Reliability study of lithium ion cell and battery pack

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Reliability Study of Lithium Ion cell and battery pack

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ABSTRACT

Lithium ion battery (LiB) is becoming the work horse for many electronics gadgets especially for portable electronics products. It is also an enabling technology for electrified transportation that can help in environmental sustainability significantly. The reliability of Lithium ion cell is of increasing concern in present-day energy storage devices where the failures of LiB not only result in severe inconvenience and enormous replacement/repair cost for the battery model/pack, but also risk catastrophic consequences such as fire hazard and possible explosion due to overcharge or high temperature .

In order to study the reliability of LiB and prevent the failures then extend its lifetime, the modelling approach is widely employed as it is an *in situ* non-destructive technique (NDT) that is necessary for some applications like Battery Management System (BMS). In this work, an electrochemistry-based electrical model (ECBE) is developed for LiB cells based on the first principle of electrochemistry from its discharge curve (i.e. the change in terminal voltage over time within a discharge cycle), and then convert the corresponding partial differential equations into circuit model. This model is able to compute the internal parameters of a cell, including its maximum initial capacity at the beginning of each discharge cycle. With the internal parameters computed, it can also produce its Nyquist plot and the plot is found to agree well with its experimental electrochemical impedance spectroscopy (EIS) spectra. Moreover, ECBE allows the performance of each component inside LiB be determined real time through its discharging curve non-destructively (i.e., terminal voltage vs. time during discharge), making it is capable of comprehensively identify the various aging causes through in-situ real time characterization. As ECBE is derived based on the first principles, it can be applied to other cell systems.

To obtain the parameters values of the circuit elements are using a non-linear regression method, Levenberg-Marquart fitting Algorithm (LMA) cum Simulated Annealing (SA). SA is employed to approximate global minima, and LMA is used to deliver rapid and accurate estimates of the local minima due to gradient-descent based algorithm. With these algorithms, the fitting can agree well with the experimental results in around 0.3 seconds computed by i7 8-core CPU.

Through this ECBE model, the status of a LiB cell and its maximum charge capacity can be determined in real time. With the computed maximum initial capacity at the beginning of each discharge cycle, State of charge (SoC) have been estimated online without the periodic

discharge of the cell fully which can introduce damage to the cell and shorten its lifespan. Furthermore, its value can also be used as an indication of state-of-health (SoH) of a battery.

The study of Quality Decision for Overcharged Li Ion Battery from reliability and safety perspective has been conducted. The definition of Quality decision is a practical and systematic approach that methodically breaks down barriers and improves the quality and timeliness of important decisions. The results show both positive electrode and the total of electrodes resistance and electrode/electrolyte resistance are degraded when cut-off voltage (COV) is excessive. However, the performance of the graphite electrode is insignificant against excessive COV. Although we enjoy the seemingly longer runtime with higher COV, the cell reliability is degrading. The battery reliability is defined as the ability of battery to consistently perform its required function. Therefore, this method can evaluate if the damage made in the cell by the excessive COV is rendering the cell from further safe usage or it is still acceptable with minor degradation in reliability and safety, thus providing a basis for quality consideration of the cell. Moreover, it also enables battery manufacturers to identify the internal components for their cells that are most vulnerable to the excessive COV so that quality improvement of their batteries can be designed and produced. Furthermore, it also alerts electric vehicles (EVs) user on the hidden safety issues of their battery pack, and enables BMS to perform reliability balancing, a new patented technique to ensure the safe and reliable operation of battery pack.

The effects of temperature on the electrochemistry in LiB and aging rate of LiB have been studied. The LiCoO_2 (LCO) prismatic Sony cell is used in this work. The findings allow us to have a better understanding of the effect of temperature and it also reveals phase transformation of the anode when LiB is operating beyond 45°C . The increasing degradation rate of the maximum charge storage of LiB during cycling at elevated temperature is found to relate mainly to the degradations at the electrodes, and that the degradation of LCO cathode is larger than graphite anode at elevated temperature. In particular, the formation and modification of the surface films on the electrodes as well as structural/phase changes of the LCO electrode, as reported in the literatures, are found to be the main contributors to the increasing degradation rate of the maximum charge storage of LiB with temperature for specific operating temperature range. Larger increases in the Warburg element and cell impedance are also found with cycling at higher temperature, but they do not seriously affect the state of health (SoH) of LiB as shown in this work.

Understand the degradation processes of the various components in LiB during cyclic aging are essential in order to improve its cycle life for its various applications. Extensive research works reported the degradation processes of the various components individually after LiB is

cycled through different number of cycles, but its time evolving nature has not been explored due to the complexity of the degradation processes and the absence of non-destructive method. Internal probing into the degradation processes in LiBs under cyclic aging has been reported. And these reported degradation mechanisms are arranged according to their possible degradation time scale, through the use of a recently developed non-destructive in-situ method of finding the degradation of the internal components in LiB during its cyclic aging. Lithium cobalt oxide (LCO) and graphite full coin cell is used in this work to demonstrate the methodology, and the time evolving degradation processes inside the coin cell is developed. The results show the degradation process in the coin cell is found to begin with the rapid SEI formation at the graphite electrode, then the LCO phase transformation, followed by the Joule heating due to the increased cell resistance and that result in the cracking and formation of SEI at the graphite electrode and surface spallation at the LCO electrode, as well as the degradation of the separator. The current density through the separator then becomes highly non-uniform, and together with the overcharging and discharging due to the decrease in the maximum charge storage capacity, Li plating occur on the electrodes. Further cycling results in the disintegration of the graphite electrode and the degradation of the inactive materials of LCO electrode that lead to the degradation of the contact of the cathode.

A Reliability-based Design Concept for Lithium-ion Battery Pack in EVs has been presented. In this work, a method on the design and analysis of lithium-ion (Li-ion) battery pack from the reliability perspective is proposed. The analysis is based on the degradation of the battery pack, which is related to the cells configuration in the battery pack and the SoH of all the Lithium ion cells in the pack. Universal Generating Function (UGF) technique is used for reliability analysis. As adding redundant battery cells to the battery pack in the production process can improve its reliability but it also increases cost, tradeoff between the numbers of the redundant battery cells, the configuration of the redundant cells and their reliability is investigated in this work. From the simulation, we conclude that the reliability could be improved by adding redundant cells as expected, and the configuration of the redundant cells has significant effect on its reliability. The proposed design concept provides a way to select the best redundant cells configuration for good pack reliability, while considering the total cost through the optimal number of the redundant cells.

The thesis details the development of the proposed ECBE model and a method on the design and analysis of Li-ion battery pack from the reliability perspective, a practical framework of electrical based online SoC estimation of LiBs, the quality decision for overcharged LiB from reliability and safety perspective, an a reliability-based design concept for Li-ion battery pack in electric vehicle. And it also includes details investigation of the effect of temperature on

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List of Abbreviations

AFM	Atomic force microscopy
BMS	Battery management system
CALCE	Centre for advanced life cycle engineering
CCCV	Constant current/constant voltage
COV	Cut-off voltage
CTS	Cell test system
DoD	Depth of discharge
ECI	Electrochemical interface
ECBE	Electrochemistry based electrical
EDX	Energy dispersive X-ray analysis
EIS	Electrochemical impedance spectrometer
EKF	Extended Kalman filter
EMF	Electromotive force
EoL	End of life
ETMS	Electrochemical thermodynamics measurement system
EV	Electric vehicle
FRA	Frequency response analyzer
GHG	Greenhouse gases
GIC	Graphite intercalation compounds
HEV	Hybrid electric vehicle
ICP	Inductively coupled plasma
KF	Kalman filter
LCO	Lithium cobalt oxide

LiB	Lithium ion battery
LiPB	Lithium polymeric battery
LMA	Levenburg-marquardt algorithm
LMO	Lithium manganese oxide
LSA	Least square algorithms
MSS	Multi-state systems
NDT	Non-destructive techniques
OCV	Open circuit voltage
PHM	Prognostic and health monitoring
PSS	Panasonic solid solution
Redox	Reduction and oxidation
RUL	Remaining useful life
SA	Simulated Annealing
SEM	Scanning electron microscopy
SEI	Solid electrolyte interphase
SoC	State-of-charge
SoH	State-of-health
SPKF	Sigma-point Kalman filter
TEM	Transmission electron microscopy
UGF	Universal generating function
XRD	X-ray diffraction

Chapter 1. Introduction

1.1 Motivation

In view of the fossil fuel depletion and the emission of greenhouse gases (GHG) with the fossil fuel, and the fact that transportation is a major source of GHG emission and usage of the fossil fuel, research and development of electric vehicles (EVs) are blooming significantly. With EVs, their energy sources can be renewable clean energy sources through the recharging of Li-ion battery packs from these clean energy sources, and no GHG emission occurs with EVs.

These EVs are driven by electric motors instead of internal combustion engines. These motors are powered by the Li-ion battery packs in the vehicles. Li-ion batteries (LiBs) are used because they have the highest energy and power densities, and their life time is sufficiently longer [1]. In fact, it is because of the LiB technology that enables EVs to be a realistic product that we see in the market today worldwide [2].

The reliability of the Li-ion battery pack is becoming increasingly important for its use in EVs as higher reliability pack will have a long lifetime can help to save cost and reduce environmentally hazard impact resulting from the electrochemistry wastes from the batteries [3]. Reliability of a battery pack depends on the reliability of the battery cell, including the number of redundant cells and their configurations.

While reliability of battery cells are being studied, and several degradation mechanisms are explored, how these mechanisms related to one another and their occurrence time scale remain unexplored. A non-destructive evaluation of the health of battery is also needed for timely monitoring and better managed, especially when they are placed in a battery pack. In fact, there is no work on the reliability of battery pack. It is with these backgrounds that this work is produced, so that our understanding of the cell degradation and its relationship to pack reliability can be better understood.

1.2 Objectives

This thesis aims to study the reliability of Lithium Ion cell and battery pack.

(1). To develop an in-situ non-destructive battery modelling method, and to comprehensively model all the electrochemical and physical processes in the cell during its cyclic aging.

- (2). To investigate the effect of abusive overcharge and high temperature on degradation rates of all the internal components in the LiB, and identify the internal component in a cell that are most vulnerable to the specific abusive operation.
- (3). To comprehensively investigate the effects of temperature on the cyclic aging rate of each component inside the LiB, and identify the various aging causes.
- (4). To investigate the degradation of the internal components in LiB during its cyclic aging, and identify the dominant aging mechanisms in a time progression sequence.
- (5). To develop a method to design Li-ion battery pack with higher reliability and analysis of Li-ion battery pack with different configurations in order to improve its cost effectiveness.

1.3 Contributions

The contributions of this research work include:

- a. The development of an electrochemistry based electrical (ECBE) model for LiB cells from their discharge curves (i.e. the change in terminal voltage as a function of discharge within a discharge cycle). This model examines the electrochemical and physical processes in a battery cell, considering both the thermodynamics and the kinetic of the processes, and converts the partial differential equations of these processes into electrical equivalent circuit. Thus all the circuit elements and their values are associated with the individual internal components in the cell, including the *emf*. The internal parameters of this model are computed at the beginning of each discharge cycle. With the computed internal parameters, its Nyquist plot agrees well with its experimental EIS spectra. A detail investigation of the impact of resting time and discharging current on the model parameters. Using the model developed in this work, we can estimate the maximum charge store capacity after every discharge cycle, and hence the SoC of a LiB cell can be determined in real time using Coulomb counting method.

The proposed ECBE model is described in details in Chapter 3 and in the following published paper.

[4] 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, 6/1/ 2014.(IF:6.227)

- b. An assessment of the internal components in a LiB cell to evaluate its reliability and safety with respect to this overcharging abuse. The identification of seemingly gain of LiB cell by having it to charge with high cut-off voltage (COV), and reveal the hidden issues associated with charging the cell with high COV. A characterization of the temperature effect on electrochemistry in LiB. The phase transition was proposed as the main cause of changes for each component in the investigated LiB cell operated above 45°C.

The effect of abusive overcharge and temperature on electrochemistry is discussed in details in Chapter 4 and in the following published papers.

[5] F. Leng, C. M. Tan, Y. Rachid, M. Kenza, and R. Wang, "Effect of overcharge on the reliability and safety of lithium-ion batteries," presented at the Asian Network for Quality Singapore, vol. 256, pp. 102-109, 2014.

[6] F. Leng, C. M. Tan, M. Pecht, and J. Zhang, "The effect of temperature on the electrochemistry in Lithium-ion batteries," in *3rd International Symposium on Next-Generation Electronics, ISNE 2014, May 7-10, 2014*, Taoyuan, Taiwan, pp. 1-4, 2014.

- c. An investigation and characterization of the effect of temperature on cycling aging rate in LiB when it is operating in the temperature range of 25 to 55 °C. The performance degradation rate of each component inside the LiB due to cycling aging at different temperatures was determined, and the degradations at the electrodes are found to be the main causes of the increasing degradation rate of irreversible capacity loss of LiB (i.e. SoH with temperature).

The effect of temperature (operating above room temperature) on the all aging rate of internal components in LiB and its underlying main aging mechanisms of each internal components are investigated in details in Chapter 5 and in the following published paper.

[7] F. Leng, C. M. Tan, and P. Michael, "Effect of Temperature on the Aging rate of Li Ion Battery Operating above Room Temperature," *Scientific Reports* 5: 08/06/online 2015. DOI:[10.1038/srep12967](https://doi.org/10.1038/srep12967) (IF:5.578)

- d. An investigation of the degradation processes of the various internal components in LiB during cyclic aging. The time evolving degradation processes of the various

internal components inside the coin cell is developed to identify the predominant degradation mechanisms at different times.

The detail investigation is provided in Chapter 6 and in the following submitted manuscript.

[8] Leng Feng, Tan Cher Ming, Rachid Yazami, and K. Maher, "Internal probing into the degradation processes in Lithium-ion batteries under cyclic aging," *Journal of Power Sources*, accepted, 2016. (IF:6.227)

- e. The development of a method on the design and analysis of Li-ion battery pack from the reliability perspective. The proposed method is employed to analyse the reliability of battery pack with various configurations of redundant cells as well as different number of redundant cell for the cost effectiveness by using UGF technique. The SoH of the LiB cells in the pack has been also taken into consideration for the analysis as well.

The proposed method and corresponding analysis are described in details in Chapter 7 and in the following published paper.

[9] Z. Liu, C. Tan, and F. Leng, "A reliability-based design concept for lithium-ion battery pack in electric vehicles," *Reliability Engineering & System Safety*, vol. 134, pp. 169-177, 2/ 2015. (IF:2.693)

1.4 Organization of the Thesis

This thesis is organized into eight chapters.

Chapter 1 gives an introduction to the motivation, objectives and contribution of the research.

The literature review on the LiB cell's basic operating principle, internal characterization, reliability, SoC and SoH definition and determination, cyclic aging process, safety and the reliability of battery packs in EV are presented in Chapter 2.

A practical framework of electrical based On-line SoC estimation of LiB is presented in Chapter 3. The ECBE model is developed as well.

In Chapter 4, the effect of abuses on electrochemistry in LiBs is discussed. The effect of overcharge and temperature on internal components in the LiB cell is discussed in details.

In Chapter 5, the effect of temperature on the aging rate of LiB operating above room temperature is shown. A comprehensive identification of the various aging causes is also presented.

In Chapter 6, internal probing into the degradation processes in LiBs under cyclic aging is provided. The reported degradation mechanisms are arranged into a progression sequence. And the main aging mechanisms in LiB at various cycles are identified.

In Chapter 7, a reliability-based design concept for Li-ion battery Pack in EVs is presented. The reliability of the battery packs with different configurations is analyzed.

Finally, the thesis ends with a conclusion and the planned future works in Chapter 8.

