in cell SoC 50% and 2%, respectively.



Figure 7.4 (a) Simulated voltage response and (b) frequency response for 1 second at 50% SoC.

In Fig. 7.4 (a), the cell voltage at 50% SoC, which is the middle of the cell discharge, shows a sine wave of 1 Hz, which is hardly distorted. In the frequency domain of Fig. 7.4 (b), few components other than the input 1 Hz component appear. Here, THD simulated at 50% cell SoC is 2.59%.



Figure 7.5 (a) Simulated voltage response and (b) frequency response for 1 second at 2% SoC.

In Fig. 7.5 (a), the cell voltage at 2% SoC, just before the complete discharge of the cell, shows a severely distorted 1 Hz sine wave. In the frequency domain of Fig. 7.5 (b), added components other than the input 1 Hz component are shown. These added frequency components are caused by system nonlinearity and cause THD to increase. Here, THD simulated in cell SoC 2% is 73.49%.

As a result, when THD is measured in the frequency response of the battery cell, a cell discharged beyond a certain limit can be detected.

### 7.4.2 THD measurement of a cell during over-discharge

The voltage and THD during the discharge of one battery cell are measured by the measurement system introduced in Chapter 3. Fig. 7.6 shows a device that connects three LIB cells in series. In this device, the bonding part of the battery socket is formed in the form of a pin, which not only reduces the contact resistance, but also provides a constant contact part, so that it has a constant contact resistance.



Figure 7.6 A photo of a device that connect three LIB cells in series.

The voltage of each cell is measured at  $V_1$ ,  $V_2$ , and  $V_3$ , the total voltage of the connected cells is measured at  $V_4$ , and  $C_{out}$  is used to control the current passing through the battery cells using electronic loads.

Table 7.3 shows the experimental conditions for measuring THD during over-discharge of a LIB cell, and Fig. 7.7 shows the measured cell voltage and THD. The lower cut-off voltage of the cell defined by the manufacturer is 2.8 V, but the cell is over-discharged up to 2.5 V for the experiment.

Parameter	Description
Test frequency	1 Hz
Initial SoC	100 %
Cell SoH	90 %
DC bias	2.6 A (1 C)
Amplitude	26 mA
Lower cut-off voltage	2.5 V

Table 7.3 Experimental conditions for THD measurement until a cell is over-discharged.


Figure 7.7 Cell voltage and THD measured until the cell is over-discharged.

Fig. 7.7 shows that THD increases when a cell is discharged below a certain voltage, as shown in the simulation result in Fig. 7.3. Table 7.4 shows THD values at different cell voltages.

Cell voltage (V)	THD (%)	
3.0	13.29	
2.9	25.5	
2.8	46.31	
2.7	86.87	
2.6	311.74	
2.5	538.78	

 Table 7.4 THD values at different cell voltages.

Table 7.4 shows that the THD increases significantly as the cell voltage decreases while the cell is over-discharged. THD increases even before the cell over-discharge begins, thus it can be used to predict and prevent cell over-discharge.

#### 7.4.3 THD measurement of the battery pack during over-discharge

THD is measured in voltage response during over-discharge of a battery pack in which three cells are connected in series.

Table 7.5 shows the experimental conditions for measuring the THD of the battery pack while one cell is over-discharged, and Fig. 7.8 shows the voltage and THD of the battery pack while one cell is over-discharged. The battery pack is over-discharged until one cell voltage reaches 2.5 V.

Table 7.5 Experimental conditions for measuring THD of a battery pack while one cell is over-discharged.

Parameter	Description	
Test frequency	1 Hz	
Initial SoC	100 %	
Cell SoH	90, 85 and 70 %	
DC bias	2.6 A (1 C)	
Amplitude	26 mA	
Lower cut-off voltage	2.5 V	



Figure 7.8 Voltage and THD of the battery pack while one cell is over-discharged.

As shown in Fig. 7.8, the battery pack voltage is 8.62 V when one cell is over-discharged to 2.50 V, which does not reach the lower limit voltage of 8.40 V. Only by measuring a decrease in the battery pack voltage, it is not possible to distinguish whether every cell voltage is uniformly lowered, or one cell is over-discharged. Nevertheless, since one cell is over-discharged, it is shown that THD measured by the voltage response of the battery pack significantly increases.

Fig. 7.9 shows the THD of the battery pack and the voltages of each cell.



Figure 7.9 THD of the battery pack and voltages of each cell while one cell is over-discharged.

Fig. 7.9 shows that THD begins to increase as one cell begins to discharge below a specific voltage. Although the charge of the other cells still remains, the THD is remarkably increased due to the overdischarge of one cell.

Table 7.6 shows increased rates of THD of the battery pack at different cell voltages while a cell with 70% SoH is over-discharged.

0		
Voltage of cell with 70% SoH (V)	THD (%)	
3.0	14.37	
2.9	14.70	
2.8	18.57	
2.7	27.14	
2.6	36.62	
2.5	49.72	

Table 7.6 THDs at different cell voltages of a cell with 70% SoH.

Table 7.6 shows that the THD of the battery pack increases as only one cell is over-discharged.

THD measured while one cell is over-discharged in a battery pack to which three cells are connected (Table 7.6) shows a lower value than THD measured while only one cell is over-discharged (Table 7.4). Nevertheless, it is shown that THD can be used to detect one cell over-discharge in the battery pack. As the over-discharge of the cell intensifies, THD increases significantly.

#### 7.4.4 THD simulation in different numbers of serial-connected cells

It is simulated that as the number of serial-connected cells increases, the degree of increase in THD due to the over-discharge of one cell decreases. In simulations in this subsection, when the other cells begin to discharge at 100% SoC, one cell begins to discharge at 50% initial SoC. The one cell discharged at 50% initial SoC, called a weak cell, reaches EoD earlier than the other cells. The number of cells connected in series is simulated from 2 to 32, and Table 7.7 shows the simulation conditions.

Parameter	Description	
DC offset	1 C	
Lower cut-off voltage	2.8 V	
Test frequency	1 Hz	
Amplitude	260 mA	
Number of series-connected cells	2 to 32	

Table 7.7	Conditions for	THD simulation	in different number	rs of series-conn	ected cells
	Conditions for	THD Simulation	in unierent number	13 01 361163-00111	etteu tens.

Fig. 7.10 illustrates the simulation result of the voltage of a battery pack consisting of 15 cells and one normal cell voltage while one weak cell reaches EoD as an example.



Figure 7.10 Battery pack voltage and normal cell voltage while one weak cell reaches EoD.

In Fig. 7.10, the solid black line represents the total voltage of the 15 cells connected in series and shows the voltage value on the left y-axis. The solid red line shows a weak cell voltage, and the solid blue line shows the voltage of one normal cell, and their voltage values are indicated on the right y-axis. It can be seen that, even though one weak cell reaches EoD and may be over-discharged, the battery pack voltage does not significantly decrease.

Fig. 7.11 illustrates the THD of the simulated battery pack voltage at different numbers of cells while the voltage of the weak cell reaches the lower cut-off. In this simulation result, the number of connected cells ranges from 2 to 32, and the darker the color of the line, the more cells it has. The x-axis indicates the voltage of the weak cell, and the y-axis indicates the THD of the battery pack voltage.



Figure 7.11 THD for weak cell voltages in different numbers of series-connected cells.

The THD of the battery pack increases as the voltage of one weak cell decreases. As the number of connected cells increases, the degree to which THD increases decreases.

Fig. 7.12 and Table 7.8 show the increased rate of THD when the weak cell voltage is 2.8 V compared to 3.4 V in different cell numbers.



Figure 7.12 THD increased rate in the different number of series-connected cells.

7	Frequency	Excitation	to the	Battery	Pack
---	-----------	------------	--------	---------	------

Number of cells	THD at 3.4 V (%)	THD at 2.8 V (%)	THD increased rate (%)
2	15.97	1074.77	6630.49
3	12.52	246.86	1872.26
4	10.11	108.19	970.44
5	8.44	61.09	624.16
6	7.23	39.52	446.88
7	6.31	27.83	340.69
8	5.61	20.77	270.51
9	5.04	16.16	220.89
10	4.57	12.99	184.04
11	4.19	10.71	155.65
12	3.86	9.03	133.88
13	3.58	7.72	115.41
14	3.34	6.69	100.14
15	3.13	5.86	87.31
16	2.94	5.19	76.37
17	2.78	4.64	66.95
18	2.63	4.18	58.74
19	2.50	3.78	51.53
20	2.38	3.45	45.16
21	2.17	2.91	34.37
22	2.08	2.70	29.77
23	1.99	2.50	25.60
24	1.92	2.33	21.81
25	1.84	2.18	18.33
26	1.78	2.05	15.15
27	1.72	1.93	12.22
28	1.66	1.82	9.51
29	1.60	1.72	6.99
30	1.55	1.63	4.66
31	1.51	1.54	2.48
32	1.46	1.47	0.45

cells are connected, the increased rate of THD at 2.8V is close to 0%. In other words, as the number of connected cells increases, the increase rate of THD of the battery pack decreases, and according to the simulation, when ca. 32 cells are connected, the THD cannot be used to detect that one cell has reached EoD. However, in actual measurements, it is expected that over-discharge can be detected even if more than 32 cells are connected. In the simulation results in Fig. 7.11, THD decreases as the cell voltage approaches 2.8V. Meanwhile, according to the actual measurement results in Fig. 7.7 and Fig. 7.8, the THD value increases more significantly during the cell is actually over-discharged. Note that the voltage response during over-discharge cannot be simulated because the behavior of a cell over-discharge with less than 0% SoC is not considered in the development of this battery model.

The higher the number of cells connected in series, the lower the rate of increase in THD. When 32

## 8 Conclusion and Future Work

This thesis deals with the LIB state monitoring method via frequency excitation. Not only single cells but also battery packs with connected cells are dealt with. Cell impedance at two frequencies is used to estimate each cell SoH and SoC, and a model for predicting cell impedance for optimization and simulation of the proposed algorithm is presented. In addition, an over-discharged cell in the battery pack can be detected as a method of measuring the frequency distortion rate.

The LIB state monitoring method proposed in this thesis can be summarized as follows:

- It can be used to estimate the battery state during operation by measuring the frequency response.
- It is a kind of simplified EIS analysis method with a specific purpose.
- It targets a specific system, not general system, thus excessive performance is not required.

• It has a fast measurement speed. Since it uses two preselected frequencies, not a wide frequency range.

• It is rather advantageous for estimating the state of LIB cells having a flat plateau in the discharge curve, which makes it difficult to measure the state.

• It can also analyze the nonlinear processes of the battery system from frequency responses, unlike EIS measurements, which are only valid for linear systems.

In Chapter 4, the cell SoH is estimated by impedance while charging or discharging a LIB cell of which SoC and temperature are unknown. Cell impedance at different frequencies is compared at different cell SoHs, SoCs, and temperatures. The lower the cell SoH, DoD, and temperature, the higher the cell impedance, and the greater the difference in impedance at the lower frequency. During charging, the cell impedance changes more, and a longer measurement time for cell SoH estimation is required than during discharging. In conclusion, the cell SoH is estimated by using the cell impedance that increases linearly as the cell degrades. When 250Hz impedance is used for cell SoH estimation, it takes about 4 seconds while discharging and about 10 minutes while charging to reach a 98% confidence level.

In Chapter 5, cell SoH estimated in Chapter 4 and the measured cell temperature are used to monitor the SoC of the LIB cells being discharged. Here, two frequencies are applied simultaneously to estimate each cell SoH and SoC. 1Hz impedance measured for cell SoC monitoring takes into account the effect of temperature and SoH. As a result, the proposed cell SoC monitoring method enables simultaneous estimation of the cell SoH and SoC whose initial value is unknown. In cells with 100% to 80% SoH, it takes 233 seconds for the cell SoC estimation to reach a 95% confidence level and 267 seconds to reach a 98% confidence level.

Chapter 6 presents a LIB cell model used to optimize and simulate state monitoring algorithms using frequency excitation. A multi-frequency signal is applied to the DC bias of a cell being discharged, and thus, the real-time cell voltage and continuous cell impedance are predicted. The continuous cell impedance prediction takes into account the effect of cell SoC, SoH, temperature and C-rate, and even when cells are discharged at different initial SoCs, cell impedance is successfully predicted. While a

fully charged cell is discharged, a prediction result of 1Hz impedance shows an average error of 1.46%, compared to the measured cell impedance, and 2.59% when discharged at different initial SoCs. In addition, the prediction result of 250 Hz impedance shows an average error of 0.48%.

The use of the proposed simulation model can save time for verification and optimization of diagnostic algorithms as well as cost for experimental devices. Simulation results are displayed in a short period of time with a simple input of each battery cell state parameter, so it is possible to determine the optimal state estimation parameters for the diagnostic algorithm and predict the results before performing a time-consuming cell test.

Chapter 7 introduces a method of detecting an over-discharged cell in a battery pack in which battery cells are connected in series. Even if every cell voltage is not measured, the presence of one overdischarged cell can be detected with THD measured in the voltage response of the battery pack. The proposed algorithm is verified through simulations and measurements. THD increases even before cell over-discharge begins and increases significantly as cell voltage decreases, which can be used as an effective factor to prevent over-discharge.

As the number of connected cells increases, the increased rate of THD due to the over-discharge of one cell decreases. And as a result of the simulation, if 32 cells are connected in series, it cannot be detected using THD that one cell has reached EoD. Nevertheless, the measurement results show that the THD value increases more significantly when the cell is actually over-discharged. In the development of the battery model used, the behavior of cells over-discharged with less than 0% SoC is not considered, thus the voltage response during over-discharging cannot be simulated. Therefore, as future work, the difference in the increased rate of THD due to the over-discharge of one cell in different numbers of cells will be compared by measurement. In addition, the simulation model will be reinforced to take into account the behavior during the over-discharge of the cell.

In this thesis, 250 Hz or 1 kHz is used for SoH estimation, and 1 Hz is used for SoC estimation. Nonetheless, the use of frequencies is not limited to them. Considerations for selecting the appropriate test frequency and test amplitude are covered in Subsection 3.2.1 and Subsection 5.1.1.

Note that in the experiments in this thesis, cell SoH is set by repetitive cycles under the same controlled conditions. Estimation accuracy for cases where cells deteriorate due to exceptional conditions such as physical shock or extreme temperature is not verified in this thesis.

DC bias has a nonlinear effect on cell impedance [298, 299], which results in a difference between the cell impedance measured by EIS and the continuous cell impedance measured during cell operation. Measurement errors increase in applications where the operating current continues to change, thus e.g., during the CV charging or during the acceleration of an EV, the cell impedance cannot be accurately measured. Nevertheless, the impedance measurement is possible during the CC charging and when the EV stops driving.

Estimating SoC using 1Hz cell impedance is possible after discharging for 267 seconds, and is not possible below ca. 10% SoC. This is due to the characteristics inherent in LIB cells, as covered in Subsection 5.2.1. However, THD is significantly increased in these areas, which can be used to prevent over-discharge, and the cell voltage measurement method can be used as an auxiliary for SoC estimation. In addition, in these areas where 1Hz impedance cannot be accurately measured, the cell voltage change is remarkable, and thus cell SoC estimation using the cell voltage is advantageous for

use. Contrariwise, the cell voltage seems to be almost flat in the intermediate SoC range. This range, the so-called flat plateau in the discharge curve of LIB cells, is particularly notorious in LFP type cells, and makes it difficult to estimate SoC using cell voltage. Nevertheless, in this flat plateau, the voltage response of the cell is the most linear, thus the cell impedance can be measured more accurately, which is rather advantageous for SoC estimation using impedance. I.e., the method of using impedance for cell SoC estimation and the method of using cell voltage have complementary effects. Since the cell voltage is already measured to obtain cell impedance, SoC estimation using the cell voltage can be used without any additional device.

To apply test frequency signals to an operating current and to measure the frequency response, additional devices to incur additional costs are required to the existing BMS. However, the proposed LIB state monitoring method does not have to be applied to every battery application. The cost of applying this method is included in the battery management cost and should be considered whether it can provide practical benefits. E.g., battery management is considered much more important in critical missions and large-capacity battery packs. Failure of critical missions or frequent replacement of expensive battery packs should be avoided, and large-capacity battery packs have a high risk of explosion due to management failures. In these cases, the damage caused by the failure of battery management can far exceed the cost of maintenance.

This study only shows the experimental results of LCO and NMC type cells. However, since the proposed method is based on EIS technology already validated in various types of battery cells in a lot of literature, it is expected that it can be applied to other types of battery cells. In the future, it would be better if this proposed method is applied to other types of cells and the results are compared.

Lastly, even though the cell state monitoring method proposed in this thesis has the advantages of considering cell temperature, cell tests are performed only between 20°C and 35°C, which are considered to be in the room temperature range. In the future, it would be better to analyze cell impedance at a wider range of temperatures for this method to be applied in a wider range.

### **9** References

[1] K. Chen, F. Zhao, H. Hao, and Z. Liu, "Synergistic Impacts of China's Subsidy Policy and New Energy Vehicle Credit Regulation on the Technological Development of Battery Electric Vehicles," *Energies*, vol. 11, no. 11, p. 3193, 2018, doi: 10.3390/en11113193.

[2] J. M. Tarascon and M. Armand, "Issues and challenges facing rechargeable lithium batteries," *Nature*, vol. 414, no. 6861, pp. 359–367, 2001, doi: 10.1038/35104644.

[3] P. Poizot and F. Dolhem, "Clean energy new deal for a sustainable world: from non-CO2 generating energy sources to greener electrochemical storage devices," *Energy Environ. Sci.*, vol. 4, no. 6, p. 2003, 2011, doi: 10.1039/C0EE00731E.

[4] L. Lu, X. Han, J. Li, J. Hua, and M. Ouyang, "A review on the key issues for lithium-ion battery management in electric vehicles," *Journal of Power Sources*, vol. 226, pp. 272–288, 2013, doi: 10.1016/j.jpowsour.2012.10.060.

[5] J. B. Goodenough and Y. Kim, "Challenges for Rechargeable Li Batteries," *Chem. Mater.*, vol. 22, no. 3, pp. 587–603, 2010, doi: 10.1021/cm901452z.

[6] M. Armand and J.-M. Tarascon, "Building better batteries," *Nature*, vol. 451, no. 7179, pp. 652–657, 2008, doi: 10.1038/451652a.

[7] "A General Discussion of Li Ion Battery Safety," *Electrochemical Society Interface*, 2012, doi: 10.1149/2.F03122if.

[8] D. Belov and M.-H. Yang, "Failure mechanism of Li-ion battery at overcharge conditions," *J Solid State Electrochem*, vol. 12, 7-8, pp. 885–894, 2008, doi: 10.1007/s10008-007-0449-3.

[9] P. Biensan *et al.*, "On safety of lithium-ion cells," *Journal of Power Sources*, 81-82, pp.
 906–912, 1999, doi: 10.1016/S0378-7753(99)00135-4.

[10] J. Kim, L. Krüger, and J. Kowal, "On-line state-of-health estimation of Lithium-ion battery cells using frequency excitation," *Journal of Energy Storage*, vol. 32, p. 101841, 2020, doi: 10.1016/j.est.2020.101841.

[11] J. Kim and J. Kowal, "A Method for Monitoring State-of-Charge of Lithium-Ion Cells Using Multi-Sine Signal Excitation," *Batteries*, vol. 7, no. 4, p. 76, 2021, doi: 10.3390/batteries7040076.

[12] J. Kim and J. Kowal, "Development of a Matlab/Simulink Model for Monitoring Cell State-of-Health and State-of-Charge via Impedance of Lithium-Ion Battery Cells," *Batteries*, vol. 8, no. 2, p. 8, 2022, doi: 10.3390/batteries8020008.

[13] J. Kim and J. Kowal, "A Method for Detecting the Existence of an Over-Discharged Cell in a Lithium-Ion Battery Pack via Measuring Total Harmonic Distortion," *Batteries*, vol. 8, no. 3, p. 26, 2022, doi: 10.3390/batteries8030026.

[14] J.-M. Tarascon and M. Armand, "Issues and challenges facing rechargeable lithium batteries," in *Materials for Sustainable Energy*, V. Dusastre, Ed.: Co-Published with Macmillan Publishers Ltd, UK, 2010, pp. 171–179.

[15] J. B. Goodenough and Y. Kim, "Challenges for rechargeable batteries," *Journal of Power Sources*, vol. 196, no. 16, pp. 6688–6694, 2011, doi: 10.1016/j.jpowsour.2010.11.074.

[16] S. Megahed and W. Ebner, "Lithium-ion battery for electronic applications," *Journal of Power Sources*, vol. 54, no. 1, pp. 155–162, 1995, doi: 10.1016/0378-7753(94)02059-C.

[17] H. Budde-Meiwes *et al.,* "A review of current automotive battery technology and future prospects," *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering*, vol. 227, no. 5, pp. 761–776, 2013, doi: 10.1177/0954407013485567.

[18] G. Bruce, P. Mardikian, and L. Marcoux, "50 to 100 Ah lithium-ion cells for aircraft and spacecraft applications," *Journal of Power Sources*, vol. 65, 1-2, pp. 149–153, 1997, doi: 10.1016/S0378-7753(97)81531-5.

[19] S. M. Mousavi G., "An autonomous hybrid energy system of wind/tidal/microturbine/battery storage," *International Journal of Electrical Power & Energy Systems*, vol. 43, no. 1, pp. 1144–1154, 2012, doi: 10.1016/j.ijepes.2012.05.060.

[20] Z. Zhou, M. Benbouzid, J. Frédéric Charpentier, F. Scuiller, and T. Tang, "A review of energy storage technologies for marine current energy systems," *Renewable and Sustainable Energy Reviews*, vol. 18, pp. 390–400, 2013, doi: 10.1016/j.rser.2012.10.006.

[21] M. Majima, S. Ujiie, E. Yagasaki, K. Koyama, and S. Inazawa, "Development of long life lithium ion battery for power storage," *Journal of Power Sources*, vol. 101, no. 1, pp. 53–59, 2001, doi: 10.1016/S0378-7753(01)00554-7.

[22] Handbook of batteries, 3rd ed. New York, NY: McGraw-Hill, 2002. [Online]. Available: http://www.loc.gov/catdir/bios/mh041/2001030790.html

[23] G. Berckmans, M. Messagie, J. Smekens, N. Omar, and L. Vanhaverbeke, "Cost Projection of State of the Art Lithium-Ion Batteries for Electric Vehicles Up to 2030," *Energies*, vol. 10, no. 9, p. 1314, 2017, doi: 10.3390/en10091314.

[24] N. Nitta, F. Wu, J. T. Lee, and G. Yushin, "Li-ion battery materials: present and future," *Materials Today*, vol. 18, no. 5, pp. 252–264, 2015, doi: 10.1016/j.mattod.2014.10.040.

[25] R. J. Brodd, *Batteries for Sustainability*. New York, NY: Springer New York, 2013.

[26] D. Anseán *et al.,* "Fast charging technique for high power LiFePO4 batteries: A mechanistic analysis of aging," *Journal of Power Sources*, vol. 321, pp. 201–209, 2016, doi: 10.1016/j.jpowsour.2016.04.140.

[27] V. Agubra and J. Fergus, "Lithium Ion Battery Anode Aging Mechanisms," *Materials* (*Basel, Switzerland*), vol. 6, no. 4, pp. 1310–1325, 2013, doi: 10.3390/ma6041310.

[28] K. Zaghib *et al.,* "Safe and fast-charging Li-ion battery with long shelf life for power applications," *Journal of Power Sources*, vol. 196, no. 8, pp. 3949–3954, 2011, doi: 10.1016/j.jpowsour.2010.11.093.

[29] H. F. Andersen *et al.,* "Silicon-Carbon composite anodes from industrial battery grade silicon," *Scientific reports*, vol. 9, no. 1, p. 14814, 2019, doi: 10.1038/s41598-019-51324-4.

[30] S. You, H. Tan, L. Wei, W. Tan, and C. Chao Li, "Design Strategies of Si/C Composite Anode for Lithium-Ion Batteries," *Chemistry (Weinheim an der Bergstrasse, Germany)*, vol. 27, no. 48, pp. 12237–12256, 2021, doi: 10.1002/chem.202100842.

[31] M. Nie and B. L. Lucht, "Role of Lithium Salt on Solid Electrolyte Interface (SEI) Formation and Structure in Lithium Ion Batteries," *J. Electrochem. Soc.*, vol. 161, no. 6, A1001-A1006, 2014, doi: 10.1149/2.054406jes.

[32] *Linden's handbook of batteries,* 4th ed. New York: McGraw-Hill, 2011. [Online]. Available: https://www.accessengineeringlibrary.com/content/book/9780071624213

[33] M. D. Levi and D. Aurbach, "The mechanism of lithium intercalation in graphite film electrodes in aprotic media. Part 1. High resolution slow scan rate cyclic voltammetric studies

and modeling," *Journal of Electroanalytical Chemistry*, vol. 421, 1-2, pp. 79–88, 1997, doi: 10.1016/S0022-0728(96)04832-2.

[34] P. Kurzweil, "Lithiumionen-Batterien," in *Elektrochemische Speicher*, P. Kurzweil and O. K. Dietlmeier, Eds., Wiesbaden: Springer Fachmedien Wiesbaden, 2018, pp. 165–263.

[35] P. Arora, R. E. White, and M. Doyle, "Capacity Fade Mechanisms and Side Reactions in Lithium-Ion Batteries," *J. Electrochem. Soc.*, vol. 145, no. 10, pp. 3647–3667, 1998, doi: 10.1149/1.1838857.

[36] B. Stiaszny, J. C. Ziegler, E. E. Krauß, M. Zhang, J. P. Schmidt, and E. Ivers-Tiffée, "Electrochemical characterization and post-mortem analysis of aged LiMn2O4–NMC/graphite lithium ion batteries part II: Calendar aging," *Journal of Power Sources*, vol. 258, pp. 61–75, 2014, doi: 10.1016/j.jpowsour.2014.02.019.

[37] *Lithium-ion batteries: Solid-electrolyte interphase*. London: Imperial College Press, 2007.