Chapter 2. LITERATURE REVIEW

2.1 Introduction

The literature review section is organized as follows. In Section 2.2, the basic operating principle of a LiB is presented where the electrochemical reactions of discharging/charging of a LiB are introduced. Section 2.3 shows the Internal Characterization of Lithium ion battery cell, in which, Electromotive force, Over-potential, Double-layer capacitance, Warburg element and Butler-Volmer element are studied in detail for the purpose of modelling. In Section 2.4 the reliability of Lithium ion battery cell is discussed, and the different Lithium ion Battery modelling methods are discussed in Chapter 2.5. The State-of-Charge and State-of-Health definition and determination are shown in Sections 2.6 and 2.7, where various SoC and SoH estimation methods are introduced and their advantages and disadvantages are discussed. Section 2.8 introduces the cyclic aging process of Lithium ion battery cell and the various aging mechanisms of anode and cathode are discussed. In Section 2.9 the safety of the Lithium ion battery cell is presented, and Overcharge and high temperature abuse of Lithium ion battery cell are discussed in the sub section. With all these knowledge on the cell, the reliability of battery packs in Electrical Vehicles is subject of Section 2.10.

2.2 The basic Operating Principles of a Lithium ion battery cell

In this section, the basic operating principle of a LiB cell will be presented. LiB cell is an electrochemical system that enables conversion of the chemical energy contained in its active materials into electrical energy and vice versa [10]. The electroactive species in the electrodes store the chemical energy. The energy is converted through electrochemical reduction and oxidation (redox) reactions, which occur at the electrodes [10] where the electrons are exchanged among the active species of electrode, transferring from outside circuit to the LiB cell.

The schematic of a LiB cell is shown in Fig.2.1. The LiB cell consists of four major components:

1. The positive electrode or anode where an oxidation reaction occurs during charge and it is termed as oxidizing electrode that picks up electrons from the outer circuit when current flows through the cell.
2. The negative electrode or cathode where a reduction reaction occurs during charge and it is termed as reducing electrode that provides electrons to the outer circuit.

3. The porous separator is a permeable membrane between a cell's anode and cathode. It is used to separate the two electrodes, preventing electrical short circuit while allow ions to travel through the electrolyte so that outer circuit can be closed for current flow. Its properties and structure will affect cell performance as well as cycle life and safety of LiB cell [11].
4. The electrolyte is liquid and serves as an intermediate carrier between anode and cathode, offering a medium for transfer of charge such as ions but it rejects electrons. By definition, the electrolyte does have leakage current, i.e. a tiny amount of electrons could hop through the bulk electrolyte at a very low statistical probability.

Fig.2.1. The Schematic of a LiB cell [12].

2.2.1 The discharging of a Lithium ion battery cell

The basic electrochemical operation of a LiB cell during discharge is shown in Fig.2.2. At discharged state, the external load is connecting to a cell, in which oxidation reaction occurs at the anode (negative electrode) where electrons are released and travel through the external load to the cathode (positive electrode), where reduction reaction occurs through the acceptance of the incoming electrons. The negative ions or anions flow to the anode and the positive ions or cations flow to the cathode. The transportation of these ions completes the close loop electric circuit.

The lithium cobalt oxide (LCO)/ highly-crystallized specialty carbon LiB cell is used as an example to study the chemical reaction on discharge as LCO is a most commonly used cathode material and the highly-crystallized specialty carbon is widely used for anode. The chemical reaction on discharge can be written as below:

Oxidation reaction occurs at anode, losses of electrons (anodic reaction)

The Lithium ions flow to the surface of active anode particles where they undergo the above electrochemical reaction and flow through electrolyte. The positive ions travel through the electrolyte via diffusion to the inter regions of active cathode particles where the reaction is shown as follows:

Reduction reaction occurs at cathode, accepts of electrons (cathodic reaction)

Fig.2.2. Basic electrochemical operation of the LiB (LCO/Carbon) cell during discharge.

2.2.2 The charging of a Lithium ion battery cell

During charge of a LiB cell, the current flows in the opposite direction and oxidation reaction occurs at the cathode and reduction at the anode, which is shown in Fig.2.3. The current flow is not spontaneous, but enforced through the voltage applied by the external charger.

Fig.2.3. Basic electrochemical operation of the LiB (LCO/Carbon) cell during charging.

The corresponding chemical reaction on charge is shown as follows:

Reduction reaction occurs at anode, accepts of electrons (cathodic reaction)

Oxidation reaction occurs at cathode, losses of electrons (anodic reaction)

The net reaction of charging/discharging of the LiB (LCO/Carbon) cell can be shown as follows:

2.3 Internal Characterization of Lithium ion battery cell

In order to develop a battery model, we need to understand the electrochemical phenomena and physical process occurring in a LiB cell, and take into consideration of both the thermodynamics and kinetic of the processes, therefore the specific physical and electrochemical phenomena will be reviewed in the this sections.

2.3.1 Electromotive force and Over-potential

By definition, a cell will stay at the equilibrium state when there is no external current flow through it, and the terminal voltage of a cell will be equal to its electromotive force (*emf*) when no external current flows through. It is an internal driving force in a battery to provide energy to application. According to the principle, the *emf* can be calculated from Nernst equation (or new developed equations derived from it). In electrochemistry, the Nernst equation is related to the reduction *emf* of a cell as the reduction of active mass concentrations at the electrode during the discharging, and its modelling includes maximum capacity of a cell after it is fully charged. This capacity is termed as cell maximum charge storage capacity throughout the thesis. The cell maximum charge storage capacity is the most important parameter need to be addressed for monitoring of cell performance as well as the study of cell aging. The detail of modelling the *emf* will be introduced in Chapter 3.

When a cell is charging or discharging, the current flows through it, and the terminal voltage of the cell will be different from its *emf* value. The illustration of estimated *emf*, over-potential and terminal voltage during discharging is shown in Fig.2.4. This is mainly due to polarization take places at the electrode/electrolyte interfaces resulting from the charge

transfer reactions in addition to another additional terms that are related the transport of electrolyte species in the bulk solution, which is likely small. The different between the terminal voltage and *emf* when the current flows is defined as the over-potential [10]. The determining factors for this over-potential will be shown in Chapter 3.

Fig.2.4. The illustration of estimated *emf*, over-potential and terminal voltage during discharging.

2.3.2 Double-layer capacitance

The charge on the surface of electrode will attract ions of opposite charge in the electrolyte and form the solvent dipoles, renders a formation an electrical double-layer with double layer capacitance as show in Fig.2.5 [10]. The amount of charge stored in this zone should not be ignored and depend on the electrode voltage [13].

Fig.2.5. Double layer capacitance [10].

2.3.3 Mass transport effect

Inside a battery cell, the ions are transported by the diffusion due to the gradient in concentration and the migration resulted from the electric field. The forces caused by these two mechanisms might not have the same directions, and the diffusion is mainly considered as main contributor for the mass transportation in most cases whereas, the migration is often impeded by. (the migration of solvated ions is often impeded by the coverage of solvent molecules.). Fig.2.6 shows where the diffusion occurs inside a cell.

Fig.2.6. Diffusion in porous electrode and in active mass of electrodes [13].

From the electrical point of view, the diffusion leads to an over-potential resulted from the changes of ion concentration at the location of charge transfer. A planar electrode in an infinite electrolyte reservoir is considered as an example of semi-infinite linear diffusion

as shown in Fig.2.7, and its impedance plot has a constant phase of -45 degree for the entire frequency range. Using a common diffusion circuit element describes this characteristic and it is called Warburg element as reported in the literature [13]. The impedance is provided by Jossen [13] as shown below:

$$Z_w = \frac{\sigma}{\sqrt{\omega}} - j \frac{\sigma}{\sqrt{\omega}} \quad (2.6)$$

Fig.2.7. Nyquist plot of semi-infinite diffusion [13].

where σ is the Warburg element coefficient, ω is the angular frequency of Z_w as well as the frequency applied to the system in an experiment and Z_w is the impedance of Warburg element.

In [13], the time domain Warburg element Z_w (Fig.2.8) is represented by pairs of RC elements as shown below:

Fig.2.8. The equivalent circuit symbol of a Warburg element [13].

Fig.2.9. Pairs of RC elements are used to represent for Warburg element [13].

2.3.4 Butler-Volmer element

The charge transfer rate of Li Ions will also determine the transfer resistance as electrons conduction in the electrodes is converted into ionic conduction at the interfaces. This is because the rate of the charge transfer determines how rapid can the conduction be continued, and hence it manifests itself as resistance to current flow. This rate is associated with the kinetic of the charge transfer, and it is determined by the Butler-Volmer equation [14]. The Butler-Volmer equation is considered as one of the most elementary principle in electrochemical kinetics of a cell. It describes how the changes of electrical current on an electrode depend on the changes of potential on the electrode, which is presented in the form of impedance. The equation of the impedance is given by [14]:

$$Z_{BV} = k \frac{Q_m}{Q_m - \int i dt} \quad (2.7)$$

2.4 The reliability of Lithium ion battery cell

In order to ensure LiB to have continuous functionality, the LiB reliability is receiving more attentions. However, the concept of battery reliability is rarely found according to the EI database, but its sub concept of diagnosis and prognosis of lithium ion battery has been vastly

investigated, and hence this section will focus on the prognostics and health monitoring of LiB.

The long life is expected by customers to last for the lifetime of the EV as it can help to save cost and reduce environmentally hazard impact resulting from the electrochemistry wastes such as cadmium, lead, mercury, copper, zinc, manganese, lithium, and potassium etc. from the batteries [3], those are considered as heavy metals will lead to soil contamination and water pollution. However, regardless of the advancement of the battery technology, battery functionality will gradually degrade over time due to battery cyclic aging, abusive operations and environmental impact [15-17]. The end of life (EoL) criteria for replacement in industry is about 80% of the maximum charge storage capacity as the degradation of capacity will follow a trend of exponential decay after the 80% threshold [16, 17]. Failures of Lithium ion batteries not only lead to the performance degradation and economy loss, but also the catastrophic hazardous events due to the extreme aging, abusive overcharge and high temperature [18-21]. Therefore, a systematic detection of the underlying degradation mechanisms is necessary, so that necessary actions can be devised to slow down or possibly stop the development of fault actions resulted from abusive conditions and battery aging. This is the essential goal of health monitoring. The definition of the battery prognostics is the time predictions when an internal component or battery system will not be able to fulfill their functional requirements in their actual life cycle conditions [16], and it ultimately determinates the remaining useful life (RUL) of the internal component or battery system [16, 17], where the RUL is defined as the time between the current moment and the moment of internal component or battery system fail in fulfilling its functionality requirements. Effectively applying the concept of health monitoring and prognostics to LiB cell can help to deal with users' concerns regarding safety issues. The understandings of the degradation mechanisms of the various components in LiB cell due to aging and abusive operations are essential to improve its cycle life for its various applications. Therefore there is a demand for approaches to investigate the underlying degradation mechanisms, and the modelling approaches are discussed in the next section.

2.5 Lithium ion Battery modelling

In order to investigate the underlying degradation mechanisms of LiB cell, the modelling approach is widely employed as *in situ* non-destructive techniques (NDT) that are necessary for prognosis and diagnosis [22]. Among the modelling approaches, there are different NDT methods which can be further divided into three groups. The first group is physical models where the chemical and physical processes within the cells are modelled. Specific degradation mechanisms such as degradation of the electrodes [23] and solid electrolyte interphase (SEI)

[24-26] were examined. The impact of each degradation mechanisms on the cell performance is investigated via linking the variations of the various components parameters in the cells to the cell performance. While their studies enhance our understanding of the degradation mechanisms in LiB, these approaches are computational intensive due to the presence of more than 15 parameters in the models generally [3]. Also, they cannot comprehensively model all the degradation mechanisms occurring during the battery life as they focus only on one or two degradation mechanisms. For example, Christensen et al.[27] developed stress-generation model to predict the fracture in the active material revealed the impact of mechanical stress occurring during the lithium intercalation process in Lithium Manganese Oxide (LMO) batteries. Ploehn et al.[28] developed a solvent diffusion model that related the formation of SEI and battery capacity loss. Ramadesigan et al.[29] provided estimation of the effective diffusion coefficient of Li-Ion in the electrolyte with cycle number. However, due to their microscopic approach, different manufacturing technologies, cell designs and raw materials used for fabrication of different batteries will result in different models, limit its practicality for industrial application.

Simplification is therefore necessary, and a second group, termed as mathematical models are developed. They can be further divided into empirical and statistical methods. The empirical methods are to predict estimators values such as capacity fade or resistance increase by fitting large amount of experimental data [22], and the accuracies of the estimations depend on both the amount and accuracy of the measurement data which can be costly [30]. The statistical methods also require large data set accomplished by complex measurements in order to determine all the possible interactions without knowing a-priori knowledge on the degradation mechanisms. Although they permit possible on-line estimation and are adjustable to different type of batteries, they take extremely long time to age batteries significantly in order to obtain the large data sets [22]. Overall, the mathematical models do not have direct physical relationship between the model parameters and the electrical characteristics of the battery, making them inappropriate for diagnosis purposes.

The last group is the electrical models, and they model battery cell using electrical equivalent circuit with the model parameters determined through different algorithms, namely least square algorithms (LSA), Levenburg-Marquardt algorithm (LMA) etc. Although LSA is a standard approach for best fit, it is a strong statistic algorithm when the population is linear, making it inappropriate for understanding the various aging mechanisms as the internal components of battery cell are not linearly independent. Thus, LMA is usually employed as a non-linear regression approach for on-line battery model parameter estimation. However, LMA can only provide the local minima [31], and thus the estimated parameters values may

not be the true values. While circuit analysis is generally faster depending on the algorithm used, not all the internal parameters in LiB are modelled individually by the equivalent circuits (and they are usually lumped together [32]), and the maximum charge storage capacity of LiB cell, which is the most important parameter for the study of LiB aging, cannot be modelled. This is because they do not model the degradation of the electromotive force (*emf*) of a cell. Also, they are not able to relate the degradation of the various cell internal components with each other, especially to the degradation of the maximum charge storage capacity (Q_m) of the cell. Thus, they are limited for LiB prognosis and diagnosis. Therefore, it is desired to develop a new model that is able to overcome the above-mentioned shortcoming of the various methods and also combine the strengths of the above-mentioned three groups of battery modelling at the same time. The detail development of the new proposed model is presented in Chapter 3. The performance indexes of a LiB cell that need to be monitored to ensure the safe operation and its lifetime are the SoC and SoH.

2.6 State-of-Charge definition and determination

SoC represents the amount of stored charge remain in a cell available for external usage, and thus it is related to the remaining operating time of the cell for a specific application and indicates the time to re-charge the cell. Accurate determination of SoC of a cell is very important for user convenience, LiBs' performance evaluation.

The determination of SoC of a LiB cell is a complex task as it will be affected by the battery type, battery manufacturing technologies, and the application in which the LiB cell is used. Let us now review the various SoC estimation methods.

Methods of SoC estimation can be classified into electrical, stochastic and thermodynamic methods [33]. In electrical methods, the commonly employed methods today are the Coulomb counting and open circuit voltage (OCV) methods. The Coulomb counting method integrates the current over time and thus the accumulated charge delivered can be obtained and used to estimate the SoC [34]. This method is simple and easy to be implemented, but its drawback is that its maximum capacity at the start of each discharge cycle must be known and this capacity degrades with prolonged charge-discharge cycle. Thus, this method often requires periodic capacity calibration where a full discharge of the cell will be performed, but such action can shorten the life of the battery significantly [35]. Another common method on the estimation of SoC is the OCV method [36], this method is not an online estimation as OCV can only be measured at open circuit. Also, OCV vs. SoC profiles can be very flat as shown in Fig.2.10, and thus large uncertainty can be generated by using OCV to estimate SoC.

Fig.2.10. OCV of lithium iron phosphate vs. SoC during discharging process [37].