[38] R. Fong, U. von Sacken, and J. R. Dahn, "Studies of Lithium Intercalation into Carbons Using Nonaqueous Electrochemical Cells," *J. Electrochem. Soc.*, vol. 137, no. 7, pp. 2009–2013, 1990, doi: 10.1149/1.2086855.

[39] J. Vetter *et al.,* "Ageing mechanisms in lithium-ion batteries," *Journal of Power Sources*, vol. 147, 1-2, pp. 269–281, 2005, doi: 10.1016/j.jpowsour.2005.01.006.

[40] G. Ning, B. Haran, and B. N. Popov, "Capacity fade study of lithium-ion batteries cycled at high discharge rates," *Journal of Power Sources*, vol. 117, 1-2, pp. 160–169, 2003, doi: 10.1016/S0378-7753(03)00029-6.

[41] D. Aurbach, B. Markovsky, I. Weissman, E. Levi, and Y. Ein-Eli, "On the correlation between surface chemistry and performance of graphite negative electrodes for Li ion batteries," *Electrochimica Acta*, vol. 45, 1-2, pp. 67–86, 1999, doi: 10.1016/S0013-4686(99)00194-2.

[42] Z. Li, J. Huang, B. Yann Liaw, V. Metzler, and J. Zhang, "A review of lithium deposition in lithium-ion and lithium metal secondary batteries," *Journal of Power Sources*, vol. 254, pp. 168–182, 2014, doi: 10.1016/j.jpowsour.2013.12.099.

[43] T. Waldmann, M. Wilka, M. Kasper, M. Fleischhammer, and M. Wohlfahrt-Mehrens, "Temperature dependent ageing mechanisms in Lithium-ion batteries – A Post-Mortem study," *Journal of Power Sources*, vol. 262, pp. 129–135, 2014, doi: 10.1016/j.jpowsour.2014.03.112.

[44] L. Somerville *et al.,* "The effect of charging rate on the graphite electrode of commercial lithium-ion cells: A post-mortem study," *Journal of Power Sources*, vol. 335, pp. 189–196, 2016, doi: 10.1016/j.jpowsour.2016.10.002.

[45] M. Petzl and M. A. Danzer, "Nondestructive detection, characterization, and quantification of lithium plating in commercial lithium-ion batteries," *Journal of Power Sources*, vol. 254, pp. 80–87, 2014, doi: 10.1016/j.jpowsour.2013.12.060.

[46] T. Ohzuku, Y. Iwakoshi, and K. Sawai, "Formation of Lithium-Graphite Intercalation Compounds in Nonaqueous Electrolytes and Their Application as a Negative Electrode for a Lithium Ion (Shuttlecock) Cell," *J. Electrochem. Soc.*, vol. 140, no. 9, pp. 2490–2498, 1993, doi: 10.1149/1.2220849.

[47] I. Laresgoiti, S. Käbitz, M. Ecker, and D. U. Sauer, "Modeling mechanical degradation in lithium ion batteries during cycling: Solid electrolyte interphase fracture," *Journal of Power Sources*, vol. 300, pp. 112–122, 2015, doi: 10.1016/j.jpowsour.2015.09.033. [48] T. G. Zavalis, M. Klett, M. H. Kjell, M. Behm, R. W. Lindström, and G. Lindbergh, "Aging in lithium-ion batteries: Model and experimental investigation of harvested LiFePO4 and mesocarbon microbead graphite electrodes," *Electrochimica Acta*, vol. 110, pp. 335–348, 2013, doi: 10.1016/j.electacta.2013.05.081.

[49] R. Deshpande, M. Verbrugge, Y.-T. Cheng, J. Wang, and P. Liu, "Battery Cycle Life Prediction with Coupled Chemical Degradation and Fatigue Mechanics," *J. Electrochem. Soc.*, vol. 159, no. 10, A1730-A1738, 2012, doi: 10.1149/2.049210jes.

[50] J.-H. Kim *et al.,* "Capacity fading mechanism of LiFePO4-based lithium secondary batteries for stationary energy storage," *Journal of Power Sources*, vol. 229, pp. 190–197, 2013, doi: 10.1016/j.jpowsour.2012.12.024.

[51] P. Liu *et al.,* "Aging Mechanisms of LiFePO[sub 4] Batteries Deduced by Electrochemical and Structural Analyses," *J. Electrochem. Soc.*, vol. 157, no. 4, A499, 2010, doi: 10.1149/1.3294790.

[52] R. Kostecki, L. Norin, X. Song, and F. McLarnon, "Diagnostic Studies of Polyolefin Separators in High-Power Li-Ion Cells," *J. Electrochem. Soc.*, vol. 151, no. 4, A522, 2004, doi: 10.1149/1.1649233.

[53] C. Peabody and C. B. Arnold, "The role of mechanically induced separator creep in lithium-ion battery capacity fade," *Journal of Power Sources*, vol. 196, no. 19, pp. 8147–8153, 2011, doi: 10.1016/j.jpowsour.2011.05.023.

[54] J. Cannarella and C. B. Arnold, "Ion transport restriction in mechanically strained separator membranes," *Journal of Power Sources*, vol. 226, pp. 149–155, 2013, doi: 10.1016/j.jpowsour.2012.10.093.

[55] A. Barai, G. H. Chouchelamane, Y. Guo, A. McGordon, and P. Jennings, "A study on the impact of lithium-ion cell relaxation on electrochemical impedance spectroscopy," *Journal of Power Sources*, vol. 280, pp. 74–80, 2015, doi: 10.1016/j.jpowsour.2015.01.097.

[56] F. M. Kindermann, A. Noel, S. V. Erhard, and A. Jossen, "Long-term equalization effects in Li-ion batteries due to local state of charge inhomogeneities and their impact on impedance measurements," *Electrochimica Acta*, vol. 185, pp. 107–116, 2015, doi: 10.1016/j.electacta.2015.10.108.

[57] S.-C. Huang, K.-H. Tseng, J.-W. Liang, C.-L. Chang, and M. Pecht, "An Online SOC and SOH Estimation Model for Lithium-Ion Batteries," *Energies*, vol. 10, no. 4, p. 512, 2017, doi: 10.3390/en10040512.

[58] E. Wood, M. Alexander, and T. H. Bradley, "Investigation of battery end-of-life conditions for plug-in hybrid electric vehicles," *Journal of Power Sources*, vol. 196, no. 11, pp. 5147–5154, 2011, doi: 10.1016/j.jpowsour.2011.02.025.

[59] R. Faria *et al.,* "Primary and secondary use of electric mobility batteries from a life cycle perspective," *Journal of Power Sources,* vol. 262, pp. 169–177, 2014, doi: 10.1016/j.jpowsour.2014.03.092.

[60] X. Han, M. Ouyang, L. Lu, and J. Li, "A comparative study of commercial lithium ion battery cycle life in electric vehicle: Capacity loss estimation," *Journal of Power Sources*, vol. 268, pp. 658–669, 2014, doi: 10.1016/j.jpowsour.2014.06.111.

[61] W. Waag, S. Käbitz, and D. U. Sauer, "Experimental investigation of the lithium-ion battery impedance characteristic at various conditions and aging states and its influence on the application," *Applied Energy*, vol. 102, pp. 885–897, 2013, doi: 10.1016/j.apenergy.2012.09.030.

[62] *Dual and joint EKF for simultaneous SOC and SOH estimation*, 2005. [Online]. Available: http://mocha-java.uccs.edu/dossier/research/2005evs21b-.pdf

[63] M. Wohlfahrt-Mehrens, C. Vogler, and J. Garche, "Aging mechanisms of lithium cathode materials," *Journal of Power Sources*, vol. 127, 1-2, pp. 58–64, 2004, doi: 10.1016/j.jpowsour.2003.09.034.

[64] R. Fu, S.-Y. Choe, V. Agubra, and J. Fergus, "Modeling of degradation effects considering side reactions for a pouch type Li-ion polymer battery with carbon anode," *Journal of Power Sources*, vol. 261, pp. 120–135, 2014, doi: 10.1016/j.jpowsour.2014.03.045.

[65] Y. Zhang and C.-Y. Wang, "Cycle-Life Characterization of Automotive Lithium-Ion Batteries with LiNiO[sub 2] Cathode," *J. Electrochem. Soc.*, vol. 156, no. 7, A527, 2009, doi: 10.1149/1.3126385.

[66] T. Q. Duong, "USABC and PNGV test procedures," *Journal of Power Sources*, vol. 89, no. 2, pp. 244–248, 2000, doi: 10.1016/S0378-7753(00)00439-0.

[67] J. Li, J. Zhang, X. Zhang, C. Yang, N. Xu, and B. Xia, "Study of the storage performance of a Li-ion cell at elevated temperature," *Electrochimica Acta*, vol. 55, no. 3, pp. 927–934, 2010, doi: 10.1016/j.electacta.2009.09.077.

[68] L. HARDWICK, H. BUQA, and P. NOVAK, "Graphite surface disorder detection using in situ Raman microscopy," *Solid State Ionics*, vol. 177, 26-32, pp. 2801–2806, 2006, doi: 10.1016/j.ssi.2006.03.032.

[69] K. Maher and R. Yazami, "A study of lithium ion batteries cycle aging by thermodynamics techniques," *Journal of Power Sources*, vol. 247, pp. 527–533, 2014, doi: 10.1016/j.jpowsour.2013.08.053.

[70] M. Ouyang *et al.,* "Low temperature aging mechanism identification and lithium deposition in a large format lithium iron phosphate battery for different charge profiles," *Journal of Power Sources*, vol. 286, pp. 309–320, 2015, doi: 10.1016/j.jpowsour.2015.03.178.

[71] B. Sood, M. Osterman, and M. Pecht, "Health monitoring of lithium-ion batteries," in 2013 IEEE Symposium on Product Compliance Engineering (ISPCE), Austin, TX, USA, 2013, pp. 1–6.

[72] F. Di Lanza Scalea *et al.,* "Non-contact ultrasonic inspection of rails and signal processing for automatic defect detection and classification," *Insight - Non-Destructive Testing and Condition Monitoring*, vol. 47, no. 6, pp. 346–353, 2005, doi: 10.1784/insi.47.6.346.66449.

[73] T. D'Orazio, M. Leo, A. Distante, C. Guaragnella, V. Pianese, and G. Cavaccini, "Automatic ultrasonic inspection for internal defect detection in composite materials," *NDT & E International*, vol. 41, no. 2, pp. 145–154, 2008, doi: 10.1016/j.ndteint.2007.08.001.

[74] E. R. Wognsen, B. R. Haverkort, M. Jongerden, R. R. Hansen, and K. G. Larsen, "A Score Function for Optimizing the Cycle-Life of Battery-Powered Embedded Systems," in *Lecture Notes in Computer Science, Formal Modeling and Analysis of Timed Systems*, S. Sankaranarayanan and E. Vicario, Eds., Cham: Springer International Publishing, 2015, pp. 305–320.

[75] K. S. Ng, C.-S. Moo, Y.-P. Chen, and Y.-C. Hsieh, "Enhanced coulomb counting method for estimating state-of-charge and state-of-health of lithium-ion batteries," *Applied Energy*, vol. 86, no. 9, pp. 1506–1511, 2009, doi: 10.1016/j.apenergy.2008.11.021.

[76] M. Berecibar, I. Gandiaga, I. Villarreal, N. Omar, J. van Mierlo, and P. van den Bossche, "Critical review of state of health estimation methods of Li-ion batteries for real applications," *Renewable and Sustainable Energy Reviews*, vol. 56, pp. 572–587, 2016, doi: 10.1016/j.rser.2015.11.042.

[77] A. Eddahech, O. Briat, and J.-M. Vinassa, "Determination of lithium-ion battery stateof-health based on constant-voltage charge phase," *Journal of Power Sources*, vol. 258, pp. 218– 227, 2014, doi: 10.1016/j.jpowsour.2014.02.020.

[78] M. Dubarry and B. Y. Liaw, "Identify capacity fading mechanism in a commercial LiFePO4 cell," *Journal of Power Sources*, vol. 194, no. 1, pp. 541–549, 2009, doi: 10.1016/j.jpowsour.2009.05.036.

[79] M. Dubarry *et al.,* "Identifying battery aging mechanisms in large format Li ion cells," *Journal of Power Sources*, vol. 196, no. 7, pp. 3420–3425, 2011, doi: 10.1016/j.jpowsour.2010.07.029.

[80] C. Weng, Y. Cui, J. Sun, and H. Peng, "On-board state of health monitoring of lithiumion batteries using incremental capacity analysis with support vector regression," *Journal of Power Sources*, vol. 235, pp. 36–44, 2013, doi: 10.1016/j.jpowsour.2013.02.012.

[81] X. Han, M. Ouyang, L. Lu, J. Li, Y. Zheng, and Z. Li, "A comparative study of commercial lithium ion battery cycle life in electrical vehicle: Aging mechanism identification," *Journal of Power Sources*, vol. 251, pp. 38–54, 2014, doi: 10.1016/j.jpowsour.2013.11.029.

[82] C. Weng, J. Sun, and H. Peng, "A unified open-circuit-voltage model of lithium-ion batteries for state-of-charge estimation and state-of-health monitoring," *Journal of Power Sources*, vol. 258, pp. 228–237, 2014, doi: 10.1016/j.jpowsour.2014.02.026.

[83] Y. Li *et al.,* "A quick on-line state of health estimation method for Li-ion battery with incremental capacity curves processed by Gaussian filter," *Journal of Power Sources*, vol. 373, pp. 40–53, 2018, doi: 10.1016/j.jpowsour.2017.10.092.

[84] L. Wang, C. Pan, L. Liu, Y. Cheng, and X. Zhao, "On-board state of health estimation of LiFePO4 battery pack through differential voltage analysis," *Applied Energy*, vol. 168, pp. 465–472, 2016, doi: 10.1016/j.apenergy.2016.01.125.

[85] C.P. Zhang, J.Z. Liu, and S.M. Sharkh, "Identification of dynamic model parameters for lithium-ion batteries used in hybrid electric vehicles," in *International Symposium on Electric Vehicles (ISEV) (31/08/09 - 31/08/09)*, 1970. [Online]. Available: https://eprints.soton.ac.uk/73265/

[86] X. Hu, S. Li, and H. Peng, "A comparative study of equivalent circuit models for Li-ion batteries," *Journal of Power Sources*, vol. 198, pp. 359–367, 2012, doi: 10.1016/j.jpowsour.2011.10.013.

[87] M.-H. Hung, C.-H. Lin, L.-C. Lee, and C.-M. Wang, "State-of-charge and state-of-health estimation for lithium-ion batteries based on dynamic impedance technique," *Journal of Power Sources*, vol. 268, pp. 861–873, 2014, doi: 10.1016/j.jpowsour.2014.06.083.

[88] D. Andre, M. Meiler, K. Steiner, C. Wimmer, T. Soczka-Guth, and D. U. Sauer, "Characterization of high-power lithium-ion batteries by electrochemical impedance spectroscopy. I. Experimental investigation," *Journal of Power Sources*, vol. 196, no. 12, pp. 5334–5341, 2011, doi: 10.1016/j.jpowsour.2010.12.102.

[89] M. Galeotti, L. Cinà, C. Giammanco, S. Cordiner, and A. Di Carlo, "Performance analysis and SOH (state of health) evaluation of lithium polymer batteries through electrochemical impedance spectroscopy," *Energy*, vol. 89, pp. 678–686, 2015, doi: 10.1016/j.energy.2015.05.148.

[90] T. Momma, M. Matsunaga, D. Mukoyama, and T. Osaka, "Ac impedance analysis of lithium ion battery under temperature control," *Journal of Power Sources*, vol. 216, pp. 304–307, 2012, doi: 10.1016/j.jpowsour.2012.05.095.

[91] U. Tröltzsch, O. Kanoun, and H.-R. Tränkler, "Characterizing aging effects of lithium ion batteries by impedance spectroscopy," *Electrochimica Acta*, vol. 51, 8-9, pp. 1664–1672, 2006, doi: 10.1016/j.electacta.2005.02.148.

[92] S. Buller, M. Thele, E. Karden, and R. W. de Doncker, "Impedance-based non-linear dynamic battery modeling for automotive applications," *Journal of Power Sources*, vol. 113, no. 2, pp. 422–430, 2003, doi: 10.1016/S0378-7753(02)00558-X.

[93] T. Osaka, D. Mukoyama, and H. Nara, "Review—Development of Diagnostic Process for Commercially Available Batteries, Especially Lithium Ion Battery, by Electrochemical Impedance Spectroscopy," *J. Electrochem. Soc.*, vol. 162, no. 14, A2529-A2537, 2015, doi: 10.1149/2.0141514jes.

[94] J. Kowal, *Spatially-resolved impedance on nonlinear inhomogenerous devices: Using the example of lead-acid batteries*. Zugl.: Aachen, Techn. Hochsch., Diss., 2010. Aachen: Shaker, 2010.

[95] E. Barsoukov and J. R. Macdonald, *Impedance Spectroscopy*: Wiley, 2005.

[96] M. E. Orazem and B. Tribollet, *Electrochemical Impedance Spectroscopy*. Hoboken, NJ, USA: John Wiley & Sons, Inc, 2008.

[97] P. Gao, C. Zhang, and G. Wen, "Equivalent circuit model analysis on electrochemical impedance spectroscopy of lithium metal batteries," *Journal of Power Sources*, vol. 294, pp. 67–74, 2015, doi: 10.1016/j.jpowsour.2015.06.032.

[98] T. N. Gucin and L. Ovacik, "Online Impedance Measurement of Batteries Using the Cross-Correlation Technique," *IEEE Trans. Power Electron.*, vol. 35, no. 4, pp. 4365–4375, 2020, doi: 10.1109/TPEL.2019.2939269.

[99] J. P. Schmidt, T. Chrobak, M. Ender, J. Illig, D. Klotz, and E. Ivers-Tiffée, "Studies on LiFePO4 as cathode material using impedance spectroscopy," *Journal of Power Sources*, vol. 196, no. 12, pp. 5342–5348, 2011, doi: 10.1016/j.jpowsour.2010.09.121.

[100] J. Illig, J. P. Schmidt, M. Weiss, A. Weber, and E. Ivers-Tiffée, "Understanding the impedance spectrum of 18650 LiFePO4-cells," *Journal of Power Sources*, vol. 239, pp. 670–679, 2013, doi: 10.1016/j.jpowsour.2012.12.020.

[101] J. R. Macdonald, "Impedance spectroscopy," *Annals of biomedical engineering*, vol. 20, no. 3, pp. 289–305, 1992, doi: 10.1007/BF02368532.

[102] N. Munichandraiah, L. Scanlon, and R. Marsh, "Surface films of lithium: an overview of electrochemical studies," *Journal of Power Sources*, vol. 72, no. 2, pp. 203–210, 1998, doi: 10.1016/S0378-7753(97)02771-7.

[103] A. Jossen, "Fundamentals of battery dynamics," *Journal of Power Sources*, vol. 154, no. 2, pp. 530–538, 2006, doi: 10.1016/j.jpowsour.2005.10.041.

[104] L. O. Valoén and J. N. Reimers, "Transport Properties of LiPF[sub 6]-Based Li-Ion Battery Electrolytes," *J. Electrochem. Soc.*, vol. 152, no. 5, A882, 2005, doi: 10.1149/1.1872737.

[105] M. S. Ding, K. Xu, S. S. Zhang, K. Amine, G. L. Henriksen, and T. R. Jow, "Change of Conductivity with Salt Content, Solvent Composition, and Temperature for Electrolytes of LiPF[sub 6] in Ethylene Carbonate-Ethyl Methyl Carbonate," *J. Electrochem. Soc.*, vol. 148, no. 10, A1196, 2001, doi: 10.1149/1.1403730. [106] L. Wang, D. Lu, M. Song, X. Zhao, and G. Li, "Instantaneous estimation of internal temperature in lithium-ion battery by impedance measurement," *Int J Energy Res*, vol. 44, no. 4, pp. 3082–3097, 2020, doi: 10.1002/er.5144.

[107] P. J. Osswald *et al.,* "Current density distribution in cylindrical Li-Ion cells during impedance measurements," *Journal of Power Sources*, vol. 314, pp. 93–101, 2016, doi: 10.1016/j.jpowsour.2016.02.070.

[108] R. Xiong, J. Tian, H. Mu, and C. Wang, "A systematic model-based degradation behavior recognition and health monitoring method for lithium-ion batteries," *Applied Energy*, vol. 207, pp. 372–383, 2017, doi: 10.1016/j.apenergy.2017.05.124.

[109] Q. Yuan, F. Zhao, W. Wang, Y. Zhao, Z. Liang, and D. Yan, "Overcharge failure investigation of lithium-ion batteries," *Electrochimica Acta*, vol. 178, pp. 682–688, 2015, doi: 10.1016/j.electacta.2015.07.147.

[110] R. A. Leising, M. J. Palazzo, E. S. Takeuchi, and K. J. Takeuchi, "Abuse Testing of Lithium-Ion Batteries: Characterization of the Overcharge Reaction of LiCoO[sub 2]/Graphite Cells," *J. Electrochem. Soc.*, vol. 148, no. 8, A838, 2001, doi: 10.1149/1.1379740.

[111] D. P. Finegan *et al.,* "Investigating lithium-ion battery materials during overchargeinduced thermal runaway: an operando and multi-scale X-ray CT study," *Physical chemistry chemical physics : PCCP*, vol. 18, no. 45, pp. 30912–30919, 2016, doi: 10.1039/C6CP04251A.

[112] F. Larsson and B.-E. Mellander, "Abuse by External Heating, Overcharge and Short Circuiting of Commercial Lithium-Ion Battery Cells," *J. Electrochem. Soc.*, vol. 161, no. 10, A1611-A1617, 2014, doi: 10.1149/2.0311410jes.

[113] Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun, and C. Chen, "Thermal runaway caused fire and explosion of lithium ion battery," *Journal of Power Sources*, vol. 208, pp. 210–224, 2012, doi: 10.1016/j.jpowsour.2012.02.038.

[114] J. Sun *et al.,* "Toxicity, a serious concern of thermal runaway from commercial Li-ion battery," *Nano Energy*, vol. 27, pp. 313–319, 2016, doi: 10.1016/j.nanoen.2016.06.031.

[115] Y. Zheng *et al.,* "Influence of over-discharge on the lifetime and performance of LiFePO 4 /graphite batteries," *RSC Adv.*, vol. 6, no. 36, pp. 30474–30483, 2016, doi: 10.1039/C6RA01677D.

[116] L. Zhang *et al.,* "Capacity fading mechanism during long-term cycling of overdischarged LiCoO2/mesocarbon microbeads battery," *Journal of Power Sources*, vol. 293, pp. 1006–1015, 2015, doi: 10.1016/j.jpowsour.2015.06.040.

[117] H. Maleki and J. N. Howard, "Effects of overdischarge on performance and thermal stability of a Li-ion cell," *Journal of Power Sources*, vol. 160, no. 2, pp. 1395–1402, 2006, doi: 10.1016/j.jpowsour.2006.03.043.

[118] H.-F. LI, J.-K. GAO, and S.-L. ZHANG, "Effect of Overdischarge on Swelling and Recharge Performance of Lithium Ion Cells," *Chin. J. Chem.*, vol. 26, no. 9, pp. 1585–1588, 2008, doi: 10.1002/cjoc.200890286.

[119] L. Zheng, L. Zhang, J. Zhu, G. Wang, and J. Jiang, "Co-estimation of state-of-charge, capacity and resistance for lithium-ion batteries based on a high-fidelity electrochemical model," *Applied Energy*, vol. 180, pp. 424–434, 2016, doi: 10.1016/j.apenergy.2016.08.016.

[120] X. Tang, Y. Wang, and Z. Chen, "A method for state-of-charge estimation of LiFePO4 batteries based on a dual-circuit state observer," *Journal of Power Sources*, vol. 296, pp. 23–29, 2015, doi: 10.1016/j.jpowsour.2015.07.028.

[121] F. Leng, C. M. Tan, R. Yazami, and M. D. Le, "A practical framework of electrical based online state-of-charge estimation of lithium ion batteries," *Journal of Power Sources*, vol. 255, pp. 423–430, 2014, doi: 10.1016/j.jpowsour.2014.01.020.

[122] A. J. Salkind, C. Fennie, P. Singh, T. Atwater, and D. E. Reisner, "Determination of state-of-charge and state-of-health of batteries by fuzzy logic methodology," *Journal of Power Sources*, vol. 80, 1-2, pp. 293–300, 1999, doi: 10.1016/S0378-7753(99)00079-8.

[123] P. Singh, R. Vinjamuri, X. Wang, and D. Reisner, "Design and implementation of a fuzzy logic-based state-of-charge meter for Li-ion batteries used in portable defibrillators," *Journal of Power Sources*, vol. 162, no. 2, pp. 829–836, 2006, doi:

10.1016/j.jpowsour.2005.04.039.

[124] S. Malkhandi, "Fuzzy logic-based learning system and estimation of state-of-charge of lead-acid battery," *Engineering Applications of Artificial Intelligence*, vol. 19, no. 5, pp. 479–485, 2006, doi: 10.1016/j.engappai.2005.12.005.

[125] M. A. Awadallah and B. Venkatesh, "Accuracy improvement of SOC estimation in lithium-ion batteries," *Journal of Energy Storage*, vol. 6, pp. 95–104, 2016, doi: 10.1016/j.est.2016.03.003.

[126] K. T. Chau, K. C. Wu, and C. C. Chan, "A new battery capacity indicator for lithium-ion battery powered electric vehicles using adaptive neuro-fuzzy inference system," *Energy Conversion and Management*, vol. 45, 11-12, pp. 1681–1692, 2004, doi: 10.1016/j.enconman.2003.09.031.

[127] C. H. Cai, D. Du, and Z. Y. Liu, "Battery state-of-charge (SOC) estimation using adaptive neuro-fuzzy inference system (ANFIS)," in *The 12th IEEE International Conference on Fuzzy Systems, 2003. FUZZ '03*, St Louis, MO, USA, May. 2003, pp. 1068–1073.

[128] Z. Chen, S. Qiu, M. Masrur, and Y. L. Murphey, "Battery state of charge estimation based on a combined model of Extended Kalman Filter and neural networks," in *The 2011 International Joint Conference on Neural Networks*, San Jose, CA, USA, Jul. 2011 - Aug. 2011, pp. 2156–2163.