As errors can occur during the SoC measurement due to noise and external disturbance, Kalman filter (KF) has also been applied to estimate the battery's SoC as a stochastic method. It has become popular due to its self-regulated and online nature. As the SoC pattern with discharging is not linear, extended Kalman filter (EKF) and sigma-point Kalman filter (SPKF) are introduced, and they have been used for the lithium polymeric battery (LiPB)-based hybrid electric vehicle (HEV) battery [38-40]. As all the stochastic methods require an accurate model of the battery's discharging behavior, various battery models [41] have been developed based on the battery electrical performances at the beginning, and these models are empirical instead of being derived based on the principle of electrochemistry, rendering their limited applicability to specific battery type without performance ageing being taken into account. Although there is a fully described model which takes into account of all the electrochemical processes [42], it is very difficult to implement in real time application as complex solution of simultaneous partial differential equations is needed.

Thermodynamics based method computes the entropy of a cell based on the variation of the terminal voltage and temperature, from which the cell's SoC can be deduced [43]. Unfortunately its in-situ online measurement is yet to be developed.

Among all the online SoC measurement methods, Coulomb counting method is the most intuitive and simple. In order to remove the necessity of calibration to determine its maximum charge storage capacity at the start of each discharge cycle, an in-situ method is proposed to provide an accurate online estimation of the maximum charge storage capacity, and this will be introduced in Chapter 3.

2.7 State-of health definition and determination

As cell continues its charge and discharge operation, the maximum charge storage capacity (Q_m) will become lower, due to various aging mechanisms as can be found in [40]. Hence, SoH is defined as Q_m (aged)/ Q_m (fresh) to represents the age of the cell. When the SoH of the cell reaches 60% [39, 44], it will be considered as dead, and no further discharging operation is to be performed to prevent fire hazard and other severe consequences.

The existing methods of SoH estimation are either the Coulomb counting or the impedance measurement methods.

The Coulomb counting method fully discharges a battery to a fixed low cut-off voltage, and integrates the current over time so that the maximum releasable capacity (Q_m (aged)) can be obtained and the estimate SoH is given by Q_m (aged)/ Q_m (fresh) [35]. This method works well for LiB [37], but its accuracy is subjected to several factors determined by the test conditions and environment such as the releasable charge is always less than the stored charge if the higher discharging C-rate applied that due to the effect of over-potential which can render energy loss and thus produces unreliable value [8, 16, 37]. This method is also very time-consuming as the measured value should be followed by a rest period of 24 hours after charge in a controlled environment, and a discharge of 0.1C to cut-off voltage [37] as recommended by battery manufacturers, and the entire testing cycle will take about two days. Meanwhile, the cell needs to be disconnected from its services. Thus, it is an offline estimation method and is energy wasteful [33]. The life of the cell will also be affected significantly with the cell frequently subjected to full discharge [35].

The impedance spectrum measurement is a widely used method in electrochemistry to characterize the dynamic behaviors of a battery [45]. It consists of applying sinusoidal excitations of wide range of frequencies on the input signal, and measures the impedance response of a cell. From the impedance measurement data, and together with an equivalent circuit for the cell, the parameters of the circuit model are obtained, and from which the SoH of the cell can be determined through some algorithms [46]. This method depends on the accuracy of the circuit model for the cell, and its measurement is done off-line as the determination of cell impedance is made by response to ac signal with pre-set amplitude (no DC current passing through). Also, it requires the EIS instrument that can be costly and not portable [33, 47].

As both the above-mentioned methods for the determination of SoH cannot be performed in dynamic operation, the estimation of the relevant parameters must be performed discretely

and thus Kalman-filtering method is needed to minimize the measurement noise and other external disturbances [48]. However, the required computational power for Kalman filter is high, and not suitable for real time SoH determination. Also, as both the existing methods of SoH determination are off-line, the on-line capability of the Kalman filter does not help to provide an in-situ real time SoH determination as battery pack requests. Using the recently developed method [47] to compute the maximum charge storage capacity of a cell directly from its discharging curve, regardless of the age of the cell, and it can thus determine the SoH of the cell in-situ after each discharge of the cell, and this proposed model will be introduced in Chapter 3. Besides monitoring the performance of LiB cell, a systematic detection of the underlying aging process also need to be taken into account so as to detect the underlying degradation mechanisms, take counter measurements to impede the developing faults and ultimately prevent the catastrophic failure from occurring, therefore the lifetime of battery can be improved.

2.8 The cyclic aging process of Lithium ion battery cell

In an effort to prolong the battery cycle life, comprehensive understanding of the underlying aging mechanisms that cause degradation in its electrical performance (i.e., Energy and Power fade) and electrochemical properties (i.e., Capacity loss and Cell Impedance increase) is necessary. As battery ages, the LiB cell could operate beyond its restricted safe and reliable operating window in terms of temperature and voltage, and this will render rapid degradation of battery performance and even result in catastrophic failures. With the understanding of the root causes from the analysis of underlying degradation processes, opportunity to slow down the development of fault and ultimately prevent the catastrophic failures from occurring can become possible, extending the lifetime and safety of LiB cell [17].

Unfortunately, the study of LiB cell aging is challenging as it is a complex system, and the process of its aging is complicated. Capacity fade and cell impedance increase do not originate from one single cause, but from several underlying processes which could depend on each other. This requires investigation of the various degradation processes in LiB cell at different time scales in order to determine the predominant degradation mechanisms at different times. Unfortunately, there are only few available literatures has been found on this topic.

Researchers have conducted extensive study on the degradation of various cell components in LiB cell after its prolonged cycling using many approaches, beside the modelling approaches we discussed above, there are some experimental approaches. The characterization techniques such as atomic force microscopy (AFM) [49], scanning electron microscopy (SEM) [50], and

transmission electron microscopy (TEM) [51], Raman spectroscopy [52] and other X-ray diffraction (XRD) and neutron techniques [52, 53] are used. These techniques are ex-situ and destructive because the investigations are conducted by cross-section the fresh and aged cells and comparing their positive and negative electrodes in order to reveal their morphological, electrical, and structural changes that occur during cycling [54]. They require complex instruments and must be done in controlled operating conditions that are both costly and not portable. Consequently, it is not possible for them to be implemented for prognosis and diagnosis purposes. Nevertheless, their investigation results provide wealth of information for degradation study of LiB which will be employed to find the main aging mechanisms of internal components of the LiB cell and these will presented in Chapter 5 and 6.

In order to improve the reliability of a cell, it always required to be able to find the underlying degradation mechanisms deal with fault propagation/degradations of components a cell. In this section, the review of cyclic aging mechanisms for LiB cell will be presented. The cyclic aging mechanisms take place at the anode and cathode very differently. Therefore, we will discuss them in two separate sections.

2.8.1 Dominate aging mechanisms of anode

2.8.1.1 Formation of the SEI Layer

The most commonly used materials for anode is graphite. The reaction between graphite and electrolyte lead to the changes at the electrode/electrolyte interface as shown in Fig.2.11. The graphite react with electrolyte through reductive electrolyte decomposition with irreversible consumption of Li-ions occurs at the interface between electrode and electrolyte, where a passive layer is grown up with decomposition product. This layer is named as Solid Electrolyte Interphase (SEI) [55], and it covers the anode's surface to protect the graphite from further electrolyte decomposition and also the possible corrosions. This process is mainly take place at charging state during the first few cycles which is normally called formation period [22, 56]. The most important function of the SEI to strip of the solution shell of Li^+ , and hence the intercalation occurs without exfoliation.

Fig.2.11. Aging mechanisms of negative electrode [22, 56].

2.8.1.2 The development of the SEI Layer

Sethuraman et al.[57] has reported the steep Li^+ surface-bulk concentration gradients at the surface of graphite occur during the early stages of intercalation processes, and the inherent increase of the Li_xC d-spacing tend to induce local stresses at the edges of graphene layers, lead to the breakage of C-C bonds. The exposed graphite edge sites react with the electrolyte to (re)form the SEI layer, and thus SEI is still continue to grow. This mechanism may cause sharply decrease in maximum charge capacity, and it is considered as surface disorder of the graphite electrode. This surface structural disorder is based on the famous Daumas-Herold mode which is proposed in 1969. They demonstrated that the intercalation/deintercalation of Li-ion take places through staging such as formation of metastable phases. The Li^+ intercalation process starts from a dilute stage-4 to a concentrated stage-1 compound. With charging/discharging cycling, the staging is developing from stage-4 back to stage-1, and within this process, the crystallization of the graphite electrode is damaged lead to surface structural disorder, and it promotes the development of SEI. This process occurs within the first several ten of cycles as reported in [57], depending on the quality of the graphite electrode. Fig.2.12 shows the development of SEI layer on the surface of carbon particles when the cell is cycled.

Fig.2.12. The development of SEI layer on the surface of carbon particle [58].

2.8.1.3 Degradation of the active anode material

In parallel to SEI formation and development, the solvent diffuses through the SEI, interacts with the graphite, and co-intercalates into the carbon structure to form a ternary graphite intercalation compound (GIC), which induces the graphite exfoliation and expansion of the carbon particle [58]. This mechanism will lead to the loss of active material of the anode, and subsequently cause the capacity fade.

2.8.1.4 Degradation of the composite electrode

In [56], the formation and development of SEI will cause the volume change of the active material of the anode, leading to gradual contact loss mechanically inside the composite electrode. This mechanism will result in an increasing in total cell resistance and subsequent capacity fading. The types of mechanical contact loss inside the composite electrode are shown below [56]:

- Between graphite particles
- Between graphite particle and current collector
- Between graphite particle and binder
- Between binder and current collector

2.8.2 Aging mechanisms of cathode

The degradation of the cathode mainly arises from the structure and phase change of the composite cathode, surface layer formation and development, and degradation of cathode inactive components.

2.8.2.1 Surface layer formation and development

There is very large debate for the existence of SEI layer on cathode. In [22, 55, 56], the SEI layer is also found created at the cathode/electrode interface, however, the thickness of SEI on LCO electrode is very thin in this initial period to be detected as reported by [22, 56]. Similar to the anode, the SEI is developing with cycling via electrolyte oxidation. In parallel to electrolyte oxidation, the metal dissolution will occur [56], causes loss of active cathode materials.

2.8.2.2 Structure change and transformation of composite cathode

As this work is focus only on the degradation of LCO electrode, the degradation mechanism for LCO electrode is reviewed here. Garbish et al.[59] has reported the off-stoichiometric compositions of $\text{Li}_{1-x}\text{CoO}_2$ is caused by the intercalation/deintercalation of Li-Ions in LiCoO_2 electrode. Consequently, transformation of hexagonal structure to cubic spinel structure occurs via an intermediate phase of H1-3. This structure transformation initiates at the LCO electrode/electrolyte interface, and continuous toward the interior of the electrode.

Moreover, the structural transformation of the LCO electrode will induce the transformation stress within the electrode. The resulting internal strain might cause spallation of the surface layer, reducing the volume for active Li intercalation, and hence a reduction in maximum charge storage capacity.

2.8.2.3 Degradation of cathode inactive components

According to Wohlfahrt-Mehrens et al.[60], the intercalation and de-intercalation of lithium-ions cause the changes in the molar volume in cathode materials, and the resulting mechanical stress will be introduced to the oxide particle, and subsequently to the cathode. The mechanical stress will be accumulated to a certain high value that can lead to degradation of inactive materials such as decomposition of binder, oxidation of conductive agent and corrosion of the current collector. That may result in a partial loss of contact within cathode.

Besides the extreme aging in a cell, the abusive operations can also cause the degradation of a cell, and reducing its lifetime. In addition, the abusive operations will also cause the safety issues. Therefore, we will focus on the safety of the LiB cell in the next section.

2.9 The safety of the Lithium ion battery cell

Battery safety is one of the main concerns for many battery-powered applications as various abusive operations can occur in a LiB cell during its operation, and these abusive operations

can cause the severe degradation, shortening the lifetimes of the battery and even catastrophic hazardous events such as fire hazard and possible explosion in some extremes cases [16-20, 50]. Fig.2.13 shows the Tesla LiB catches fire due to the abusive operation.

Fig.2.13. Tesla Model S catches fire at 4th Oct of 2013[61].

Among these abusive operations, the high temperature and overcharge are considered the most important safety issues that can cause the catastrophic failures. Let us now look at these two abusive operations more closely in this section.

2.9.1 Overcharge abuse of Lithium ion battery cell

The LiB cells will be overcharged due to the terminal voltage of the cell is not accurately monitored by the charging control system or the battery is aged, or the breakdown of the battery charger etc. The overcharge causes a drastic reduction in thermal stability of the cathode and decomposition of the electrolyte leading to swell, rupture, catch fire, explore at extreme condition [19, 20]. Fig.2.14 to Fig.2.17 shows the catastrophic hazardous events caused by overcharge abuse.

Fig.2.14. Pouch cell swelling due the overcharge abuse [62].

Fig.2.15. Cylindrical cell rupture due the overcharge abuse [5].

Fig.2.16. Pouch cell catch fire due the overcharge abuse [63].

Fig.2.17. Pouch cell explored due the overcharge abuse (Take by author).

Therefore, it is considered to be one of the major failure mechanisms for LiB. As reported in many literatures, the unwanted chemical reaction between cathode or anode and electrolyte will generate more heat with release of increasing amount of gas products. The remaining heat inside the cell will accumulated locally, and induces other exothermic reactions, casing the catastrophic hazardous events through thermal runaway [5, 19, 20]. Therefore, study the degradation mechanisms of the overcharge abuse with detailed investigation of each component of the cell is needed and it will be discussed in Chapter 4.

2.9.2 High temperature abuse of Lithium ion battery cell

The electric vehicles (EVs) and hybrid electric vehicles (HEVs) requires higher power density and energy density LiBs, as well as its ability to work over a wide range of temperature. Temperature is an important aspect of LiB, which has a significant impact on the performance, safety and cycle life of LiB cells. The high temperature leads to decrease in the stabilization of electrodes and electrolytes, and induces unexpected side reaction that generating more heat, and ultimately trigger thermal runaway similar as the overcharge abuse[64]. Beside these, the high temperature cycling will also lead to decrease in the stabilization of SEI layer, breakdown of electrolyte salt, change in charge transfer kinetics, and enhancement of surface reactivity [64-66]. Therefore, it requires a systematic investigation of the impact of temperature on internal components of LiB that can help to improve battery design to combat these failure mechanisms and thus the operational temperature range and its lifetime can be extended. Such work will be presented in Chapter 4.

2.9.3 High temperature cycling abuse of Lithium ion battery cell

Several researches on the effect of temperature on battery degradation of various cell components in LiB have been conducted recently. Markevich et al.[67] studied the degradation of carbon negative electrode at elevated temperature (up to 80°C); Gabrisch et al.[68] studied the degradation of thermally aged LiCoO₂ and LiMn₂O₄ cathode; Handel et al.[69] studied the thermal aging of electrolytes and investigated the degradation product from electrolyte and the influence of the housing material; Schalkwijk et al.[66] investigated the temperature effect on the degradation at electrode/electrolyte interface, and Ramadass et al.[70]. studied the capacity fade of Sony 18650 cells with LiCoO₂/Graphite electrode materials at room temperature, 45°C, 50°C and 55°C respectively. These work focus on the effect of temperature on individual component in LiB.

The study of temperature on the LiB cell as entire entity was done by Bodenness et al.[18] and Thomas et al.[71]. Using X-ray diffraction (XRD), Nuclear Magnetic Resonance, Scanning Electron Microscopy (SEM) and X-ray Photo-electron Spectroscopy, Bodenness et al.[18] studied the effect of high temperature on the aging process of electrode's binder, electrodes/electrolyte interfaces, and positive active material. Their results indicated a formation of a binder layer at the surface of the positive electrode and led to a poor Li-re-intercalation. They also showed several changes in the composition of the SEI, when the LiBs were cycled at 60°C and 80°C and 120°C respectively and observed the disappearance of carbonate species and the increase of inorganic species at the surface of negative electrode. The modification of the SEI composition layer is proposed as a cause for the capacity loss and

impedance increase at high temperature, in addition to the binder on the electrode surface of the positive electrode.