[129] L. Rui-hao, S. Yu-kun, and J. Xiao-fu, "Battery state of charge estimation for electric vehicle based on neural network," in *2011 IEEE 3rd International Conference on Communication Software and Networks*, Xi'an, China, May. 2011 - May. 2011, pp. 493–496.

[130] X. Wu, L. Mi, W. Tan, J. L. Qin, and M. N. Zhao, "State of Charge (SOC) Estimation of Ni-MH Battery Based on Least Square Support Vector Machines," *AMR*, 211-212, pp. 1204–1209, 2011, doi: 10.4028/www.scientific.net/AMR.211-212.1204.

[131] J. C. Álvarez Antón, P. J. García Nieto, F. J. de Cos Juez, F. Sánchez Lasheras, M. González Vega, and M. N. Roqueñí Gutiérrez, "Battery state-of-charge estimator using the SVM technique," *Applied Mathematical Modelling*, vol. 37, no. 9, pp. 6244–6253, 2013, doi: 10.1016/j.apm.2013.01.024.

[132] Y. Chen, B. Long, and X. Lei, "The Battery State of Charge Estimation Based Weighted Least Squares Support Vector Machine," in *2011 Asia-Pacific Power and Energy Engineering Conference*, Wuhan, China, Mar. 2011 - Mar. 2011, pp. 1–4.

[133] Y. Zheng, L. Lu, X. Han, J. Li, and M. Ouyang, "LiFePO4 battery pack capacity estimation for electric vehicles based on charging cell voltage curve transformation," *Journal of Power Sources*, vol. 226, pp. 33–41, 2013, doi: 10.1016/j.jpowsour.2012.10.057.

[134] J. Xu, B. Cao, Z. Chen, and Z. Zou, "An online state of charge estimation method with reduced prior battery testing information," *International Journal of Electrical Power & Energy Systems*, vol. 63, pp. 178–184, 2014, doi: 10.1016/j.ijepes.2014.06.017.

[135] T. O. Ting, K. L. Man, E. G. Lim, and M. Leach, "Tuning of Kalman filter parameters via genetic algorithm for state-of-charge estimation in battery management system," *TheScientificWorldJournal*, vol. 2014, p. 176052, 2014, doi: 10.1155/2014/176052.

[136] M. W. Yatsui and H. Bai, "Kalman filter based state-of-charge estimation for lithiumion batteries in hybrid electric vehicles using pulse charging," in *2011 IEEE Vehicle Power and Propulsion Conference*, Chicago, IL, USA, Sep. 2011 - Sep. 2011, pp. 1–5.

[137] Z. Chen, Y. Fu, and C. C. Mi, "State of Charge Estimation of Lithium-Ion Batteries in Electric Drive Vehicles Using Extended Kalman Filtering," *IEEE Trans. Veh. Technol.*, vol. 62, no. 3, pp. 1020–1030, 2013, doi: 10.1109/TVT.2012.2235474.

[138] M. Mastali, J. Vazquez-Arenas, R. Fraser, M. Fowler, S. Afshar, and M. Stevens,
"Battery state of the charge estimation using Kalman filtering," *Journal of Power Sources*, vol.
239, pp. 294–307, 2013, doi: 10.1016/j.jpowsour.2013.03.131.

[139] R. Xiong, H. He, F. Sun, and K. Zhao, "Evaluation on State of Charge Estimation of Batteries With Adaptive Extended Kalman Filter by Experiment Approach," *IEEE Trans. Veh. Technol.*, vol. 62, no. 1, pp. 108–117, 2013, doi: 10.1109/TVT.2012.2222684.

[140] X. Hu, F. Sun, and Y. Zou, "Comparison between two model-based algorithms for Liion battery SOC estimation in electric vehicles," *Simulation Modelling Practice and Theory*, vol. 34, pp. 1–11, 2013, doi: 10.1016/j.simpat.2013.01.001.

[141] W. He, N. Williard, C. Chen, and M. Pecht, "State of charge estimation for electric vehicle batteries using unscented kalman filtering," *Microelectronics Reliability*, vol. 53, no. 6, pp. 840–847, 2013, doi: 10.1016/j.microrel.2012.11.010.

[142] F. Sun, X. Hu, Y. Zou, and S. Li, "Adaptive unscented Kalman filtering for state of charge estimation of a lithium-ion battery for electric vehicles," *Energy*, vol. 36, no. 5, pp. 3531–3540, 2011, doi: 10.1016/j.energy.2011.03.059.

[143] J. Du, Z. Liu, and Y. Wang, "State of charge estimation for Li-ion battery based on model from extreme learning machine," *Control Engineering Practice*, vol. 26, pp. 11–19, 2014, doi: 10.1016/j.conengprac.2013.12.014.

[144] J. Li, J. Klee Barillas, C. Guenther, and M. A. Danzer, "A comparative study of state of charge estimation algorithms for LiFePO4 batteries used in electric vehicles," *Journal of Power Sources*, vol. 230, pp. 244–250, 2013, doi: 10.1016/j.jpowsour.2012.12.057.

[145] Z. He, Y. Liu, M. Gao, and C. Wang, "A joint model and SOC estimation method for lithium battery based on the sigma point KF," in *2012 IEEE Transportation Electrification Conference and Expo (ITEC)*, Dearborn, MI, USA, Jun. 2012 - Jun. 2012, pp. 1–5.

[146] Y. Zhang, C. Zhang, and X. Zhang, "State-of-charge estimation of the lithium-ion battery system with time-varying parameter for hybrid electric vehicles," *IET Control Theory & Applications*, vol. 8, no. 3, pp. 160–167, 2014, doi: 10.1049/iet-cta.2013.0082.

[147] M. Charkhgard and M. H. Zarif, "Design of adaptive  $H\infty$  filter for implementing on state-of-charge estimation based on battery state-of-charge-varying modelling," *IET Power Electronics*, vol. 8, no. 10, pp. 1825–1833, 2015, doi: 10.1049/iet-pel.2014.0523.

[148] S. Schwunk, N. Armbruster, S. Straub, J. Kehl, and M. Vetter, "Particle filter for state of charge and state of health estimation for lithium–iron phosphate batteries," *Journal of Power Sources*, vol. 239, pp. 705–710, 2013, doi: 10.1016/j.jpowsour.2012.10.058.

[149] Y. He, X. Liu, C. Zhang, and Z. Chen, "A new model for State-of-Charge (SOC) estimation for high-power Li-ion batteries," *Applied Energy*, vol. 101, pp. 808–814, 2013, doi: 10.1016/j.apenergy.2012.08.031.

[150] A. Eddahech, O. Briat, and J. M. Vinassa, "Adaptive voltage estimation for EV Li-ion cell based on artificial neural networks state-of-charge meter," in *2012 IEEE International Symposium on Industrial Electronics*, Hangzhou, China, May. 2012 - May. 2012, pp. 1318–1324.

[151] H. Xiaosong, S. Fengchun, Z. Yuan, and P. Huei, "Online estimation of an electric vehicle Lithium-Ion battery using recursive least squares with forgetting," in *Proceedings of the 2011 American Control Conference*, San Francisco, CA, Jun. 2011 - Jul. 2011, pp. 935–940.

[152] I.-S. Kim, "The novel state of charge estimation method for lithium battery using sliding mode observer," *Journal of Power Sources*, vol. 163, no. 1, pp. 584–590, 2006, doi: 10.1016/j.jpowsour.2006.09.006.

[153] B. Xia, C. Chen, Y. Tian, W. Sun, Z. Xu, and W. Zheng, "A novel method for state of charge estimation of lithium-ion batteries using a nonlinear observer," *Journal of Power Sources*, vol. 270, pp. 359–366, 2014, doi: 10.1016/j.jpowsour.2014.07.103.

[154] J. Xu, C. C. Mi, B. Cao, J. Deng, Z. Chen, and S. Li, "The State of Charge Estimation of Lithium-Ion Batteries Based on a Proportional-Integral Observer," *IEEE Trans. Veh. Technol.*, vol. 63, no. 4, pp. 1614–1621, 2014, doi: 10.1109/TVT.2013.2287375.

[155] X. Chen, W. Shen, Z. Cao, and A. Kapoor, "A novel approach for state of charge estimation based on adaptive switching gain sliding mode observer in electric vehicles," *Journal of Power Sources*, vol. 246, pp. 667–678, 2014, doi: 10.1016/j.jpowsour.2013.08.039.

[156] I.-S. Kim, "Nonlinear State of Charge Estimator for Hybrid Electric Vehicle Battery," *IEEE Trans. Power Electron.*, vol. 23, no. 4, pp. 2027–2034, 2008, doi: 10.1109/TPEL.2008.924629.

[157] L. Wang, L. Wang, and Y. Li, "A Novel State-of-Charge Estimation Algorithm of EV Battery Based on Bilinear Interpolation," in *2013 IEEE Vehicle Power and Propulsion Conference* (*VPPC*), Beijing, China, Oct. 2013 - Oct. 2013, pp. 1–4.

[158] X. Hu, F. Sun, and Y. Zou, "Estimation of State of Charge of a Lithium-Ion Battery Pack for Electric Vehicles Using an Adaptive Luenberger Observer," *Energies*, vol. 3, no. 9, pp. 1586– 1603, 2010, doi: 10.3390/en3091586.

[159] T. Bruen and J. Marco, "Modelling and experimental evaluation of parallel connected lithium ion cells for an electric vehicle battery system," *Journal of Power Sources*, vol. 310, pp. 91–101, 2016, doi: 10.1016/j.jpowsour.2016.01.001.

[160] J. A. Abu Qahouq, "Online battery impedance spectrum measurement method," in 2016 IEEE Applied Power Electronics Conference and Exposition (APEC), Long Beach, CA, 2016, pp. 3611–3615.

[161] W. Waag, C. Fleischer, and D. U. Sauer, "On-line estimation of lithium-ion battery impedance parameters using a novel varied-parameters approach," *Journal of Power Sources*, vol. 237, pp. 260–269, 2013, doi: 10.1016/j.jpowsour.2013.03.034.

[162] C. Fleischer, W. Waag, H.-M. Heyn, and D. U. Sauer, "On-line adaptive battery impedance parameter and state estimation considering physical principles in reduced order equivalent circuit battery models part 2. Parameter and state estimation," *Journal of Power Sources*, vol. 262, pp. 457–482, 2014, doi: 10.1016/j.jpowsour.2014.03.046.

[163] D. A. Howey, P. D. Mitcheson, V. Yufit, G. J. Offer, and N. P. Brandon, "Online Measurement of Battery Impedance Using Motor Controller Excitation," *IEEE Trans. Veh. Technol.*, vol. 63, no. 6, pp. 2557–2566, 2014, doi: 10.1109/TVT.2013.2293597.

[164] Y.-P. Yang, J.-J. Liu, and C.-H. Tsai, "Improved estimation of residual capacity of batteries for electric vehicles," *Journal of the Chinese Institute of Engineers*, vol. 31, no. 2, pp. 313–322, 2008, doi: 10.1080/02533839.2008.9671384.

[165] W. Waag and D. U. Sauer, "Adaptive estimation of the electromotive force of the lithium-ion battery after current interruption for an accurate state-of-charge and capacity determination," *Applied Energy*, vol. 111, pp. 416–427, 2013, doi: 10.1016/j.apenergy.2013.05.001.

[166] J. C. Álvarez Antón, P. J. García Nieto, F. J. de Cos Juez, F. Sánchez Lasheras, C. Blanco Viejo, and N. Roqueñí Gutiérrez, "Battery State-of-Charge Estimator Using the MARS Technique," *IEEE Trans. Power Electron.*, vol. 28, no. 8, pp. 3798–3805, 2013, doi: 10.1109/TPEL.2012.2230026.

[167] J. A. A. Qahouq and Z. Xia, "Single-Perturbation-Cycle Online Battery Impedance Spectrum Measurement Method With Closed-Loop Control of Power Converter," *IEEE Trans. Ind. Electron.*, vol. 64, no. 9, pp. 7019–7029, 2017, doi: 10.1109/tie.2017.2686324.

[168] R. Koch, R. Kuhn, I. Zilberman, and A. Jossen, "Electrochemical impedance spectroscopy for online battery monitoring - power electronics control," in *2014 16th European Conference on Power Electronics and Applications*, Lappeenranta, Finland, 2014, pp. 1–10.

[169] S. K. Dam and V. John, "High-Resolution Converter for Battery Impedance Spectroscopy," *IEEE Trans. on Ind. Applicat.*, vol. 54, no. 2, pp. 1502–1512, 2018, doi: 10.1109/TIA.2017.2771498.

[170] T.-T. Nguyen, V.-L. Tran, and W. Choi, "Development of the intelligent charger with battery State-Of-Health estimation using online impedance spectroscopy," in *2014 IEEE 23rd International Symposium on Industrial Electronics (ISIE)*, Istanbul, Turkey, 2014, pp. 454–458.

[171] Y.-D. Lee, S.-Y. Park, and S.-B. Han, "Online Embedded Impedance Measurement Using High-Power Battery Charger," *IEEE Trans. on Ind. Applicat.*, vol. 51, no. 1, pp. 498–508, 2015, doi: 10.1109/TIA.2014.2336979.

[172] X. Wei, X. Wang, and H. Dai, "Practical On-Board Measurement of Lithium Ion Battery Impedance Based on Distributed Voltage and Current Sampling," *Energies*, vol. 11, no. 1, p. 64, 2018, doi: 10.3390/en11010064.

[173] A. Waligo and P. Barendse, "A comparison of the different broadband impedance measurement techniques for lithium-ion batteries," in *2016 IEEE Energy Conversion Congress and Exposition (ECCE)*, Milwaukee, WI, USA, 2016, pp. 1–7.

[174] J. P. Christophersen, J. Morrison, W. Morrison, and C. Motloch, "Rapid Impedance Spectrum Measurements for State-of-Health Assessment of Energy Storage Devices," *SAE Int. J. Passeng. Cars - Electron. Electr. Syst.*, vol. 5, no. 1, pp. 246–256, 2012, doi: 10.4271/2012-01-0657.

[175] H. Piret, P. Granjon, N. Guillet, and V. Cattin, "Tracking of electrochemical impedance of batteries," *Journal of Power Sources*, vol. 312, pp. 60–69, 2016, doi: 10.1016/j.jpowsour.2016.02.006.

[176] R. Al Nazer, V. Cattin, P. Granjon, M. Montaru, and M. Ranieri, "Broadband Identification of Battery Electrical Impedance for HEVs," *IEEE Trans. Veh. Technol.*, vol. 62, no. 7, pp. 2896–2905, 2013, doi: 10.1109/TVT.2013.2254140.

[177] Z. Geng, T. Thiringer, Y. Olofsson, J. Groot, and M. West, "On-board Impedance Diagnostics Method of Li-ion Traction Batteries Using Pseudo-Random Binary Sequences," in 2018 20th European Conference on Power Electronics and Applications (EPE'18 ECCE Europe), 2018, pp. 1–9. [178] J. Sihvo, D.-I. Stroe, T. Messo, and T. Roinila, "Fast Approach for Battery Impedance Identification Using Pseudo-Random Sequence Signals," *IEEE Trans. Power Electron.*, vol. 35, no. 3, pp. 2548–2557, 2020, doi: 10.1109/TPEL.2019.2924286.

[179] E. Locorotondo *et al.,* "Electrochemical Impedance Spectroscopy of Li-Ion battery onboard the Electric Vehicles based on Fast nonparametric identification method," in *2019 IEEE International Conference on Environment and Electrical Engineering and 2019 IEEE Industrial and Commercial Power Systems Europe (EEEIC / I&CPS Europe)*, Genova, Italy, 2019, pp. 1–6.

[180] X. Wang, X. Wei, Q. Chen, J. Zhu, and H. Dai, "Lithium-ion battery temperature online estimation based on fast impedance calculation," *Journal of Energy Storage*, vol. 26, p. 100952, 2019, doi: 10.1016/j.est.2019.100952.

[181] M. Nakayama, K. Fukuda, Y. Ohmori, K. Wakahara, T. Araki, and K. Onda, "Battery Impedance Measurement by Laplace Transformation of Charge or Discharge Current/Voltage," *IEEJ Trans. PE*, vol. 125, no. 12, pp. 1279–1286, 2005, doi: 10.1541/ieejpes.125.1279.

[182] A. Rahmoun, M. Loske, and A. Rosin, "Determination of the Impedance of Lithium-ion Batteries Using Methods of Digital Signal Processing," *Energy Procedia*, vol. 46, pp. 204–213, 2014, doi: 10.1016/j.egypro.2014.01.174.

[183] D. Klotz, M. Schönleber, J. P. Schmidt, and E. Ivers-Tiffée, "New approach for the calculation of impedance spectra out of time domain data," *Electrochimica Acta*, vol. 56, no. 24, pp. 8763–8769, 2011, doi: 10.1016/j.electacta.2011.07.096.

[184] Y. Hoshi, N. Yakabe, K. Isobe, T. Saito, I. Shitanda, and M. Itagaki, "Wavelet transformation to determine impedance spectra of lithium-ion rechargeable battery," *Journal of Power Sources*, vol. 315, pp. 351–358, 2016, doi: 10.1016/j.jpowsour.2016.03.048.

[185] M. Itagaki, M. Ueno, Y. Hoshi, and I. Shitanda, "Simultaneous Determination of Electrochemical Impedance of Lithium-ion Rechargeable Batteries with Measurement of Charge-discharge Curves by Wavelet Transformation," *Electrochimica Acta*, vol. 235, pp. 384–389, 2017, doi: 10.1016/j.electacta.2017.03.077.

[186] B. Bullecks, R. Suresh, and R. Rengaswamy, "Rapid impedance measurement using chirp signals for electrochemical system analysis," *Computers & Chemical Engineering*, vol. 106, pp. 421–436, 2017, doi: 10.1016/j.compchemeng.2017.05.018.

[187] C. Gabrielli, F. Huet, M. Keddam, and J. F. Lizee, "Measurement time versus accuracy trade-off analyzed for electrochemical impedance measurements by means of sine, white noise and step signals," *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, vol. 138, no. 1, pp. 201–208, 1982, doi: 10.1016/0022-0728(82)87141-6.

[188] B. Liebhart, L. Komsiyska, and C. Endisch, "Passive impedance spectroscopy for monitoring lithium-ion battery cells during vehicle operation," *Journal of Power Sources*, vol. 449, p. 227297, 2020, doi: 10.1016/j.jpowsour.2019.227297.

[189] B. A. Boukamp, "A Linear Kronig-Kramers Transform Test for Immittance Data Validation," *J. Electrochem. Soc.*, vol. 142, no. 6, pp. 1885–1894, 1995, doi: 10.1149/1.2044210.

[190] E. Karden, S. Buller, and R. W. de Doncker, "A method for measurement and interpretation of impedance spectra for industrial batteries," *Journal of Power Sources*, vol. 85, no. 1, pp. 72–78, 2000, doi: 10.1016/S0378-7753(99)00385-7.

[191] W. Huang and J. A. Qahouq, "An Online Battery Impedance Measurement Method Using DC–DC Power Converter Control," *IEEE Trans. Ind. Electron.*, vol. 61, no. 11, pp. 5987–5995, 2014, doi: 10.1109/TIE.2014.2311389.

[192] X. Wang, X. Wei, Q. Chen, and H. Dai, "A Novel System for Measuring Alternating Current Impedance Spectra of Series-Connected Lithium-Ion Batteries With a High-Power Dual Active Bridge Converter and Distributed Sampling Units," *IEEE Trans. Ind. Electron.*, vol. 68, no. 8, pp. 7380–7390, 2021, doi: 10.1109/TIE.2020.3001841.

[193] E. Din, C. Schaef, K. Moffat, and J. T. Stauth, "A Scalable Active Battery Management System With Embedded Real-Time Electrochemical Impedance Spectroscopy," *IEEE Trans. Power Electron.*, vol. 32, no. 7, pp. 5688–5698, 2017, doi: 10.1109/TPEL.2016.2607519.

[194] M. A. Varnosfaderani and D. Strickland, "Online impedance spectroscopy estimation of a dc–dc converter connected battery using a switched capacitor-based balancing circuit," *J. eng.*, vol. 2019, no. 7, pp. 4681–4685, 2019, doi: 10.1049/joe.2018.8069.

[195] L. Raijmakers, K. M. Shivakumar, M. Donkers, M. Lammers, and H. J. Bergveld, "Crosstalk Interferences on Impedance Measurements in Battery Packs \* \*This work has received financial support from the Dutch Ministry of Economic Affairs under the grant A green Deal in Energy Materials (ADEM) and from the Horizon 2020 programme of the European Union under the grant Integrated Components for Complexity Control in affordable electrified cars (3Ccar-662192)," *IFAC-PapersOnLine*, vol. 49, no. 11, pp. 42–47, 2016, doi: 10.1016/j.ifacol.2016.08.007.

[196] Y. Nishimura *et al.,* "A development and evaluation of high accurate AC impedance measurement system by an application specific LSI," 60th, ROMBUNNO.2A13, 2019. [Online]. Available: https://jglobal.jst.go.jp/en/detail?JGLOBAL ID=202002288617703590

[197] K. Jiang, X. Liu, G. Lou, Z. Wen, and L. Liu, "Parameter sensitivity analysis and cathode structure optimization of a non-aqueous Li–O2 battery model," *Journal of Power Sources*, vol. 451, p. 227821, 2020, doi: 10.1016/j.jpowsour.2020.227821.

[198] L. Liu and P. Guan, "Phase-Field Modeling of Solid Electrolyte Interphase (SEI) Evolution: Considering Cracking and Dissolution during Battery Cycling," *ECS Trans.*, vol. 89, no. 1, pp. 101–111, 2019, doi: 10.1149/08901.0101ecst.

[199] V. S. Bagotsky, *Fundamentals of Electrochemistry*. Hoboken, NJ, USA: John Wiley & Sons, Inc, 2005.

[200] Z. B. Stoynov and D. E. Vladikova, "MEASUREMENT METHODS | Electrochemical: Impedance Spectroscopy," in *Encyclopedia of Electrochemical Power Sources*: Elsevier, 2009, pp. 632–642.

[201] J. Ojarand, M. Min, and P. Annus, "Crest factor optimization of the multisine waveform for bioimpedance spectroscopy," *Physiological measurement*, vol. 35, no. 6, pp. 1019–1033, 2014, doi: 10.1088/0967-3334/35/6/1019.

[202] B. Sanchez, G. Vandersteen, R. Bragos, and J. Schoukens, "Optimal multisine excitation design for broadband electrical impedance spectroscopy," *Meas. Sci. Technol.*, vol. 22, no. 11, p. 115601, 2011, doi: 10.1088/0957-0233/22/11/115601.

[203] T. Breugelmans *et al.,* "Odd random phase multisine EIS as a detection method for the onset of corrosion of coated steel," *Electrochemistry Communications*, vol. 12, no. 1, pp. 2–5, 2010, doi: 10.1016/j.elecom.2009.10.008.

[204] S. J. Kwon, E. Park, J. Lim, J. Choi, and J. Kim, Eds., *Performance Analysis and Degradation Characteristics of NCM LIB for ESS*, 2018.

[205] S. Liu, X. Liu, R. Dou, W. Zhou, Z. Wen, and L. Liu, "Experimental and simulation study on thermal characteristics of 18,650 lithium–iron–phosphate battery with and without spot–

welding tabs," *Applied Thermal Engineering*, vol. 166, p. 114648, 2020, doi: 10.1016/j.applthermaleng.2019.114648.

[206] Q. Zhang, D. Wang, B. Yang, X. Cui, and X. Li, "Electrochemical model of lithium-ion battery for wide frequency range applications," *Electrochimica Acta*, vol. 343, p. 136094, 2020, doi: 10.1016/j.electacta.2020.136094.

[207] M. A. Rahman, S. Anwar, and A. Izadian, "Electrochemical model parameter identification of a lithium-ion battery using particle swarm optimization method," *Journal of Power Sources*, vol. 307, pp. 86–97, 2016, doi: 10.1016/j.jpowsour.2015.12.083.

[208] W. Sung and C. B. Shin, "Electrochemical model of a lithium-ion battery implemented into an automotive battery management system," *Computers & Chemical Engineering*, vol. 76, pp. 87–97, 2015, doi: 10.1016/j.compchemeng.2015.02.007.

[209] A. P. Schmidt, M. Bitzer, Á. W. Imre, and L. Guzzella, "Experiment-driven electrochemical modeling and systematic parameterization for a lithium-ion battery cell," *Journal of Power Sources*, vol. 195, no. 15, pp. 5071–5080, 2010, doi: 10.1016/j.jpowsour.2010.02.029.

[210] S. K. Rahimian, S. Rayman, and R. E. White, "State of Charge and Loss of Active Material Estimation of a Lithium Ion Cell under Low Earth Orbit Condition Using Kalman Filtering Approaches," *J. Electrochem. Soc.*, vol. 159, no. 6, A860-A872, 2012, doi: 10.1149/2.098206jes.

[211] K. A. Smith, C. D. Rahn, and C.-Y. Wang, "Control oriented 1D electrochemical model of lithium ion battery," *Energy Conversion and Management*, vol. 48, no. 9, pp. 2565–2578, 2007, doi: 10.1016/j.enconman.2007.03.015.

[212] K. Rahul, J. Ramprabhakar, and S. Shankar, "Comparative study on modeling and estimation of State of Charge in battery," in *2017 International Conference On Smart Technologies For Smart Nation (SmartTechCon)*, Bangalore, 2017, pp. 1610–1615.

[213] J. Wei, G. Dong, and Z. Chen, "Remaining Useful Life Prediction and State of Health Diagnosis for Lithium-Ion Batteries Using Particle Filter and Support Vector Regression," *IEEE Trans. Ind. Electron.*, vol. 65, no. 7, pp. 5634–5643, 2018, doi: 10.1109/TIE.2017.2782224.

[214] L. Chen *et al.,* "A Novel State-of-Charge Estimation Method of Lithium-Ion Batteries Combining the Grey Model and Genetic Algorithms," *IEEE Trans. Power Electron.*, vol. 33, no. 10, pp. 8797–8807, 2018, doi: 10.1109/TPEL.2017.2782721.