Thomas et al.[71] used scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), inductively coupled plasma (ICP), and measurements of electrode thickness to compare the aged and fresh materials of cathodes and anodes, and they showed morphological and structural changes of the electrodes during cycling. Further study on the chemical reactions of degradation was also done using X-ray diffraction (XRD). For the $\text{Li}_x\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2/\text{Li}_y\text{Mn}_2\text{O}_4$ blend cathodes and graphite/carbon anodes system (commercial 18650 cells), they showed that the capacity loss is mainly related to the SEI film growth on the anode, and the elevated temperatures accelerate the degradation of the cathode and formation of SEI on anode. The SEI was found to be the main contributor to the increase in the cell internal resistance.

While Bodness et al.[18] and Thomas et al.[71] investigated the aging of various cell components at elevated temperature and provided useful information for the aging of LiB cycled at high temperature, their techniques involve disassembly of battery and complex instrument that is costly and not portable, making their methods not possible to be implemented in some practical applications which required a real time investigation such as those demanded by the battery management system (BMS) of EV. An *in situ* non-destructive technique (NDT) will be better for the field applications. Also, the respective degree of contribution of each component in LiB cell to the overall degradation rate of LiB cell performance at different temperatures and how their respective degradation rates of each component in LiB cell manifest in term of the electrical performance of LiB cell are not presented. In fact, the studies on the effect of temperature on the aging of LiB are reported as described earlier, the comprehensively investigating of the effect of temperature on the aging rate of internal components in LiB cell is not reported, and thus this will be investigated in Chapter 5.

2.10 The reliability of battery packs in Electrical Vehicles

EVs are now commercial products, there are three main challenges that are being researched into, namely the limited driving range, long batteries charging time and high cost of the battery pack [2]. All these challenges are closely link to the applications of the Li-ion battery pack in EVs. The high cost of the pack in turn is related to the reliability of the pack because if the pack has low charge/discharge cycle life time, the replacement frequency of the pack will be high, and this will increase the operating cost of the EVs.

Currently, the battery pack of EV contains more than 100 Li-ion cells, and when one cell becomes aged, other cells will have to carry the load and this can cause other cells to degrade rapidly. On the other hand, due to the safety consideration, one cannot open the pack and replace the aged cells in the pack. Thus, when a few cells get aged, the entire pack will have to be replaced and sent to the workshop, and this increases the operating cost of EVs significantly and unnecessarily.

The above-mentioned situations will happen even with the use of reliable cells, and thus to reduce the unnecessary replacement of the pack and to prolong the life span of the pack, redundant cells are designed in the pack [72].

Several works reported the reliability study of battery packs, and they can be divided into the following categories of focus. The references quoted below are the typical papers selected for each category:

1. Thermal management of battery pack to improve pack reliability.

The temperature in battery pack is an important factor which affects the safety and reliability of the cells when the vehicle is running. Using thermal management in BMS can improve the reliability of the battery pack. In this category of research works, the heat generation model, the methods of cooling and air flow in the battery packs are investigated [73-76].

2. Cell redundancy and configuration to improve pack reliability.

In order to improve the reliability of the battery packs, different configurations of cells and the use of cell redundancy, coupled with appropriate designs of DC/DC converters are proposed [19, 77, 78]. However, no quantitative relationship between the pack reliability and redundant cells configuration is discussed.

3. Prognostic and health management for battery packs.

Since there are inevitable differences in the cells, a cell in battery packs could become overcharged and/or over-discharged. This could in turn reduce the lifetime of the packs. Generally speaking, the health state of an individual degraded cell is difficult to detect in a battery pack. To ensure safe driving, the battery packs are routinely replaced even though they do not exhibit any problems, but this will increase the maintenance cost for the drivers. Prognostic and health monitoring (PHM) technology is thus proposed to monitor the battery pack in the EVs. It can monitor the battery pack states during their operations, and extend their useful lives correspondingly [79].

A number of these small sizing rechargeable LiB cells are connected in series and parallel to form a battery pack for higher output voltage or current capacity [2]. With so many Li Ion cells in a pack, BMS is developed to ensure the safe operation of the cells in the battery pack [72, 73].

2.10.1 Battery Management System

Although the performances of LiB cell are superior, they are quite unforgiving when operating outside their safe operating area, with the consequences ranging from larger degradation rates to dangerous events such as fire hazard and explosion. Therefore, BMS is essential for the proper operation of a battery pack.

The BMS system is a system to measure and monitor a battery pack during its operation to ensure each cell in the pack is operating within its own safe operation region, including the prevention of its overcharging/overdischarging during operation.

Some of the functions in a BMS are the monitoring of current, voltage, temperature and SoC; SoH, remaining run-time information, battery cells balancing; over current protection; over and under voltage protection; and thermal protection [80]. Fig.2.18 shows a block diagram of a BMS.

The safety and reliability need to be addressed at cell, pack, and ultimately vehicle levels. The failure occurs at one level may trigger much more severe failure at an upper level . Therefore the safety and reliability of LiB at cell level is essential for the battery pack and SoC and SoH of the cells are the most important parameters for a BMS of battery pack.

Fig.2.18. A circuit block diagram of a BMS [80].

Chapter 3. A Practical Framework of electrical based On-line SoC Estimation of Lithium-Ion Battery

3.1 Introduction

As discussed in Chapters 1 and 2, in all battery operated devices and system that requires continuous operations, estimation of the battery SoC is important so that user can have a clue on the remaining useable time they can use further. Uncertainties in SoC estimation can cause the user to be highly conservative, but frequent re-charging can shorten the lifespan of the battery. On the other hand, if re-charging is done too late, an over-discharge may occur which also shorten the life of the battery. While Coulomb counting method (also called Coulometry) is useful to estimate the SoC on-line, its accuracy depends on how well the value of its initial maximum capacity is known. Presently, this capacity is obtained by the periodic discharge of the cell fully but this can introduce damage to the cell and shorten its lifespan. In this chapter, we develop an ECBE model for LiB cell based on the principle of electrochemistry so that the maximum charge storage capacity can be obtained simply through its discharging curve, i.e. the change in terminal voltage over time within a discharging cycle.

This chapter is organized in the following manner. Section 3.2 introduces the decomposition of the battery discharging curve and Section 3.3 discusses the experimentation and result analysis. Section 3.4 shows the application of the battery model and this chapter ends with a summary in Section 3.5.

As only the battery discharge curve is available during battery operation, the estimation will be done by extracting the information contained in the discharge curve. Thus decomposition of the curve into different components is necessary and it is the first step in the model development.

3.2 .Decomposition of battery discharging curve

The discharging terminal voltage contains much information about the battery's working state. It is well understood that the terminal voltage can be decomposed into the electromotive force (*emf*) and the over-potential.

3.2.1 Derivation of emf expression

emf represents the battery's ability to provide a certain voltage. It is the difference in equilibrium potentials between the two electrodes. emf is often measured as the open circuit voltage of the battery and is in ideal cases described by the Nernst's equation [10].

To model the emf voltage change during discharging, Coleman et al.[34] presented a linear relationship between the emf voltage and SoC based on their experimental data, but such linear relationship is applicable to a limited range of SoC, and it is empirical with the data set they have.

In fact, during discharging, the active mass concentrations at the electrodes reduces, render the reduction in its emf , and such active mass concentration reduction need to be taken into account to reflect the mechanism underlying.

Limit the work to the LiB cell of intercalation type reaction instead of displacement or conversion type reaction, the emf expression derived by Pop et al.[81] is employed, based on the Nernst Equation as given below:

$$V_{emf} = E_{eq}^+ - E_{eq}^- \quad (3.1)$$

where

$$E_{eq}^+ = E_0^+ - \frac{RT}{F} \left[\ln \left(\frac{x_{Li}}{1 - x_{Li}} \right) + U_j^+ x_{Li} - \zeta_j^+ \right] \quad (3.2)$$

$$E_{eq}^- = E_0^- - \frac{RT}{F} \left[\ln \left(\frac{z_{Li}}{1 - z_{Li}} \right) + U_j^- z_{Li} - \zeta_j^- \right] \quad (3.3)$$

However, and this model is not applicable to Lithium iron phosphate (LFP) battery as its discharge curve is too flat. Here R is the gas constant, F is the Faraday constant, T is temperature at the electrode in K , x_{Li} and z_{Li} are the mole fractions of Li^+ ion inside the positive and negative electrodes respectively. U_j^+ and U_j^- are the dimensional interaction energy coefficients in the respective electrodes, and ζ_j^+ and ζ_j^- are dimensionless constants accounting for the phase transition in the equilibrium potential of the two electrodes(The detail explanations can be seen in Ref. [81]). Superscripts $+$ and $-$ refer to positive and negative electrodes respectively. Subscript j is used to represent the phase change at the electrodes, and such phase change is found to occur at SoC below 20% (i.e. x_{Li} below 0.75

and z_{Li} below 0.25) for the Li-ion batteries with a $LiCoO_2$ electrode[81]. As the terminal voltage of LiB will drop abruptly when SoC is below 20% for the ageing battery [2] and this value vary with battery chemistry, the situation of SoC >20% is considered for practical consideration and hence the subscripts in Eqs.(3.1) to (3.3) are dropped in the subsequent equations.

If Q_m is the maximum amount of electrochemically active $Li+$ ion inside a battery, and the maximum capacities of the positive and negative electrodes are denoted as Q_{max}^+ and Q_{max}^- , then according to the work of Pop et al.[81],

$$Q_{max}^+ = m_1 Q_m, m_1 \leq 1 \quad (3.4)$$

$$Q_{max}^- = m_2 Q_m, m_2 \leq \frac{1}{2} \quad (3.5)$$

And Eq.(3.4-3.5) are applicable to certain battery chemistry and the initial value of m_1 and m_2 vary with battery chemistry. If Q_m is the maximum amount of electrochemically active $Li+$ ion inside a battery, and the maximum capacities of the positive and negative electrodes are denoted as Q_{max}^+ and Q_{max}^- , then according to the work of Pop et al.[81],

Here $m_1=1$ and $m_2=1/2$ for fresh *NMC* battery, and corresponds to the chemical reaction of the full cell as schematized below:

In Eq.(3.6) C_6 and $Li(NMC)O_2$ denote the composition of the anode and the cathode at the cell's discharged state respectively, whereas LiC_6 and $Li_{0.5}(NMC)O_2$ refer to the same electrodes composition at the cell's charged state.

Denote Q_0^- as the amount of $Li+$ ions inside the negative electrode in a fully discharged battery, and Q_z^- as the charge stored in the negative electrode for a given SoC, and consider the minimum SoC for practical application to be above 20% (in order to prevent over-discharge so as to maintain the battery lifespan), equation in [81] becomes

$$Q_z^- = Q_0^- + SoC \times \left(Q_m - Q_0^- - \frac{Q_{max}^+}{2} \right) = SoC \times Q_m \left(1 - \frac{m_1}{2} \right) \quad (3.7)$$

since $Q_0^- \ll Q_m$ and for $SoC > 20\%$.

But z_{Li} and x_{Li} are given as [81],

$$z_{Li} = \frac{Q_z^-}{Q_{\max}^-} \quad (3.8)$$

$$x_{Li} = \frac{Q_m - Q_z^-}{Q_{\max}^+} \quad (3.9)$$

Hence

$$z_{Li} = SoC \frac{2 - m_1}{2m_2} \quad (3.10)$$

$$x_{Li} = \frac{Q_m \left[1 - SoC \times \frac{2 - m_1}{2} \right]}{m_1 Q_m} = \frac{2 - SoC(2 - m_1)}{2m_1} \quad (3.11)$$

and

$$\begin{aligned} V_{emf} &= E_{eq}^+ - E_{eq}^- \\ &= E_0 - \frac{RT}{F} \left\{ \ln \left[\frac{[2 - (2 - m_1)SoC][2m_2 - (2 - m_1)SoC]}{[2m_1 - 2 + (2 - m_1)SoC][(2 - m_1)SoC]} \right] + \left[\frac{U^+}{m_1} - \frac{2 - m_1}{2m_1m_2} \times SoC \times (m_2U^+ - m_1U^-) \right] + \varepsilon \right\} \end{aligned} \quad (3.12)$$

where $\varepsilon = \zeta^+ - \zeta^-$, and $SoC = \frac{Q_m - \int idt}{Q_m}$

3.2.2 Over-potential

The discharge over-potential results from the voltage drop due to electrodes potential and the internal impedances of a cell, there are three types of over-potential models available for LiB, namely the electrochemical, mathematical and electrical models [82]. Electrochemical models typically are computationally time consuming and are thus not suitable for online estimation. Mathematical models use stochastic approaches or empirical equations, and have no direct relation between the model parameters and the electrical characteristics of the batteries. Electrical models are the most intuitive for use in circuit simulations and online estimation of

battery states. Within the electrical models there are three different categories, namely the Thevenin-based, impedance-based and runtime-based models.

Thevenin-based model assumes the OCV is constant, but the *emf* or OCV is decreasing due to the decrease in SoC as mentioned earlier, it cannot represent the actual battery operation. Impedance-based models are usually obtained from fitting complicated equivalent networks to their EIS spectrum and are thus work only for fixed SoC and temperature setting [83], and cannot be used to predict battery runtime. Runtime-based model assumes a constant discharge current, and is not suitable for practical electric vehicle applications. Chen et al.[83] attempted to combine the three electrical models, but the relationship of OCV with SoC is obtained through curve fitting. In fact, almost all the equivalent circuits are derived from the measurement data without consideration of the mechanisms occurring in the battery during discharging.

Fig.3.1. EIS spectrum of Panasonic's CGR18650CH LiB cell at various OCV under Lab's ambient temperature of 23 °C. The solid line in different colour represents the impedance at various OCV(with corresponding SoCs) [4].

Fig.3.2. EIS measurement and data acquisition system (Picture drawn by J.Xu at the EEE – Nanyang Technological University).

From the typical EIS spectrum of LiB cell as shown in Fig.3.1 and the electrochemical dynamics of charge transfer and diffusion in the battery, the simple Randle's model can be expanded as shown in Fig.3.3 to construct an equivalent circuit of a battery based on the understanding of the mechanisms within the battery during discharging.

Fig.3.3. Simple Randles' Model for Electrochemical cell [84].

Solartron model 1400A with a Frequency Response Analyser (FRA) and an electrochemical interface (ECI) are used for our EIS measurement shown in Fig.3.2. The battery cell is initially charged or discharged to the pre-set terminal voltage, and it is then withdrawn from the DC supply and rest for 2 hours in order to attain a stable terminal voltage. An AC voltage of 5 mV over a span of frequencies from 0.001 Hz to 100 KHz is then applied to the cell without any DC current through the cell. In the simple Randles' model [84] shown in Fig.3.3, the series resistance represents the ohmic resistance of the electrolyte and the electrodes, the RC circuit represents the charge transfer resistance R_{CT} and the double layer capacitor C_{DL} . One should also add the Warburg element as the mass transport of active mass is mostly

diffusion limited [13], and the Warburg element in this proposed model belongs to the case of semi-infinite diffusion layer as revealed from experimental EIS spectrum of the LiB cell studied, Thus the corresponding impedance of Warburg element is given by[13]

$$Z_w = \frac{\sigma}{\sqrt{\omega}} - j \frac{\sigma}{\sqrt{\omega}} \quad (3.13)$$

With the consideration of this mixed kinetic and charge transfer control, an equivalent circuit is constructed as in Fig.3.4 [41, 85]. Here the Warburg element is placed outside the C_{DL} because the element describes the diffusion of the ions in electrolyte while C_{DL} and R_{CT} are modelling the process at the electrodes.

Fig.3.4. Equivalent circuit with mixed kinetic and charge transfer control[4].

In a continuous discharging operation of battery, reduction in the active mass concentration at the porous electrode will occur. This reduction will change the *emf* due to the Nernst Equation which can only be applied for zero current, and this has been accounted for it in the previous section. This is a thermodynamics effect. The reduction in the active mass concentration also affects the kinetics of electrochemical reactions at the electrodes, and thus affects the over-potential [86]. Such effect can be taken into account by including the Butler-Volmer term in our model, and the corresponding impedance presented by this term is given by [14]

$$Z_{BV} = k \frac{Q_m}{Q_m - \int i dt} \quad (3.14)$$

where the symbols Q_m have the same meaning as in Eq.(3.12), and k is called the rate of constant of electrode reaction.

Since the Butler-Volmer term accounts for the process at the electrodes, Z_{BV} should be in series with R_{CT} , and therefore the equivalent circuit model for a LiB cell is as shown in Fig.3.5.

Fig.3.5. Equivalent Circuit Model based on EIS spectrum[4].

3.2.3 Temporal model of Discharge Curve

Based upon the understanding of the mass transport and electrochemical kinetics in the cell, and together with the EIS spectrum, an equivalent circuit of a cell as shown in Fig.3.5 can be constructed. This equivalent circuit is however a frequency approach. In actual online application, only the electrical characteristics in time domain is available, and temporal approach must be adopted if SoC information is to be extracted online from the discharge curve of a battery cell [41].

For temporal approach, the Warburg element is to be represented using R/C sub-circuit. Through the inverse Laplace transform of the Warburg impedance, it is found that the temporal expression of the Warburg impedance is as follows [87]:

$$Z_{\omega} = \sum_{n=1}^{\infty} \frac{1}{C_{\omega}} \exp \frac{-t}{R_n C_{\omega}} \quad (3.15)$$

and

$$R_n = \frac{8k_1}{(2n-1)^2 \pi^2} \quad (3.16)$$

$$C_{\omega} = \frac{k_1}{2k_2^2} \quad (3.17)$$

Where the k_1 and k_2 are the fitting parameters and can be identified from Spectroscopy. Thus, the temporal equivalent circuit of the LiB cell can be represented in Fig.3.6:

Fig.3.6. Temporal Equivalent circuit of LiB cell in this work[4].

The equivalent circuit shown in Fig.3.6 is however too complex for obtaining time domain relationship between the terminal voltage and discharging current of the cell. On the other hand, since the time constant due to C_{DL} (in the order of 10^{-3} milliseconds to 10 seconds) is much smaller than that due to the Warburg element and the Butlet-Volmer term (in the order of 1 second to 10^4 hours) as shown by Jossen [13], and the goal here is to obtain the value of Q_m , the initial exponential decay (just 0.03 seconds) of the discharging curve can be ignored, and the following circuit (without C_{DL}) is thus used to fit the latter part of the discharging curve and obtain the parameters values of the circuit elements using a non-linear regression method, LMA cum SA. SA [88] is employed to approximate global minima, and LMA is used to delivers rapid and accurate estimates of the global minima due to gradient-descent based algorithm [89]. With these algorithms, the fitting can agree well with the experimental results in around 0.3 seconds computed by i7 8-core CPU.

Theoretically, n should be infinity in order to have the RC circuit to represent the Warburg element. Practically, the value of n should be determined such that so long as the estimated values of the parameters in the equivalent circuit shown in Fig.3.7 converge. Thus, SA cum

LMA are applied to fit the circuit of Fig.3.7 and the actual discharging curve with different values of n so as to determine the required number of n and at the same time, to obtain the parameters values.

With the equivalent circuit and the *emf* expression, the terminal voltage of a LiB cell can now be written as follows:

$$V_{terminal} = V_{emf} - \eta \quad (3.18)$$

where V_{emf} is given by Eq.(3.12), and the over-potential η is given below, based on the equivalent circuit in Fig.3.7.

$$\eta(t) = i(t) \left(R_e + R_{CT} + k \frac{Q_m}{Q_m - \int_0^t i(\tau) d\tau} + \sum_{n=1}^{\infty} \left(1 - \exp\left(-\frac{t}{R_n C_w}\right) \right) R_n \right) \quad (3.19)$$

Fig.3.7. Modified Temporal Equivalent Circuit[4].

As this is a first attempt to relate the electrochemical processes in LiB to the components in electrical equivalent circuit, this work is limited to the following situation:

- The self-discharge behaviour of the battery is not considered. This can be considered only if the electrochemistry process of the self-discharging is well understood.
- The temperature of the battery during discharging is assumed to be constant. This will be considered in future work with experimental data. The model in this work

can easily be extended to include the temperature effect by making the components in the equivalent circuit to be temperature dependent.

- SoC is always above 20% for practical consideration. Extension to SoC all the way to 0% will be considered in future.
- No high discharging current (i.e. $<10A$) so that Peukert effect is insignificant.

3.3 Experimentation and Analysis

3.3.1 Testing

In order to obtain the discharging curves of LiB, the following experiments are performed. Panasonic's CGR18650CH LiB is selected for all the experiments, Table 3.1 shows the specification of the CGR18650CH LiB obtained from the manufacturer. The PSS series adopts nickel and the manganese in the positive electrode [4].

Table 3.1: CGR18650CH LiB specification[4].

Battery	Characteristics
Series	Panasonic Solid Solution (PPS)
Chemical System	LiNiMnCoO ₂ (NMC)
Nominal voltage	3.6V
Capacity	2,250mAh Typical
Charging Condition	CCCV 4.2V max.0.7 C-rate (1500mA), 110mA cut-off 25 °C
Discharging Condition	CONSTANT CURRENT, 3.0V cut-off 25 °C
Max discharge current	10A (25 °C)
Diameter(with tube)/Max.	18.6 (mm)
Height(with tube)/Max	65.2 (mm)
Approx.Weight	44 (g)

BaSyTec 32 channels Cell Test System (CTS) and BaSyTest Battery-Test-Software Version 5.6.1.20 are used for the experiments. The battery characteristics shown in Table 3.1 are added and stored in the BaSyTec's database, so that each battery under test can have its individual signature in the database. In order to obtain a good connection with lower contact resistance, spot welding machine is used to connect the battery cell to CTS. A general battery testing system is shown in Fig.3.8.

Fig.3.8. Battery testing system set-up for discharging test and the corresponding test data analysis.

A general set-up in the Test Control Software for all experiments in this work is programmed as follows:

- All fresh battery cells are firstly discharged to the cut-off voltage of 3V as specified in the battery specification.
- The charging process is carried out at a fixed charging rate of 0.7C in CC mode and a voltage of 4.2V in CV mode with a charge-termination current of 110mA, according to the company specification shown in Table 3.1. Since this work focus only on the discharging process, the charging condition is fixed for all cases.
- The terminal voltage and current of the cell are continuously monitored and recorded every 20 seconds to obtain sufficient number of data points used in the fitting process.
- In order to provide fast SoC estimation, 10 minutes is chosen as battery rest time after charging before the discharging experiments. The typical long rest periods reported in the literatures are not chosen since it is not suitable in practical applications such as EV [90]. In order to justify the use of such short rest time, the effect of rest time on the accuracy of SoC estimation will be discussed in the later part of this Section.
- All the experiments are performed under Lab's constant ambient temperature of 23°C.

Model verification and the determination of n using constant discharging current are to be carried out first. Specific time varying current will then be used once our model parameters and n values are determined.

3.3.2 Constant Discharging Current

The experimental discharge curve of Panasonic's CGR18650CH LiB with constant discharging current of 2C is shown in Fig.3.9. Table 3.2 lists out the best fitted parameters values for different n , and Fig.3.10 to Fig.3.11 shows the variation of the key parameters values vs. n . Here $m_1=1$ and $m_2=0.5$ as expected from a fresh battery.

To simplify the fitting, the emf expression in Eq.(3.12) is re-written as follows.

$$V_{emf} = \alpha + \beta - \frac{RT}{F} \left\{ \ln \frac{[2 - (2 - m_1)SoC][2m_2 - (2 - m_1)SoC]}{[2m_1 - 2 + (2 - m_1)SoC][(2 - m_1)SoC]} \right\} \quad (3.20)$$

$$\text{where } \alpha = E_0 - \frac{RT}{F} \left[\frac{U^+}{m_1} + \varepsilon \right], \text{ and } \beta = \frac{RT}{F} \left[\frac{2 - m_1}{2m_1m_2} \times SoC \times (m_2U^+ - m_1U^1) \right]$$

Fig.3.9. Comparison of Experimental and computed discharge curve of Panasonic's CGR18650CH LiB cell. Discharge curve of tested cell at 2C under Lab's ambient temperature of 23 °C until the terminal voltage drop to cut-off voltage of 3V[4].

Fig.3.10. Variation of R_1 and R_1C_w R_1C_w with different value of n [4].

Fig.3.11. Variation of $R_e + R_{CT}$ and Q_m with different value of n [4].

Table 3.2: Estimation of battery discharging model's parameters for different number of RC groups[4].

n	R_1 (Ω)	$R_1 C_w$ (s)	$R_e + R_{CT}$ (Ω)	Q_m (Ah)	m_1	m_2	k (Ω)	α	β	$rmse$ (V)
1	0.643	2298	0.0315	2.1812	1.0	0.5	0.0028	3.955	1.0989	0.0045
2	1.212	8915	0.0526	2.1480	1.0	0.5	0.0016	4.047	0.9737	0.0053
3	0.960	13075	0.0520	2.1216	1.0	0.5	0.0009	4.043	0.5155	0.0064
4	0.989	19211	0.0458	2.1102	1.0	0.5	0.0006	4.014	0.3761	0.0069
5	0.407	10837	0.0489	2.0716	1.0	0.5	0.0000	4.029	0.0001	0.0106
6	0.414	11606	0.0465	2.0848	1.0	0.5	0.0002	4.026	0.0002	0.0110
7	0.154	1653	0.0436	2.1060	1.0	0.5	0.0005	4.057	0.0000	0.0134
8	0.148	1518	0.0435	2.1127	1.0	0.5	0.0006	4.062	0.0000	0.0136
9	0.146	1473	0.0432	2.1157	1.0	0.5	0.0007	4.062	0.0000	0.0137
10	0.144	1445	0.0426	2.1178	1.0	0.5	0.0007	4.062	0.0000	0.0139
11	0.143	1426	0.0424	2.1194	1.0	0.5	0.0007	4.063	0.0000	0.0140
12	0.142	1409	0.0425	2.1209	1.0	0.5	0.0008	4.064	0.0000	0.0140
13	0.142	1400	0.0423	2.1217	1.0	0.5	0.0008	4.064	0.0000	0.0141
14	0.141	1387	0.0422	2.1229	1.0	0.5	0.0008	4.065	0.0000	0.0142
15	0.141	1380	0.0420	2.1236	1.0	0.5	0.0008	4.065	0.0000	0.0142
16	0.141	1376	0.0418	2.1242	1.0	0.5	0.0008	4.065	0.0000	0.0143
17	0.140	1369	0.0417	2.1249	1.0	0.5	0.0008	4.065	0.0000	0.0143
18	0.140	1369	0.0417	2.1249	1.0	0.5	0.0008	4.065	0.0000	0.0143

From Fig.3.10 to Fig.3.11 and Table 3.2, it can be seen that when n is small, the parameters values fluctuate, and they converge when n is greater than 15. Although $n=3$ is the commonly used in many literatures, the experimental results show that it is insufficient to ensure good accuracy in the estimation. In fact, the computation time for the RC group of $n=15$ is only 0.3 seconds which is insignificantly small. The final n and model parameters' values for the LiB studied are listed in Table 3, and it can also be seen that the fitting accuracy is very good from Table 3 and Fig.3.9.

Therefore, given a discharge curve of a LiB cell, the Q_m can be determined after each discharge cycle without the need to fully discharge the cell.

Table 3.3: Estimation of battery discharging model's parameters using 15 of RC groups for the Warburg elements[4].

n	R_l (Ω)	$R_l C_w$ (s)	$R_e + R_{CT}$ (Ω)	Q_m (Ah)	m_1	m_2	k (Ω)	α	β	$rmse$ (V)	$Accuracy$
15	0.141	1380	0.042	2.1236	1.0	0.5	0.0008	4.065	0	0.0142	0.9964

Since the proposed model is derived based on the electrochemistry processes in the battery discharging process, the proposed model is expected to provide the same experimental EIS spectrum with the parameters determined from the discharge curve. This also serves to further verify the accuracy of the proposed model.

C_{DL} and R_e are firstly estimated from the experimental EIS spectrum by using the equivalent circuit in Fig.3.4, and then together with the model parameters from Table 3.3, the Nyquist plot of the LiB cell at various frequencies with the battery terminal voltage at 4.0V (with a corresponding SoC) is computed. The comparison of the computed and experimental EIS spectrums is shown in Fig.3.12, and one can see a good agreement in the comparison.

Fig.3.12. Comparison of Experimental and computed EIS spectrum of Panasonic's CGR18650CH LiB cell at 4V OCV[4].

3.3.3 Rest time experiments

In order to obtain stable terminal voltage of LiB, a rest period of at least 12 hours after the battery is fully charged is specified, i.e. the battery can start to discharge only after the rest period. The purpose of the rest period is to regain the chemical equilibrium at the electrodes and compensates for the self-discharge after charging [37]. In order to mimic practical application, the experiments performed in this work are done, however, with the rest time of only 10 minutes as mentioned earlier. In order to examine the impact of such short rest time, the following rest time experiments are conducted.

A cell is discharged at 2C-rates with different rest time (10 minutes, 30 minutes, 1 hour, 6 hours and 12 hours) after it is fully charged. The respective discharging curves at different rest time conditions are used to estimate the model parameters, and the results are shown in Table 3.4.

Table 3.4: Estimation of battery discharging model's parameters at different rest time condition[4].

Rest time	R_1 (Ω)	$R_1 C_w$ (s)	$R_e + R_{CT}$ (Ω)	Q_m (Ah)	m_1	m_2	$rmse$ (V)	$Accuracy$
10 minutes	0.323	8252	0.0012	2.19	1.0	0.5	0.0120	0.9973
30 minutes	0.315	8259	0.0013	2.18	1.0	0.5	0.0122	0.9972
1 hour	0.315	8165	0.0011	2.17	1.0	0.5	0.0129	0.9969
6 hours	0.315	8187	0.0014	2.17	1.0	0.5	0.0116	0.9960
12hours	0.315	8184	0.0016	2.17	1.0	0.5	0.0114	0.9966

The battery is in a state of non-equilibrium when current flows in and out during charging and discharging. This non-equilibrium causes the average concentration of the reacting species in the bulk and at the electrode surface to be different. A mass transport effect is mainly responsible for this difference, and diffusion is commonly treated as main contributor for the mass transport effect [10, 13]. This diffusion results in locally changed ion concentration at the location of charge transfer reaction, therefore the reaction rate at the electrode is influenced by mass transport process [13, 42]. With longer rest period, the ion concentration at the electrodes decreases and distributes more uniformly into the electrolyte, and hence this implies a smaller Warburg coefficient. This is indeed observed in Table 3.4 where a decrease in the values of R_1 and $R_1 C_w$ can be seen. Also, due to the increased concentration of cation

at the cathode side after charging, the cell's capacity appears to be higher. As the cell rests, the capacity decreases to its stable value. In other word, the proposed model does reflect the non-equilibrium process in the battery cell in consistent with the electrochemistry.

From Table 3.4, it can therefore be seen that the values of the model parameters are indeed influenced by the length of rest period, but the impact is insignificant. For example, the different in Q_m estimation is less than 0.5%, and thus the inaccuracy of SoC estimation resulted from short rest period is very small. To speed up the experimentation, 10 minutes rest period is employed in all the experiments in this work.

3.3.4 Effect of Discharging Current

The previous experiments are performed at a constant discharging current of 2C. In most practical applications, the discharging current varies during operation, and additional experiments are therefore conducted with discharging current of 1C, 1.5C and 2C to examine the impact of the discharging current on the model parameters. The results are shown in Table 3.5.

Table 3.5: Model Parameters determined from discharging curves at different discharging currents[4].