[215] C. Zhang, Y. Zhu, G. Dong, and J. Wei, "Data-driven lithium-ion battery states estimation using neural networks and particle filtering," *Int J Energy Res*, 2019, doi: 10.1002/er.4820.

[216] R. Xiong, H. He, and K. Zhao, "Research on an Online Identification Algorithm for a Thevenin Battery Model by an Experimental Approach," *International Journal of Green Energy*, vol. 12, no. 3, pp. 272–278, 2015, doi: 10.1080/15435075.2014.891512.

[217] S. Sepasi, R. Ghorbani, and B. Y. Liaw, "Improved extended Kalman filter for state of charge estimation of battery pack," *Journal of Power Sources*, vol. 255, pp. 368–376, 2014, doi: 10.1016/j.jpowsour.2013.12.093.

[218] R. Xiong, F.-C. Sun, and H.-W. He, "Data-driven State-of-Charge estimator for electric vehicles battery using robust extended Kalman filter," *Int.J Automot. Technol.*, vol. 15, no. 1, pp. 89–96, 2014, doi: 10.1007/s12239-014-0010-1.

[219] A. Baba and S. Adachi, "SOC Estimation of HEV/EV Battery Using Series Kalman Filter," *Electr Eng Jpn*, vol. 187, no. 2, pp. 53–62, 2014, doi: 10.1002/eej.22511.

[220] F. Sun, R. Xiong, and H. He, "Estimation of state-of-charge and state-of-power capability of lithium-ion battery considering varying health conditions," *Journal of Power Sources*, vol. 259, pp. 166–176, 2014, doi: 10.1016/j.jpowsour.2014.02.095.

[221] Y. Bao, W. Dong, and D. Wang, "Online Internal Resistance Measurement Application in Lithium Ion Battery Capacity and State of Charge Estimation," *Energies*, vol. 11, no. 5, p. 1073, 2018, doi: 10.3390/en11051073.

[222] B. Xia, Z. Sun, R. Zhang, and Z. Lao, "A Cubature Particle Filter Algorithm to Estimate the State of the Charge of Lithium-Ion Batteries Based on a Second-Order Equivalent Circuit Model," *Energies*, vol. 10, no. 4, p. 457, 2017, doi: 10.3390/en10040457.

[223] Y. Wang, C. Liu, R. Pan, and Z. Chen, "Modeling and state-of-charge prediction of lithium-ion battery and ultracapacitor hybrids with a co-estimator," *Energy*, vol. 121, pp. 739–750, 2017, doi: 10.1016/j.energy.2017.01.044.

[224] X. Zhang, J. Lu, S. Yuan, J. Yang, and X. Zhou, "A novel method for identification of lithium-ion battery equivalent circuit model parameters considering electrochemical properties," *Journal of Power Sources*, vol. 345, pp. 21–29, 2017, doi: 10.1016/j.jpowsour.2017.01.126.

[225] X. Hu, H. Yuan, C. Zou, Z. Li, and L. Zhang, "Co-Estimation of State of Charge and State of Health for Lithium-Ion Batteries Based on Fractional-Order Calculus," *IEEE Trans. Veh. Technol.*, vol. 67, no. 11, pp. 10319–10329, 2018, doi: 10.1109/TVT.2018.2865664.

[226] J. Tian, R. Xiong, and Q. Yu, "Fractional-Order Model-Based Incremental Capacity Analysis for Degradation State Recognition of Lithium-Ion Batteries," *IEEE Trans. Ind. Electron.*, vol. 66, no. 2, pp. 1576–1584, 2019, doi: 10.1109/TIE.2018.2798606.

[227] Y. Wang, G. Gao, X. Li, and Z. Chen, "A fractional-order model-based state estimation approach for lithium-ion battery and ultra-capacitor hybrid power source system considering load trajectory," *Journal of Power Sources*, vol. 449, p. 227543, 2020, doi: 10.1016/j.jpowsour.2019.227543.

[228] M. R. Jongerden and B. R. Haverkort, "Which battery model to use?," *IET Softw.*, vol. 3, no. 6, p. 445, 2009, doi: 10.1049/iet-sen.2009.0001.

[229] R. Rao, S. Vrudhula, and D. N. Rakhmatov, "Battery modeling for energy-aware system design," *Computer*, vol. 36, no. 12, pp. 77–87, 2003, doi: 10.1109/MC.2003.1250886.

[230] Y. Hu, S. Yurkovich, Y. Guezennec, and B. J. Yurkovich, "Electro-thermal battery model identification for automotive applications," *Journal of Power Sources*, vol. 196, no. 1, pp. 449–457, 2011, doi: 10.1016/j.jpowsour.2010.06.037.

[231] B. Wu, V. Yufit, M. Marinescu, G. J. Offer, R. F. Martinez-Botas, and N. P. Brandon, "Coupled thermal–electrochemical modelling of uneven heat generation in lithium-ion battery packs," *Journal of Power Sources*, vol. 243, pp. 544–554, 2013, doi:

10.1016/j.jpowsour.2013.05.164.

[232] Y.-H. Chiang, W.-Y. Sean, and J.-C. Ke, "Online estimation of internal resistance and open-circuit voltage of lithium-ion batteries in electric vehicles," *Journal of Power Sources*, vol. 196, no. 8, pp. 3921–3932, 2011, doi: 10.1016/j.jpowsour.2011.01.005.

[233] H. Liu, Z. Wei, W. He, and J. Zhao, "Thermal issues about Li-ion batteries and recent progress in battery thermal management systems: A review," *Energy Conversion and Management*, vol. 150, pp. 304–330, 2017, doi: 10.1016/j.enconman.2017.08.016.

[234] A. Garg, X. Peng, M. L. P. Le, K. Pareek, and C. Chin, "Design and analysis of capacity models for Lithium-ion battery," *Measurement*, vol. 120, pp. 114–120, 2018, doi: 10.1016/j.measurement.2018.02.003.

[235] S. Rohr *et al.,* "Quantifying Uncertainties in Reusing Lithium-Ion Batteries from Electric Vehicles," *Procedia Manufacturing*, vol. 8, pp. 603–610, 2017, doi: 10.1016/j.promfg.2017.02.077.

[236] M. F. Samadi and M. Saif, "Nonlinear model predictive control for cell balancing in Liion battery packs," in *2014 American Control Conference*, Portland, OR, USA, Jun. 2014 - Jun. 2014, pp. 2924–2929.

[237] T. Bruen, J. Marco, and M. Gama, "Model Based Design of Balancing Systems for Electric Vehicle Battery Packs," *IFAC-PapersOnLine*, vol. 48, no. 15, pp. 395–402, 2015, doi: 10.1016/j.ifacol.2015.10.057.

[238] J.-C. Lin, "Development of a New Battery Management System with an Independent Balance Module for Electrical Motorcycles," *Energies*, vol. 10, no. 9, p. 1289, 2017, doi: 10.3390/en10091289.

[239] M. Daowd, M. Antoine, N. Omar, P. Lataire, P. van den Bossche, and J. van Mierlo, "Battery Management System—Balancing Modularization Based on a Single Switched Capacitor and Bi-Directional DC/DC Converter with the Auxiliary Battery," *Energies*, vol. 7, no. 5, pp. 2897– 2937, 2014, doi: 10.3390/en7052897.

[240] M. S. Yusof, S. F. Toha, N. Kamisan, N. Hashim, and M. A. Abdullah, "Battery Cell Balancing Optimisation for Battery Management System," *IOP Conf. Ser.: Mater. Sci. Eng.*, vol. 184, p. 12021, 2017, doi: 10.1088/1757-899X/184/1/012021.

[241] J. Xu, S. Li, C. Mi, Z. Chen, and B. Cao, "SOC Based Battery Cell Balancing with a Novel Topology and Reduced Component Count," *Energies*, vol. 6, no. 6, pp. 2726–2740, 2013, doi: 10.3390/en6062726.

[242] G. Carpinelli, F. Mottola, D. Proto, and P. Varilone, "Minimizing unbalances in low-voltage microgrids: Optimal scheduling of distributed resources," *Applied Energy*, vol. 191, pp. 170–182, 2017, doi: 10.1016/j.apenergy.2017.01.057.

[243] W. Han and L. Zhang, "Battery Cell Reconfiguration to Expedite Charge Equalization in Series-Connected Battery Systems," *IEEE Robot. Autom. Lett.*, vol. 3, no. 1, pp. 22–28, 2018, doi: 10.1109/LRA.2017.2728204.

[244] H. Rahimi-Eichi, U. Ojha, F. Baronti, and M.-Y. Chow, "Battery Management System: An Overview of Its Application in the Smart Grid and Electric Vehicles," *EEE Ind. Electron. Mag.*, vol. 7, no. 2, pp. 4–16, 2013, doi: 10.1109/MIE.2013.2250351.

[245] N. Lotfi, P. Fajri, S. Novosad, J. Savage, R. Landers, and M. Ferdowsi, "Development of an Experimental Testbed for Research in Lithium-Ion Battery Management Systems," *Energies*, vol. 6, no. 10, pp. 5231–5258, 2013, doi: 10.3390/en6105231.

[246] S. Orcioni, A. Ricci, L. Buccolini, C. Scavongelli, and M. Conti, "Effects of variability of the characteristics of single cell on the performance of a lithium-ion battery pack," in 2017 13th Workshop on Intelligent Solutions in Embedded Systems (WISES), Hamburg, Germany, Jun. 2017 - Jun. 2017, pp. 15–21.

[247] M. Daowd, N. Omar, P. van den Bossche, and J. van Mierlo, "Passive and active battery balancing comparison based on MATLAB simulation," in *2011 IEEE Vehicle Power and Propulsion Conference*, Chicago, IL, USA, Sep. 2011 - Sep. 2011, pp. 1–7.

[248] D.-H. Zhang *et al.*, "Balancing Control Strategy for Li-Ion Batteries String Based on Dynamic Balanced Point," *Energies*, vol. 8, no. 3, pp. 1830–1847, 2015, doi: 10.3390/en8031830.

[249] Q. Kong, M. Ruan, and Y. Zi, "A health management system for marine cell group," *IOP Conf. Ser.: Earth Environ. Sci.*, vol. 69, p. 12081, 2017, doi: 10.1088/1755-1315/69/1/012081.

[250] W. D. Toh, B. Xu, J. Jia, C. S. Chin, J. Chiew, and Z. Gao, "Lithium Iron Phosphate
(LiFePO4) Battery Power System for Deepwater Emergency Operation," *Energy Procedia*, vol. 143, pp. 348–353, 2017, doi: 10.1016/j.egypro.2017.12.695.

[251] D. D. Artakusuma, H. Afrisal, A. I. Cahyadi, and O. Wahyunggoro, "Battery management system via bus network for multi battery electric vehicle," in *2014 International Conference on Electrical Engineering and Computer Science (ICEECS)*, Kuta, Bali, Indonesia, Nov. 2014 - Nov. 2014, pp. 179–181.

[252] Z. Xi and X. Zhao, "Data Driven Prognostics With Lack of Training Data Sets," in *Volume 2A: 41st Design Automation Conference*, Boston, Massachusetts, USA, 08022015.

[253] X. Zhang, Y. Wang, C. Liu, and Z. Chen, "A novel approach of remaining discharge energy prediction for large format lithium-ion battery pack," *Journal of Power Sources*, vol. 343, pp. 216–225, 2017, doi: 10.1016/j.jpowsour.2017.01.054.

[254] F. Zhang, M. M. U. Rehman, R. Zane, and D. Maksimovic, "Hybrid balancing in a modular battery management system for electric-drive vehicles," in *2017 IEEE Energy Conversion Congress and Exposition (ECCE)*, Cincinnati, OH, Oct. 2017 - Oct. 2017, pp. 578–583.

[255] J. Li, A. M. Gee, M. Zhang, and W. Yuan, "Analysis of battery lifetime extension in a SMES-battery hybrid energy storage system using a novel battery lifetime model," *Energy*, vol. 86, pp. 175–185, 2015, doi: 10.1016/j.energy.2015.03.132.

[256] J. Rivera-Barrera, N. Muñoz-Galeano, and H. Sarmiento-Maldonado, "SoC Estimation for Lithium-ion Batteries: Review and Future Challenges," *Electronics*, vol. 6, no. 4, p. 102, 2017, doi: 10.3390/electronics6040102.

[257] M. Gokdag and M. Akbaba, "An active battery cell balancing topology without using external energy storage elements," in *2015 6th International Conference on Modeling, Simulation, and Applied Optimization (ICMSAO)*, Istanbul, Turkey, May. 2015 - May. 2015, pp. 1–5.

[258] N. Omar *et al.,* "Rechargeable Energy Storage Systems for Plug-in Hybrid Electric Vehicles—Assessment of Electrical Characteristics," *Energies,* vol. 5, no. 8, pp. 2952–2988, 2012, doi: 10.3390/en5082952.

[259] X. Cui, W. Shen, Y. Zhang, C. Hu, and J. Zheng, "Novel active LiFePO4 battery balancing method based on chargeable and dischargeable capacity," *Computers & Chemical Engineering*, vol. 97, pp. 27–35, 2017, doi: 10.1016/j.compchemeng.2016.11.014.