Discharging Current	R_l (Ω)	$R_l C_w$ (s)	$R_e + R_{CT}$ (Ω)	Q_m (Ah)	m_1	m_2	$rmse$ (V)	$Accuracy$
2C	0.140	1360.65	0.000874	2.13	1	0.5	0.0144	0.996
1.5C	0.159	1533.19	0.000108	2.18	1	0.5	0.0148	0.996
1C	0.175	2045.91	0.000176	2.17	1	0.5	0.0153	0.996

Larger discharging current forces the diffusion of the ionic species to move faster in the electrolyte, and thus the measured Warburg element will be smaller as seen in Table 3.5. With larger discharging current, it is proposed that the charge stored in the negative electrode, Q_z^- in Eq.(3.7) will also be smaller as too many charges arriving at the negative electrode per unit time will render inefficient storage of charges. Therefore, z_{Li} in Eq.(3.8) will be smaller, and thus for a given m_1 , the apparent SoC will be smaller. But the total charge delivered as obtained from Coulomb counting method is fixed, and based on the SoC formulae, the apparent Q_m will be smaller with large discharging current as observed in Table 3.5.

Since discharging current affect the model parameters, the values in Table 3.5 are used to determine the discharge curve of the LiB cell with step change in the discharging current, with 30 minutes in between the step change. Comparison of the computation and experimental results are shown in Fig.3.13 and the maximum error in the battery voltage is 0.0808V with the root mean square error of only 0.0326V, which is very small. The larger deviation occur at lower battery voltage (or correspondingly lower SoC) is due possibly to the fact that the proposed model is developed with SoC limited to above 20%.

With the results shown in Fig.3.13, it can be seen that the proposed model can be extended to varying discharging current if the discharging current is discretized. As the model parameters are affected by the discharging current as shown in Table 3.5, one has to obtain the relationship of these parameters values with the discharging current levels. Experimental verification are being performed and the results will be reported in future as this work focus only the framework developed for in-situ online battery parameters estimation.

Fig.3.13. Comparison of our computed and experimental discharge curve for varying discharging current.

Fig.3.14. An implementation flow-chart of SoC estimation.

3.4 Application of the Battery Model

As mentioned earlier, the main problem with the Coulomb counting method is the knowledge of Q_m . Using the model developed in this work, one can determine the Q_m easily after every discharge cycle, and hence the estimation of SoC using Coulomb counting method can be accurate with the above flow-chart. The method is fast and accurate, taking approximately 0.3011 seconds, and can easily be implemented in most practical applications.

3.5 Summary

In this chapter, a practical electrical framework is developed for in-situ online battery parameters estimation, based on the electrochemistry principle in the battery during discharging. The model developed is able to provide the maximum charge capacity online after each discharge cycle without the need to fully discharge a cell which can shorten the lifespan of a cell.

Experimental verification of the model developed shows good agreement, both in temporal as well as frequency space in the form of EIS spectrum. Its application to time varying current during discharging is also shown through step current change with slightly different model parameters as they are affected by the discharging currents. Application to actual time varying current is possible through a database or calibration curves of the model parameters values at different discharging currents.

Chapter 4. Effect of abuse on electrochemistry in Lithium ion batteries

4.1 Introduction

As discussed in Chapters 1 and 2, the several abusive operations can happen to a LiB cell during its operation, and overcharge is considered as another common abuse that may lead to its severe degradation and even catastrophic failure via thermal runaway and subsequent fire hazard with possible explosion in extreme cases as discussed above. This becomes a primary concern for battery users, and hence a non-destructive method is required to access the damaging effect of the overcharging in order to decide if one should change the cell from the reliability and safety perspective. From battery manufacturers point of view, if one can identify the internal components in a cell that are most vulnerable to excessive cut-off voltage (COV), they can improve their cells so as to make the cell more robust against this abuse. Unfortunately, such a method is not available in the market.

Chapter 2 also shows that the operating ambient temperature of LiB must be well controlled as its performance, health and safety depends critically on the temperature. High temperature can lead to shortened lifetimes or catastrophic failure of the battery via thermal runaway similar as abusive overcharge .

While one can design a cooling system for the LiB system, a detail understanding of the temperature effect on each component inside LiB cell will be useful to improve its design and could extend its usability if its allowable operation temperature range can be extended. Unfortunately, such understanding is lacking.

The performance of each component inside a LiB can be determined through estimating recent developed ECBE [5] model parameters by using discharging curves(i.e. terminal voltage vs time during galvanostatic discharging) at different test conditions . Principle of optimization is employed for the determination where the target for optimization is the error between the computed voltage vs. time curve using the various values of the components and the experimental voltage vs. time curve. The goal is to have the minimum absolute error, i.e. zero. The computation in ECBE model is using SA to obtain approximated global minima. The near optimal values of these components are then used as initial guesses for the subsequently non-linear regression method for refinement of the values. The non-linear regression method employed is LMA as it is generally used for on-line estimation as mentioned earlier. The detail description of model computation can be found in Chapter 3, we

employ this model to examine the effect of excessive COV on the degradation of each component experimentally and examine how the performance of each component will be affected if LiB is operating at different temperature. The findings will help us to be one step forward in our understanding of the effect of the overcharge and thermal abuses on LiB cell.

This chapter is organized in the following manner. In Section 4.2, the quality decision for overcharged Li Ion Battery from reliability and safety perspective is presented, and the experimentation of overcharged tests is shown in Section 4.2.1. The results and analysis of overcharged LiB are provided. in Section 4.2.2. In Section 4.3, the effect of temperature on the electrochemistry in Lithium-ion batteries is investigated, and its experimentation is shown in Section 4.3.1. The results and analysis of the effect of temperature on the electrochemistry in Lithium-ion batteries is discussed in Section 4.3.2. Finally, summary is given in Section 4.4.

4.2 Quality Decision for Overcharged Li Ion Battery from reliability and safety perspective

4.2.1 Experimentation

In this work, the discharging curves of LiB cells are obtained experimentally. LiB coin cells (LIR2032) rated ~44mAh as shown in Fig.4.1. are used for experiments. The electrodes materials are graphite anode and lithium cobalt oxide (LCO) cathode, and it is one of the most commonly used cathode material in commercial LiB [91].

Fig.4.1. The coin cell (LIR2032) used in this work.

Arbin Instruments battery cyclers are used for the overcharging experiments, and the set-up for experiments in this work is programmed as follows :

- All fresh battery cells are firstly discharged to a cut-of voltage of 2.75V.
- They are then charged abusively at C/4-rate (i.e. 11mA) to COV between 4.2V and 4.9V (specification of max COV is 4.2)

- They are rested for 160s after charging for the their overvoltage stabilization
- For the discharging experiments, they were discharged at a constant current of $C/4$ to a COV of 2.75V at constant room temperature of 23°C unless otherwise stated.
- The terminal voltages and charging/discharging currents of the entire tested cells are continuously monitored and recorded at every 20seconds interval.

4.2.2 Results and analysis

Fig.4.2 shows the discharging curves of the LiB cells after excessive COV. From the discharging curves, we can see that the higher the COV, the longer the discharging time to reach 2.75V, except when the COV is above 4.7V. The rates of change of the terminal voltages for all cases are almost the same. Thus, this may indicated a benefit of having higher COV as cell can be used for longer time per charging.

Fig.4.2. Discharging curves of LIR2032 cells subjected to different charge cut-off voltages (COV).

However, it is reported that when cell is overcharged at excessive COV, it is indeed stressed, and its life will be reduced, and both the cell reliability and safety are compromised [37]. As LiB cells use volatile and flammable organic electrolytes, irreversible decomposition of the electrolyte may occur and this will trigger the gas evolution reaction at high COV, and leads the continuously swell and rupture of the cells eventually. The overcharged cell behaves as a resistor at high voltages, dissipating excess energy as heat. The locally accumulated heat due to increasing of cell resistance as a result of degradation at electrodes, leading to the catastrophic failure such as fire hazard and possible explosion of battery by thermal runaway at extreme conditions [19, 92-94]. These accidents resulted from the extreme COV as shown in Fig.4.3. This is attributed to the following degradation of the internal components in the LiB cells as revealed by our ECBE method as follows.

Fig.4.3. The accidents caused by extreme overcharging abuse.

Fig.4.4 shows that the maximum initial capacity of a cell increase with COV, and this explains the observed “enhanced” runtime of the discharging curves with higher COV as observed in Fig.4.2. This increase is a result of more lithium ions are extracted from electrode due to overcharging.

Fig.4.4. Maximum initial capacity vs. excessive COV.

The m_1 and m_2 represent efficiencies of anode and cathode in providing their stored Li ion for discharging respectively. The decrease in m_1 with excessive COV can be seen in Fig.4.5, and this implies that anode electrode is degraded when COV is excessive. However, the performance of the graphite electrode is insignificant against excessive COV as seen in Fig.4.6. Here we have to take note that graphite electrode is anode during charging, and as our results are extracted from discharging curve, the anode mentioned from the extraction using ECBE is referred to the LCO electrode.

Fig.4.5. m_1 of cobalt-oxide electrode (anode) vs excessive COV.

Fig.4.6. m_2 of graphite electrode (cathode) vs excessive COV.

For the interfaces, besides the double layer resistances R_{ct} (includes the SEI layer), the charge transfer rate of Li Ions will also determine the transfer resistance as electrons conduction in the electrodes is converted into ionic conduction at the interfaces. This is because the rate of the charge transfer determines how rapid can the conduction be continued, and hence it manifests itself as resistance to current flow. This rate is associated with the kinetic of the charge transfer, and it is determined by the Butler-Volmer equation [14]. The sum of ohmic resistance of electrode and charge transfer resistance decreases with COV and then increases for COV above 4.3 as shown in Fig.4.7. While the chemical kinetic explanation of the phenomena is beyond the scope of this work, the increase of $R_e + R_{ct}$ increases the localized heating of the anode due to Joule heating. Thus the localized temperature of anode is expected to be higher for higher COV above 4.3 V, and this could explain the degradation observed in anode as in Fig.4.5. This localized high temperature at anode could also be one of the reasons

for higher Q_m as the chemical reaction rate is going to be higher at higher temperature according to the Arrhenius relation.

As COV is further increased to beyond 4.5V, the localized high temperature can become so high that dissociation of the electrolyte next to electrode occurs, and the formation of solid electrolyte interface (SEI) is enhanced (this is also reflected as an increase in R_{ct}). The much higher localized temperature at the electrode is also evidenced by the higher rate of increase in Q_m with respect to COV when COV is above 4.5V. With formation of thicker SEI, the charge transfer at the electrode will be retarded, and hence one can see a sharp decrease in K values as shown in Fig.4.8 when COV is above 4.5V. This thick SEI also tends to protect the anode from the electrolyte and thus its degradation stop when COV is above 4.5V as shown in Fig.4.5. However, with thicker SEI, most part of the charging voltage will be dropped across the SEI, and the electric field in the SEI can become too high at COV above 4.5 V that causes it to breakdown, trigger the full cell thermal runaway [95]. It is to be noted that the above degradation happen with only one excessive COV charging. One could expect that with continuous excessive COV charging, the electrode resistance will increase continuously, and the localized temperature at anode will continue to increase. While we enjoy the seemingly longer runtime with higher COV, the cell reliability is degrading, and at some point in time, the high localized temperature can trigger some safety issue. In a mild case, we will see a swelling of the Li Ion cell in our hand phones due to larger thermal expansion, but in a severe case, fire and explosion can occur as have been observed in electric vehicles incident [96].

As our method can provide real time on-line non-destructive assessment of the internal components in a Li Ion cell, battery manufacturers can identify the weakest components that are most vulnerable to the excessive COV. This method can also be incorporated into BMS and once a cell is in an unsafe situation as defined by the R_e+R_{ct} , a bypass of the cell can be initiated according to the new technology of reliability balancing developed recently [97]. Thus our method is possible to help both battery manufacturers and BMS producers to improve their products quality over time and safety.

Fig.4.7. The sum of ohmic resistance of electrode and charge transfer resistance vs. excessive COV.

Fig.4.8. Charge transfer rate constant vs. excessive COV.

4.3 The effect of temperature on the electrochemistry in Lithium-ion batteries

Temperature is known to have significant impacts on the performance, safety and cycle lifetime of LiB cell. However, the detail effect of temperature on LiB cell is not known. In this section, we present the temperature effect of each component in LiB cell using the electrochemistry based model developed recently.

4.3.1 Experimentation

The LiB cell studied in this work is the prismatic cell from Sony. Its specification is shown in

Table 4.1. Fig.4.9 shows the photo of the cells used in this work.

The charge and discharge cycles were performed in CALCE. A standard constant current/constant voltage charging profile with a fixed current rate of 0.5C until the voltage reach 4.2V, followed by maintaining 4.2V until charging current dropped to below 0.05A, was used for all the cells under study. For the discharging experiments, all the cells were discharged at a constant current of 0.5C to cut-off voltage of 2.7V at the ambient temperature of 25 °C, 35 °C, 45 °C and 55 °C respectively. Fig.4.10 shows a typical example of the discharging curve of a cell. The red curve is computed by the battery model used in this work, and one can see good agreement between the computed and experimental discharge curve. Note here that the model is valid up to 20% SoC (80% depth of discharge (DoD)), and the initial fast discharging portion (the beginning portion of the discharging curve from 100% to 92% SoC) is excluded in the model.

Table 4.1: Sony Prismatic LiB specification is provided to distributors by manufacturers.

Battery	Characteristics
Series	Prismatic cell
Chemical System	LCO
Nominal voltage	3.6V
Capacity	1,350mAh Typical
Charging Condition	CCCV 4.2V max.0.5 C-rate (675mA), 50mA cut-off 25°C
Discharging Condition	CONSTANT CURRENT, 2.7V cut-off 25°C
Dimensions (mm)	6.6 x 33.8 x 50
Approx.Weight	28(g)

Fig.4.9. The prismatic cell used in this work.

Fig.4.10. Comparison of Experimental and computed discharge curve of the Sony prismatic cell, where the green solid line is the experimental discharge curve of testing cell and the simulated curve is the red dashed line.

4.3.2 Results and Analysis

4.3.2.1 Temperature effect on maximum initial capacity

Fig.4.11 shows that the maximum charge storage capacity increases with temperature. This increase is expected from enhanced electrochemical reduction-oxidation (redox) at anode and cathode as shown by [10, 37]. The increase is significant after 35 °C, and it slows down after 45 °C. The slowing down is due to the reduced activity of the anode as represented by the reduced value of m_1 as can be seen in Fig.4.12. The performance of the graphite electrode is stable against the temperature as seen in Fig.4.13. The detail mechanism of the reduced activity of the anode at high operating temperature remains to be explored, and it could possibly link to the enhanced formation of SEI and graphite intercalation compounds(GIC) of anode material at high temperature [98].

The significant increase within 35-45 °C in the maximum initial capacity seen from Fig.4. 11 imply one can extract more charges if the LiB is to be operated within the temperature range. It also indicates that if the Q_m is computed at lower temperature (below 35 °C), the coulomb counting method to compute the SoC will be underestimated, and this will always happen as the temperature of cell will increase during its operation.

Fig.4.11. Maximum initial capacity vs. temperature.

Fig.4.12. m_1 of cobalt-oxide electrode vs. temperature.

Fig.4.13. m_2 of graphite electrode vs. temperature.

4.3.2.2 Temperature effect on electrolyte

The diffusivity of active Li ion in the electrolyte increases with temperature [98], and this together with increased migrating number of active Li^+ that flow through the electrolyte due to the increase in Q_m will render a decrease in the apparent resistance of the electrolyte as shown in Fig.4.14. The effect of the larger increase in Q_m within 35-45 °C on the electrolyte resistance can be seen vividly in Fig.4.14.

Fig.4.14. Warburg element resistance vs. temperature.

The increase in Warburg element capacitance with temperature can be seen in Fig.4.15, and it can be explained by the increasing number of ionic charge stored (due to the increase in Q_m) in the two electrodes which serve as the two “plates” of the Warburg element capacitance. One can again see the correlation between the larger increase in Q_m within 35-45 °C and larger increase in the capacitance in the same temperature range.

Fig.4.15. Warburg element capacitance vs. temperature.

Fig.4.16. Warburg RC time constant vs. temperature.

Fig.4.16 shows the plot of the Warburg RC time constant, and one can see that increasing the temperature will increase the RC, and this implies that the response to the change in current deliver from LiB will become slower.

4.3.2.3 Temperature effect on electrode/electrolyte interface

Fig.4.17 shows the decrease of the electrodes cum electrode/electrolyte interface resistance with temperature. The decrease is not due to the increase in the Q_m as the decrease is not significant in the temperature range of 35-45 °C. In fact, this decrease is due to the change in the charge transfer rate constant at the electrode as can be seen in Fig.4.18 which shows the rate constant K vs. temperature. As increase in Q_m should be decrease in this series resistance within the temperature range of 35-45 °C (Fig.4.17) does not show a significant trend as in

Fig.4.11, one can see that the resistance shown in Fig.4.17 is mainly contributed by the interface resistance [98, 99].

The increase in K with temperature shown in Fig.4.18 is expected as higher temperature will enhance the charge transfer process [98, 99].

Fig.4.17. The sum of ohmic resistance of electrodes cum electrode/electrolyte interface resistance.

Fig.4.18. Rate constant vs. temperature.

Fig.4.19. Discharging curve of estimated *emf* and terminal voltage.

In examining Fig.4.14 and Fig.4.17, we can see that the total series resistance of LiB is mainly due to the interface resistance. As the over-potential of the cell increase with time as shown in Fig.4.19, and the total series resistance decreases with temperature, one can expect a significant increase in power dissipation within the LiB as given by V^2/R where V is over-potential and R is the series resistance. As R decreases significantly if LiB is discharging beyond 45°C , it is expected the internal accumulated heat and the temperature inside the LiB will be higher. Based on above analysis, the much smaller value of R will be obtained if the LiB is operated at a higher temperature level than 55°C and the results indeed has been found in [64], one can expected the internal heat and temperature of LiB will be much higher, and thus thermal runaway can happen beyond 55°C as indeed observed [64].

Detail investigation on the mechanism of the decrease in the electrode/electrolyte resistance beyond 55°C can help us to determine the on-set of thermal runaway, providing a good measure of the state of safety for LiB.

4.4 Summary

The seeming gain of LiB cell by charging to high COV has been identified, and it reveals the hidden issues associated with charging to high COV, with the use of recently developed ECBE battery model. And hence, the misconception of higher COV to enhance the runtime is clarified. With the proposed method, it is able to provide real time on-line non-destructive assessment of the internal components in a LiB cell to evaluate its safety and reliability with respect to this abusive overcharge. This proposed method provides a way to characterize the degradation level of each internal electrochemical component in LiB and the weakest material that is most vulnerable to the excessive COV can be identified ultimately. However, that the microscopic interpretation of the eight fitting parameters can only be speculative at this point.

The performance of each component inside LiB has been determined at different temperature with use of above mentioned method. The results show that the phase transition after 45 °C was identified as the main course of changes for each component of the LiB cell. The possible root causes of thermal runaway can be understood from the performance of each component estimated by using the proposed method. Therefore, it is possible to provide early warning of the battery thermal runaway and thus the safe operation of the LiB cell can be improved.

Chapter 5. Effect of Temperature on the Aging rate of Li Ion Battery Operating above Room Temperature

5.1 Introduction

In Chapter 4, the use of an ECBE in this work help to measure the effects of the desired temperature range of 25 to 55 °C on the aging behavior of cycled LiB. The Catastrophic failures due to excessive temperature variations especially high temperatures can cause a thermal runaway reaction that ignites a fire and consequently cause an explosion [64, 100]. Different operating temperatures will also affect the performance of LiB over time at different rates and therefore reduce its lifetime accordingly. Hence, implementation of efficient cooling system is being used for LiB system, but an understanding of the temperature effects on the degradation rate of each component inside LiB will be useful for improving the design of LiB system and extending the LiB's lifetime. The LiB's usability can also be expanded if its allowable operation temperature range is extended. Unfortunately, there are only few available literatures on this topic.

In this chapter, the performance degradation rate for each component in an LiB cell will be examined when it is operating at different temperatures from 25 to 55°C using the recently developed ECBE [4]. Unlike the various reported equivalent circuit models where the models are developed to fit the reported experimental data, ECBE model is developed based on the first principle of electrochemistry, and then convert the corresponding partial differential equations into circuit model. It is verified by the electrochemical impedance spectrometer (EIS) which is the most popular aging characterization tool for different type of LiB cells [4]. EIS employs electrical model to comprehensively understand the different aging behavior in electrochemical system, but its measurement can only be done off-line in frequency-domain with laboratory experiment that is usually inaccessible to field application. Also, complex solution of simultaneous partial differential equations is needed to determine the values of the different components in LiB using EIS [4]. On the other hand, ECBE allows the performance of each component inside LiB be determined real time through its discharging curve nondestructively (i.e., terminal voltage vs. time during discharge), making it suitable for field applications. As ECBE is derived based on the first principles, it can be applied to other cell systems.

The rest of chapter is organized as follows: The experimentation is given in Section 5.2, and the effect of temperature on the aging rate of the maximum charge storage capacity is shown in Section 5.3.1. In Sections 5.3.2 and 5.3.3 the effect of temperature on the aging rate of

electrodes will be discussed. Section 5.3.4 shows effect of temperature on the aging rate of the electrolyte. The overview of the temperature effect on aging rates is provided in Section 5.3.5. Summary is given in Section 5.4.

5.2 Experimentation

The LiB cell studied in this work is a prismatic cell from Sony. Its specifications are shown in Table 5.1, and Fig.5.1 shows a photo of the cell used in this work. The charge and discharge cycles of LiB cell were performed using an Arbin BT2000 battery testing system in the Centre for Advanced Life Cycle Engineering (CALCE) at the University of Maryland, College Park. The fresh cells are firstly discharged to the cut-off voltage of 2.7V as specified in the battery specification which corresponds to 100% depth of discharge. A standard constant current/constant voltage (CCCV) charging profile with a fixed current rate of 0.5C until the voltage reach 4.2V, followed by maintaining at 4.2V until the charging current dropped to below 0.05A, was used for all the cells under study. The cells are rested for 120s after charging for stabilization of its terminal voltage.

For the discharging experiments, four cells were discharged at a constant current of 1C to a cut-off voltage of 2.7V. One cell was cycled at 25°C, a separate cell was cycled at 35°C, a third cell was cycled at 45°C and fourth cell at 55°C. The terminal voltage and current of the cells are monitored on-line to ensure safety and recorded every 30s as input parameters for fitting process. The charging/discharging profile was repeated up to 260 cycles. Six particular cycle numbers, namely 1, 50, 100, 150, 200, and 250 were selected to investigate the cycled cells. Fig.5.2 shows a typical discharge curve of a lithium-ion cell. The red curve (the curve with data points on it) is computed using the ECBE battery model. SA [88] is used to obtain an approximated global minima of the ECBE model parameters, and non-linear regression method, LMA is employed to provide a rapid and accurate estimate of the local minima [105, 106]. Fig.5.3 shows the flow chart of the computation in ECBE model. With these algorithms, a good agreement can be seen between the computed and experimental discharge curves. Note that the ECBE model is valid up to 20% SoC, and the initial fast discharging portion (From 100% of SoC to about 95% of SoC) is excluded from the model. Here SoC is computed as Q/Q_m where Q_m is the initial maximum charge stored in LiB and it is computed using the ECBE model [4], and $Q = Q_m - \int_0^t id\tau$ as evaluated using the Coulomb counting method.

Fig.5.4 shows the ECBE model, where R_e is the combined ohmic resistance of the electrodes and the electrode/electrolyte interface, C_{dl} is the double layer capacitance, R_{ct} is the total charge transfer resistances at the electrodes, K is the charge transfer rate constant at the

electrodes embedded in the Butler-Volmer impedance (Z_{BV}), and R_n and C_w are the Warburg element in the electrolyte.

Fig.5.1. A prismatic cell used in this work. (Picture taken by M. Pecht at the CALCE - University of Maryland The red arrow indicates out direction from battery bottom to the top).

Table 5.1: Sony Prismatic LiB specification is provided to distributors by manufacturers.

Battery	Characteristics
Series	Prismatic cell
Chemical System	LCO
Nominal Voltage	3.6V
Capacity	1,350mAh Typical
Charging Condition	CCCV 4.2V max.0.5 C-rate (675mA), 50mA cut-off 25°C
Discharging Condition	CONSTANT CURRENT, 2.7V cut-off 25°C
Dimensions (mm)	6.6 x 33.8 x 50
Approx.Weight	28(g)

Fig.5.2. Comparison of an experimental and computed discharge curve (using ECBE model) of a Sony prismatic cell.

Fig.5.3. The flow chart of the computation in ECBE model [4].

Fig.5.4. Electrochemistry-based electrical model [4].

5.3 Results and Analysis

5.3.1 Effect of temperature on the aging rate of the maximum charge storage capacity

By investigating the maximum charge storage capacity (Q_m) and the effects of temperature variation and cyclic aging on the degradation of Q_m , valuable results may be generated to aid in the determination of appropriate usage conditions. Fig.5.5 shows that Q_m gradually decreases with an increasing number of cycles as expected. The degradation mechanisms for this irreversible capacity loss with cycle aging are found to be related to one or more of the following, namely structural changes of the insertion electrode, electrolyte decomposition, active materials dissolution, phase changes in the insertion electrode and passive film formation over electrodes and the current collector surface [58, 107].

To be specified, the degradation of an LCO electrode includes its structural changes during cycling, and surface film formation and its subsequent modification on the electrode [56]. For the graphite electrode, the major degradation mechanisms is the formation and growth of the film at solid electrolyte interface (SEI) due to electrolyte decomposition and the solvent co-intercalation process at the graphite electrode [56, 58]. A closer look at Fig.5.5 reveals that the higher the temperature, the larger the Q_m , except a drop at 55°C. Basically, temperature increases LiB's performance in a short term by increasing its capacity. But it also increases the degradation rate of Q_m as shown in Fig.5.5.

The increasing degradation rate of Q_m during cycling with temperature is because the degradation mechanisms of irreversible capacity loss are accelerated by elevated temperature, as reported in many studies [56, 58]. While the degradation mechanisms of different components in LiB, namely the electrodes, the electrolyte, their interfaces, and the separator, that result in the irreversible capacity loss are known, the order of important of these components' degradations is unknown. The investigation of this order of important is an objective of this chapter, and the manifestation of these degradations on the electrical performance of LiB is another objective of this chapter that has not been explored.

Fig.5.5. Maximum charge storage capacity as a function of temperature. The maximum charge storage capacity corresponds to different cycle numbers.

5.3.2 Effect of temperature on the aging rate of LCO electrode

The LCO electrode, which is the cathode during discharging, is made from LiCoO_2 (LCO) , the most commonly used material for composite electrodes [3]. Fig.5.6 shows the degradation of m_1 of an LCO electrode with cycling at different temperatures ranging from 25°C to 55°C . The definition of m_1 is the effectiveness of the LCO electrode in storing Li-ions [4].

The degradation of m_1 can be due to two mechanisms. One is the formation of surface film and its subsequent modification on the electrode, and another one is the structural/phase changes of the electrode. Zhang et al.[108] and Ramadass et al.[70] observed the formation of the surface film as a result of the oxidation at the electrode/electrolyte interface. Maher et al.[52] identified the structural and phase changes of the LCO electrode. The presence of surface film (also called SEI) lowers the reaction rate of both Li^+ insertion and de-intercalation [108], and the structural/phase change of the electrode from a hexagonal phase (less stable, but active) to a cubic phase or spinel structure (less active) also reduces the charge transfer rate. Hence, both mechanisms result in a decrease in the charge transfer rate (K) with cycling. This charge transfer rate shows the rate of Li^+ transport as it goes from electrode to electrolyte and from electrolyte to electrode [65]. The above-mentioned two mechanisms will reduce the transport rate, and this is indeed observed in Fig.5.7. Both will also increase the electrode's impedance, and again this is observed in Fig.5.8.

Fig.5.6.The aging of m_1 of cobalt-oxide electrode vs. temperature. The percentage degradations vs. cycle number at different temperatures are shown in the inserted Table.

Fig.5.7.The aging of rate constant vs. temperature. The percentage degradations vs. cycle number at different temperatures are shown in the inserted Table.

Fig.5.8. The total resistance of electrodes resistance and electrode/electrolyte resistance aging vs. temperature. The percentage degradations vs. cycle number at different temperatures are shown in the inserted Table.

In fact, two different degradation mechanisms are observed in Fig.5.7, namely the large initial drop in K value, followed by a slower decrease in the K value after 100 cycles. For the two mechanisms mentioned above, our current analysis cannot identify which of the two will occur first. On the other hand, a closer examination of Fig.5.7 shows that the rate of decrease of the K value after 100 cycles is not significantly affected by temperature when the temperature range is 35-55°C. This information could shed some light on the identification of the dominant mechanism in the later part of the cycling aging.

As the decrease in the value of K and the increase of the electrode impedance are due to the same mechanisms, their dependency on temperature are expected to be the same, and this can be seen in Fig.5.7 and Fig.5.8.

5.3.3 Effect of temperature on the aging rate of graphite electrode

Graphite is the most important anode electrode material in LiB as it has high capacity, flat potential profile and possess several advantages such as low cost, long life cycle, low volume expansion and safety [109, 110]. Fig.5.9 shows the degradation of the m_2 of the graphite electrode with cycling under various temperatures. The m_2 in the ECBE model represents the effectiveness of the graphite electrode in providing its stored Li-ions [4].

Fig.5.9.The aging of m_2 of graphite electrode vs. temperature. The percentage degradations vs. cycle number at different temperatures are shown in the inserted Table.

The degradation of m_2 is found mainly due to the formation of the SEI and its growth on the surface of the graphite electrode with cycling [66]. This SEI is developed through reductive electrolyte decomposition accompanied by irreversible consumption of lithium ions that leads to the irreversible capacity loss with the eventual release of gaseous products. Since this SEI layer is not completely permeable for lithium ions, the amount of Li-ions that can be provided from this electrode reduces with the continuous growth of the SEI at the graphite electrode [111]. This SEI will also result in a decrease in the charge transfer rate (K) and an increase in the cell impedance, as in the case of an LCO electrode. Another possible mechanism for the aging of the graphite electrode is that the solvent can co-intercalate into the carbon, causing the exfoliation of the carbon and the subsequent expansion of the carbon particles which form a ternary graphite intercalation compounds (GIC). The development of the (GIC) leads to the loss of active material, and it will also contribute to the irreversible capacity loss [58]. However, development of the GIC will not affect the charge transfer rate [58, 108].

If LiB is operating at a higher temperature, the growth rate of SEI will be increased, and this will impede the delivery of the Li-ions from the graphite electrode. Higher temperature will also enhance the formation of GIC. Therefore, both mechanisms will cause a larger degradation of m_2 at higher operating temperatures as shown in Fig.5.9, and this finding is consistent with Waldmann et al.[71].

A careful examination of the inserted Tables in Fig.5.6 and Fig.5.9 reveal that the degradation rates for both electrodes during cycling are quite similar at 25°C. But the degradation rate of

LCO electrode is affected more when the temperature is above 25°C. This implies that the rate of degradation of the LCO electrode is more temperature dependent than that of the graphite electrode, and this can also be seen from the larger increase in the slope of degradation for the LCO electrode.