[260] M. M. Hoque, M. A. Hannan, and A. Mohamed, "Voltage equalization control algorithm for monitoring and balancing of series connected lithium-ion battery," *Journal of Renewable and Sustainable Energy*, vol. 8, no. 2, p. 25703, 2016, doi: 10.1063/1.4944961.

[261] A. U. Schmid, L. Eringer, I. Lambidis, and K. P. Birke, "Electrochemical balancing of lithium-ion cells by nickel-based cells," *Journal of Power Sources*, vol. 367, pp. 49–56, 2017, doi: 10.1016/j.jpowsour.2017.09.011.

[262] O. Capron, J. Jaguemont, R. Gopalakrishnan, P. van den Bossche, N. Omar, and J. van Mierlo, "Impact of the Temperature in the Evaluation of Battery Performances During Long-Term Cycling—Characterisation and Modelling," *Applied Sciences*, vol. 8, no. 8, p. 1364, 2018, doi: 10.3390/app8081364.

[263] R. Mizanur, M. M. Rashid, A. Rahman, A. H. M. Zahirul Alam, S. Ihsan, and M. S. Mollik, "Analysis of the internal temperature of the cells in a battery pack during SOC balancing," *IOP Conf. Ser.: Mater. Sci. Eng.*, vol. 184, p. 12014, 2017, doi: 10.1088/1757-899X/184/1/012014.

[264] W. F. Bentley, "Cell balancing considerations for lithium-ion battery systems," in *The Twelfth Annual Battery Conference on Applications and Advances*, Long Beach, CA, USA, Jan. 1997, pp. 223–226.

[265] J. Kim, J. Shin, C. Chun, and B. H. Cho, "Stable Configuration of a Li-Ion Series Battery Pack Based on a Screening Process for Improved Voltage/SOC Balancing," *IEEE Trans. Power Electron.*, vol. 27, no. 1, pp. 411–424, 2012, doi: 10.1109/TPEL.2011.2158553.

[266] M. Dubarry, A. Devie, and B. Y. Liaw, "Cell-balancing currents in parallel strings of a battery system," *Journal of Power Sources*, vol. 321, pp. 36–46, 2016, doi: 10.1016/j.jpowsour.2016.04.125.

[267] G. Qi, X. Li, and D. Yang, "A control strategy for dynamic balancing of lithium iron phosphate battery based on the performance of cell voltage," in *2014 IEEE Conference and Expo Transportation Electrification Asia-Pacific (ITEC Asia-Pacific)*, Beijing, China, Aug. 2014 - Sep. 2014, pp. 1–5.

[268] J. R. Belt, C. D. Ho, T. J. Miller, M. A. Habib, and T. Q. Duong, "The effect of temperature on capacity and power in cycled lithium ion batteries," *Journal of Power Sources*, vol. 142, 1-2, pp. 354–360, 2005, doi: 10.1016/j.jpowsour.2004.10.029.

[269] I. Aizpuru, U. Iraola, J. M. Canales, E. Unamuno, and I. Gil, "Battery pack tests to detect unbalancing effects in series connected Li-ion cells," in *2013 International Conference on Clean Electrical Power (ICCEP)*, Alghero, Italy, Jun. 2013 - Jun. 2013, pp. 99–106.

[270] Q. Ouyang, J. Chen, J. Zheng, and H. Fang, "Optimal Cell-to-Cell Balancing Topology Design for Serially Connected Lithium-Ion Battery Packs," *IEEE Trans. Sustain. Energy*, vol. 9, no. 1, pp. 350–360, 2018, doi: 10.1109/TSTE.2017.2733342.

[271] Z. Xi, R. Jing, X. Yang, and E. Decker, "State of Charge Estimation of Lithium-Ion Batteries Considering Model Bias and Parameter Uncertainties," in *Volume 1A: 34th Computers and Information in Engineering Conference*, Buffalo, New York, USA, 08172014.

[272] M. Mathew, Q. H. Kong, J. McGrory, and M. Fowler, "Simulation of lithium ion battery replacement in a battery pack for application in electric vehicles," *Journal of Power Sources*, vol. 349, pp. 94–104, 2017, doi: 10.1016/j.jpowsour.2017.03.010.

[273] T. Huria, M. Ceraolo, J. Gazzarri, and R. Jackey, "High fidelity electrical model with thermal dependence for characterization and simulation of high power lithium battery cells," in *2012 IEEE International Electric Vehicle Conference*, Greenville, SC, Mar. 2012 - Mar. 2012, pp. 1–8.

[274] T. R. Ashwin, Y. M. Chung, and J. Wang, "Capacity fade modelling of lithium-ion battery under cyclic loading conditions," *Journal of Power Sources*, vol. 328, pp. 586–598, 2016, doi: 10.1016/j.jpowsour.2016.08.054.

[275] Y. Zheng, M. Ouyang, L. Lu, J. Li, X. Han, and L. Xu, "On-line equalization for lithiumion battery packs based on charging cell voltages: Part 2. Fuzzy logic equalization," *Journal of Power Sources*, vol. 247, pp. 460–466, 2014, doi: 10.1016/j.jpowsour.2013.09.012.

[276] J. Gallardo-Lozano, E. Romero-Cadaval, M. I. Milanes-Montero, and M. A. Guerrero-Martinez, "A novel active battery equalization control with on-line unhealthy cell detection and cell change decision," *Journal of Power Sources*, vol. 299, pp. 356–370, 2015, doi: 10.1016/j.jpowsour.2015.09.005. [277] W. Han and L. Zhang, "Mathematical analysis and coordinated current allocation control in battery power module systems," *Journal of Power Sources*, vol. 372, pp. 166–179, 2017, doi: 10.1016/j.jpowsour.2017.10.046.

[278] F. Altaf, L. Johannesson, and B. Egardt, "Evaluating the Potential for Cell Balancing Using a Cascaded Multi-Level Converter Using Convex Optimization\*," *IFAC Proceedings Volumes*, vol. 45, no. 30, pp. 100–107, 2012, doi: 10.3182/20121023-3-FR-4025.00024.

[279] V. A. Hentunen, V. Erkkilä, and S. Jenu, "Smart system of renewable energy storage based on INtegrated EVs and bAtteries to empower mobile, Distributed and centralised Energy storage in the distribution grid," 2010.

[280] J. Gallardo-Lozano, E. Romero-Cadaval, M. I. Milanes-Montero, and M. A. Guerrero-Martinez, "Battery equalization active methods," *Journal of Power Sources*, vol. 246, pp. 934– 949, 2014, doi: 10.1016/j.jpowsour.2013.08.026.

[281] Y. Zheng, W. Gao, M. Ouyang, L. Lu, L. Zhou, and X. Han, "State-of-charge inconsistency estimation of lithium-ion battery pack using mean-difference model and extended Kalman filter," *Journal of Power Sources*, vol. 383, pp. 50–58, 2018, doi: 10.1016/j.jpowsour.2018.02.058.

[282] Y. Xing, E. W. M. Ma, K. L. Tsui, and M. Pecht, "Battery Management Systems in Electric and Hybrid Vehicles," *Energies*, vol. 4, no. 11, pp. 1840–1857, 2011, doi: 10.3390/en4111840.

[283] N. Williard, W. He, C. Hendricks, and M. Pecht, "Lessons Learned from the 787 Dreamliner Issue on Lithium-Ion Battery Reliability," *Energies*, vol. 6, no. 9, pp. 4682–4695, 2013, doi: 10.3390/en6094682.

[284] Heidi Fisk & Johan Leijgård, "A Battery Management Unit," [Online]. Available: https://odr.chalmers.se/bitstream/20.500.12380/125124/1/125124.pdf

[285] N. Bouchhima, M. Schnierle, S. Schulte, and K. P. Birke, "Active model-based balancing strategy for self-reconfigurable batteries," *Journal of Power Sources*, vol. 322, pp. 129–137, 2016, doi: 10.1016/j.jpowsour.2016.05.027.

[286] Y. Barsukov, "Battery cell balancing: What to balance and how," *Texas Instruments*, 2-1, 2009.

[287] G. E. Mog and E. P. Ribeiro, "Total harmonic distortion calculation by filtering for power quality monitoring," in 2004 IEEE/PES Transmision and Distribution Conference and Exposition: Latin America (IEEE Cat. No. 04EX956), Sao Paulo, Brazil, Nov. 2004, pp. 629–632.

[288] J. J. Giner-Sanz, E. M. Ortega, and V. Pérez-Herranz, "Total harmonic distortion based method for linearity assessment in electrochemical systems in the context of EIS," *Electrochimica Acta*, vol. 186, pp. 598–612, 2015, doi: 10.1016/j.electacta.2015.10.152.

[289] M. Kiel, O. Bohlen, and D. U. Sauer, "Harmonic analysis for identification of nonlinearities in impedance spectroscopy," *Electrochimica Acta*, vol. 53, no. 25, pp. 7367–7374, 2008, doi: 10.1016/j.electacta.2008.01.089.

[290] Q. Mao and U. Krewer, "Sensing methanol concentration in direct methanol fuel cell with total harmonic distortion: Theory and application," *Electrochimica Acta*, vol. 68, pp. 60–68, 2012, doi: 10.1016/j.electacta.2012.02.018.

[291] Q. Mao and U. Krewer, "Total harmonic distortion analysis of oxygen reduction reaction in proton exchange membrane fuel cells," *Electrochimica Acta*, vol. 103, pp. 188–198, 2013, doi: 10.1016/j.electacta.2013.03.194.

[292] Q. Mao, U. Krewer, and R. Hanke-Rauschenbach, "Total harmonic distortion analysis for direct methanol fuel cell anode," *Electrochemistry Communications*, vol. 12, no. 11, pp. 1517–1519, 2010, doi: 10.1016/j.elecom.2010.08.022.

[293] E. Ramschak, V. Peinecke, P. Prenninger, T. Schaffer, W. Baumgartner, and V. Hacker, "Online stack monitoring tool for dynamically and stationary operated fuel cell systems," *Fuel Cells Bulletin*, vol. 2006, no. 10, pp. 12–15, 2006, doi: 10.1016/S1464-2859(06)71207-X.

[294] T. Kadyk, R. Hanke-Rauschenbach, and K. Sundmacher, "Nonlinear frequency response analysis of PEM fuel cells for diagnosis of dehydration, flooding and CO-poisoning," *Journal of Electroanalytical Chemistry*, vol. 630, 1-2, pp. 19–27, 2009, doi: 10.1016/j.jelechem.2009.02.001.

[295] Y.-H. Lee, J. Kim, and S. Yoo, "On-line and real-time diagnosis method for proton membrane fuel cell (PEMFC) stack by the superposition principle," *Journal of Power Sources*, vol. 326, pp. 264–269, 2016, doi: 10.1016/j.jpowsour.2016.06.113.

[296] D. K. Y. Wong and D. R. MacFarlane, "Harmonic impedance spectroscopy. Theory and experimental results for reversible and quasi-reversible redox systems," *J. Phys. Chem.*, vol. 99, no. 7, pp. 2134–2142, 1995, doi: 10.1021/j100007a051.

[297] S. Okazaki, S. Higuchi, and S. Takahashi, "Second-Order Harmonic in the Current Response to Sinusoidal Perturbation Voltage for Lead-Acid Battery: An Application to a State-of-Charge Indicator," *J. Electrochem. Soc.*, vol. 132, no. 7, pp. 1516–1520, 1985, doi: 10.1149/1.2114157.

[298] J. Huang, H. Ge, Z. Li, and J. Zhang, "Dynamic Electrochemical Impedance Spectroscopy of a Three-Electrode Lithium-Ion Battery during Pulse Charge and Discharge," *Electrochimica Acta*, vol. 176, pp. 311–320, 2015, doi: 10.1016/j.electacta.2015.07.017.

[299] Y. Abe, N. Hori, and S. Kumagai, "Electrochemical Impedance Spectroscopy on the Performance Degradation of LiFePO4/Graphite Lithium-Ion Battery Due to Charge-Discharge Cycling under Different C-Rates," *Energies*, vol. 12, no. 23, p. 4507, 2019, doi: 10.3390/en12234507.

# **10** Appendix

In this thesis, a total of seven cells are used for measurement. Table 10.1 shows which cells are used in which figure and which cell SoH.

Cell number	Product name	SoH (%) (used figure)
Cell #1	Samsung ICR 18650-26F	100 (3.1, 3.2, 3.3)
Cell #2	Samsung ICR 18650-26F	90 (3.1), 85 (7.6, 7.7)
Cell #3	Samsung ICR 18650-26F	80 (3.1), 70 (7.6, 7.7)
Cell #4	Samsung ICR 18650-26F	100 (4.1, 4.2), 100 to 73 (4.3), 73 (4.4, 4.5)
Cell #5	Samsung ICR 18650-26F	100 to 80 (5.2, 5.7, 5.8), 80 (5.4, 5.5, 5.6, 5.9, 5.10)
Cell #6	Samsung ICR 18650-26F	95 (6.2, 6.4, 6.5, 6.8, 6.9, 6.10, 6.11, 6.12), 90 (7.5, 7.6, 7.7)
Cell #7	Bexel INR 18650-2600 SP01	100 to 70 (4.6, 4.7, 4.8)

Table 10.1 Cells used in the measurements and the SoH at the time.