The degradation rates of the electrodes increase with temperature, as discussed earlier. A larger jump in the cell resistance in the early stages of cycling is observed at high operating temperatures, as can be seen from 0 to 50 cycles in Fig.5.8. This is believed to be due to the increasing rate of SEI formation at the electrodes at higher temperature where Schalkwijk et al.[66] have elaborated on the mechanism of SEI formation at different temperatures. Beyond 50 cycles, binder decomposition, oxidation of the conductive agent, and corrosion of the current collector will also contribute to the impedance increase, causing another large increase in the resistance at high operating temperature, as can be seen from 100 to 150 cycles in Fig.5.8 [56].

5.3.4 Effect of temperature on the aging rate of the electrolyte

The aging of the electrolyte can be analyzed through the change in the Warburg element. This Warburg element models the electrolyte as a dielectric of a parallel plate capacitor with the two electrodes as the two plates of a capacitor. It models the electrolyte system as a series of R_w and C_w where R_w is related to the resistance of the electrolyte and C_w is related to the capacitance of the equivalent parallel plate capacitor.

As temperature increases from 25°C to 55°C, the diffusivity of active Li-ions in the electrolyte increases [98], and the Li-ion concentrations that flows through the electrolyte also increases [4] due to the increase in Q_m as a result of the enhanced electrochemical reduction-oxidation (redox) at anode and cathode at elevated temperature [10, 37], thus a decrease in the resistance of the electrolyte is expected when the cell is initially cycled, as observed in Fig.5.10.

Fig.5.10.The aging of Warburg element resistance vs. temperature. The percentage degradations vs. cycle number at different temperatures are shown in the inserted Table.

On the other hand, the Warburg element capacitance increases with temperature as shown in Fig.5.11. This can be explained by the increasing number of ionic charge stored (due to the increase in Q_m) in the two electrodes, i.e. $C = \frac{Q_m}{V}$, and for a given V , which is the voltage across the two terminals of LiB, increase in Q_m will result in an increase in C .

The degradation rate of R_n (i.e., the increase in the value of R_n) due to cycling is larger at higher temperatures. This may be due to the increasing degradation rate of the maximum charge storage capacity with cycling at higher temperatures. The increasing degradation rate of separators at higher temperatures is also a possible reason for the increase in R_n [71].

The decrease in the Warburg element capacitance with cycling can be seen in Fig.5.11. One plausible cause is the formation of SEI on the electrodes and separator that decrease the available surface of the active materials during cycling, i.e. the effective area of the equivalent parallel capacitor is reduced. Another possible reason is due to the formation of SEI layer which modifies the capacitor model of the electrolyte into two capacitors in series, where one of them is having the electrolyte as dielectric, and another one is having the SEI as its dielectric. If the relative permittivity of the electrolyte is ϵ_1 , and that of the SEI film is ϵ_2 , the effective capacitance will be $\left(\frac{\epsilon_2}{\epsilon_1 + \epsilon_2}\right)$, which is always less than 1. As temperature increases the SEI film will also grow faster and thicker, which directly correspond to the decreasing rate of capacitance when cycling and temperature increase.

Multiplication of $R_n C_w$ will result in a graph shown in Fig.5.12, and one can see that increasing the temperature will increase the rate of RC, and this implies that the response to the change in current deliver from LiB will become slower at high temperature.

Fig.5.11. The aging of Warburg element capacitance vs. temperature. The percentage degradations vs. cycle number at different temperatures are shown in the inserted Table.

Fig.5.12. The aging of Warburg RC time constant vs. temperature. The percentage degradations vs. cycle number at different temperatures are shown in the inserted Table.

5.3.5 Overview of the temperature effect on aging rates

From the above analysis, it was found that higher temperature will increase the degradation rates of all the components in a LiB, and this is consistent with the work of Waldmann et al.[71]. Careful examination of the Tables inserted in the Figures that show the degradation as a percentage of each component in a LiB reveals that temperature has the largest impact on the degradation rate of the Warburg element with cycling, and followed by the cell impedance. The degradation rate of the charge transfer rate is less impacted by the operating temperature.

As the operating temperature of LiB changes from 25 to 55°C, the degradation rate of maximum charge storage after 260 cycles is found to increase from 4.22% to 13.24 %. At the component level, for the same change in the operating temperature, the degradation rate of the Warburg element resistance after 260 cycles increases from 49.40% and 584.07% (Fig.5.10) which is the highest change; and that for the cell impedance ranks second, increasing from 33.64% to 93.29% (Fig.5.8). As for the charge transfer rate, the change in its degradation rate decreases from 68.64% to 56.19% (Fig.5.7).

From the change in the degradation of the various components, and compare with the change in the degradation of Q_m , which also represent the degradation rate of the SoH of LiB cell, we can conclude that SoH degradation is not affected much by the degradation of the Warburg element and cell impedance, as large changes in their values can only result in a small change in the Q_m . This seems to contradict some studies [70, 108] which state that higher cell impedance is the cause of charge capacity loss. The discrepancy may be explained as follows.

In most cases, Q_m is determined via Coulomb counting method where Q_m is represented by integrating the discharge current with respect to time until the LiB is fully discharged which correspond to the terminal voltage of around 3-2.5V, depending on the battery type. It is observed that with higher cell impedance, the Q_m so determined will be smaller, and this was attributed to the loss of energy to the cell impedance resulting in lesser Q_m to flow out of the LiB for integration [37, 58]. The loss of energy is in the form of i^2R . However, this would mean that the temperature of the cell increase slightly, and since Q_m increase with the cell temperature as we have observed earlier [4], such explanation is questionable. Furthermore, as it is evident that the determined Q_m (commonly called Q_d , the discharge capacity) using the Coulomb counting method is higher when the discharging current is smaller [37], and since lower discharging current will implies lower energy loss, the increase in the cell temperature will be smaller, hence Q_m should be decreased with smaller discharging current as compared to larger discharging current, and this contradict to the experimental observation.

We proposed that the observation of lower Q_m for cell with higher impedance may be due to larger internal voltage drop in LiB. Thus, when the external voltage of LiB is dropped to 2.7V where it is set as the voltage where all the stored charges are discharged, the actual voltage within the LiB is actually higher than 2.7V, and hence not all the stored charges in the cell are extracted to the external circuit. Consequently, the determined Q_m is smaller than the actual Q_m in the cell. With this explanation, when the discharging current is smaller, the internal voltage drop in the LiB will also be smaller for a given cell impedance, and thus the external 2.7V will be closer to the actual voltage within the LiB, implying that the remaining stored charges in LiB will be lesser when the discharging is stopped 2.7V, thus the determined Q_m is higher. In other words, the observation of higher cell impedance cause a lower Q_m is a measurement artefact instead of cause and effect relationship.

On the other hand, the determination of Q_m in this work is computed from the ECBE model, and hence the effect of internal voltage drop due to cell impedance will not affect our calculation. Fig.5.13 shows comparison of the Q_m determined using the Coulomb counting method at different discharging currents versus the Q_m determined using the ECBE model. It can be inferred that the trend of Q_d using the Coulomb counting method is very similar to the value determined using the ECBE model when the discharging current is small, indicating that the Q_m from ECBE model is close to the actual charge capacity of the LiB. The slight reduction in Q_m determined from the ECBE model, as seen in Fig.5.13, is due to the excessive charges reaching the negative electrode per unit time that render an inefficient storage of charges in the electrode as reported [4].

Fig.5.13. Discharge capacity (Q_d) measured by ETMS vs. maximum charge storage capacity (Q_m) estimated by ECBE.

From the above analysis, we can see that when SoH is degraded significantly, where $SoH = Q_m(current)/Q_m(fresh)$, the cell impedance would have been increased very significantly, and this will result in an increase in Joule heating of the cell and lead to thermal runaway and thus possibly create a fire hazard. Therefore, a limited allowable SoH degradation value should be imposed for safety consideration.

Also, as our method is able to detect the degradation of SoH in real time and simple measurement, it will be useful for LiB prognostics and diagnostics as illustrated in Fig.5.14. This information will also allow the determination of remaining useful life of LiB which will be reported in our future work.

Fig.5.14. An advanced battery management technology with prognosis and diagnosis capability.

5.4 Summary

In this chapter, the effect of temperature on cycling aging rate in LiB cell has been detected and characterized with the use of ECBE model which is treated as a non-destructive in-situ approach in this work. We determinate the performance of degradation rate of each component inside the LiB cell due to cycling aging at different temperatures. Based on the estimated results, it can be seen that the elevated operating temperature will enhance the degradation rates of all components in the LiB. The increasing degradation rates of the Warburg element and cell impedance are in particular sensitive to the operating temperature. Moreover, it is also showed that the increase in the degradation rate of irreversible capacity loss of LiB (i.e. SoH) with temperature is mainly due to the formation and modification of the surface films on the electrodes and to the structural/phase changes of the LCO electrode. The selection of the SoC range in the study fall in the “pseudo” solid solution regions in the LCO and GIC. Therefore, the model calculations and degradation phenomena remain stable in trends primarily due to lithium loss in the aging. The interpretations of the results are still required for the further experimental verification, and hence validity might not be universal.

Chapter 6. Internal probing into the degradation processes in Lithium-ion batteries under cyclic aging

6.1 Introduction

As discussed in Chapter 2, the cycle life of LiB is one of the most important characteristics for its use in HEV/EV as long cycle life can help to save cost and reduce environmentally hazard impact resulting from the electrochemistry wastes from the batteries [3].

In order to overcome the above-mentioned shortcoming of the various methods discussed in Chapter 2, the ECBE model is used to examine the electrochemical and physical processes in a battery cell, considering both the thermodynamics and the kinetic of the processes, and converts the partial differential equations of these processes into electrical equivalent circuit. Thus all the circuit elements and their values are associated with the individual internal components in the cell, including the *emf*. Their values are then determined experimentally from the cycling experiments of the cells. The principle of the ECBE model is as follows. During discharging, Li Ions are moving from anode to cathode, thus the thermodynamics equilibrium states of the electrodes are altered, according to the Nernst Equation. The change of the states depends on the health of the electrodes which can be characterized by m_1 and m_2 for cathode and graphite anode respectively, according to the work of Pop [81]. The physical meaning of m_1 is the effectiveness of the cathode in storing Li ions [6], and m_2 represents the effectiveness of the graphite electrode in providing its stored Li ions [6]. This alteration of the thermodynamics equilibrium states renders a decrease in the electromotive force (*emf*) of the cell as discharging continues as represented in Fig.1. For fresh electrodes, $m_1=1$ and $m_2=0.5$. During prolonged charging and discharging cycling, the electrodes will degrade, and both m_1 and m_2 will reduce. Consequently, m_1 and m_2 represent the degradation states of the electrodes, and the decreasing rates of m_1 and m_2 represent the degradation rates of the electrodes.

Besides the decreasing in the *emf*, the impedance of a cell will cause a voltage drop as discharging current flows through, and the voltage drop is termed as over-potential. Looking at a general cell structure, there are several components that account for the over-potential, namely the electrodes' resistances, double layers at the interfaces of electrode/electrolyte, and the electrolyte itself. For the interfaces, besides the double layer resistances (include the SEI layer), the charge transfer rate of Li Ions will also determine the transfer resistance as electrons conduction in the electrodes is converted into ionic conduction at the interfaces.

This is because the rate of the charge transfer determines how rapid can the conduction be continued, and hence it manifests itself as resistance to current flow. This rate is associated with the kinetic of the charge transfer, and it is determined by the Butler-Volmer equation [14].

On the electrolyte resistance, it consists of two parts. Since resistance basically represents how easy ions can travel in a medium, and in electrolyte, Li Ions are traveling via diffusion, the diffusion rate through the electrolyte itself and through the separator are the governing factors in determining the resistance. This diffusion is characterized by the Warburg element in the cell as shown by the electrochemical impedance spectrometer (EIS) [4, 13], and its corresponding time domain representation will be a series of RC network as shown in Fig.6.1[13].

With the above understanding, the over-potential is thus modelled as a series of electronic components as shown in Fig.6.1. The physical significance of each component can be summarized in Table.6. 1. As the model associates each component with the electrochemical activities in the cell, and this model is thus termed as (ECBE). For detail derivation of the model, readers can refer to the work reported in [4].

Table.6. 1: Physical significance of each electronic component in the ECBE model [4, 7].

S/No	Component in the Model	Physical significance with respect to a cell
1	R_e	Electrodes' resistances
2	R_{CT}	Charge transfer resistance
3	C_{dl}	Double layer capacitance
4	Z_{BW}	Butler-Volmer impedance
5	Z_w	Warburg element impedance

The values of each component can be determined from a discharging curve. Principle of optimization is employed for the determination where the target for optimization is the error between the computed voltage vs. time curve using the various values of the components and the experimental voltage vs. time curve. The goal is to have the minimum absolute error, i.e. zero. To ensure global optimization, adjustment of these components values are first done

using SA [88] to obtain an approximated global minima. The near optimal values of these components are then used as initial guesses for the subsequently non-linear regression method for refinement of the values. The non-linear regression method employed is LMA as it is generally used for on-line estimation as mentioned earlier. The flow chart for the determination of the components values is shown in Fig.5.3

From Table.6. 1, we can see that if m_1 is decreasing, it represents that cathode is degrading, likewise for m_2 and anode. Table.6. 2 summarized the implications of the value of each component with respect to the degradation in the cell.

In other word, this ECBE model combines the strengths of the above-mentioned three groups of battery modeling, and it enables us to study the degradation of the internal components of the cell in-situ and non-destructively. It allows us to determine the cell degradation characteristics in time-domain. ECBE model is able to comprehensively investigate the on-going degradation processes of electrodes, electrolyte and electrode/electrolyte interface during battery utilization simultaneously without complex instrument as in EIS, making it ideal for battery in-situ prognosis and diagnosis. The applications of ECBE in determining the degradation mechanisms can be found in [5-7, 101].

As ECBE can provide the values of the individual internal components of LiB in-situ and non-destructively, it will be used to investigate the evolution of the internal components degradation as LiB is cycled in this work.

Table.6. 2: Implications on the cell degradation from the components values.

S/No	Components	Implications
1	m_1	Its reduction represents degradation in cathode's effectiveness in accepting Li ion. Examples of degradation are the structural change of the LCO electrode from a hexagonal phase (less stable, but active) to a cubic phase or spinel structure (less active) [59, 102], formation of surface film as a result of the oxidation at the electrode/electrolyte interface [70], degradation of inactive materials in LCO electrode [60].
2	m_2	Its reduction represents degradation in anode's effectiveness in delivering Li ion. Examples of degradation are formation of surface film and its subsequent modification on the graphite electrode [66], contact loss of active materials on the graphite electrode due to volume charges with cycling [56].
3	k in Z_{BW}	Its reduction represents degradation at the electrodes' interface that affect the charge transfer kinetics. Examples of degradation are the formation of SEI builds up significant mass-transfer and charge transfer barriers at the graphite electrode/electrolyte interface [57], structural change of the LCO electrode from a hexagonal phase (less stable, but active) to a cubic phase or spinel structure (less active) etc.
4	$R_e + R_{CT}$	The increase in the value represents degradation of the electrodes materials as well as interfaces. Examples of degradation are the formation of SEI and increase in thickness of the SEI film that increase the total cell resistance, structural transformation of the LCO electrode [59], Lithium plating [103], degradation of inactive materials in LCO electrode [60] and contact loss of active materials on the graphite electrode due to volume charges with cycling [56].
5	R_n in Z_w	The increase in the value represent slower diffusion rate that can be due to reduced conductivity of the electrolyte [7] or the degradation in the separator that reduce the ionic passage rate through the separator [104]. Examples of the degradation are the decrease in Q_m renders a reduction in the active ionic species through the electrolyte [7], Lithium plating [103], chocking and closure of pores in the separator by decomposition products, spallation products from electrodes and disintegrated carbon particles [104].
6	C_w in Z_w	A change in this value represent a change in the capacitance represented by the two series connected capacitors, one is anode and separator, and another one is separator and cathode. Examples of degradation are Lithium plating [103], chocking and closure of pores in the separator by decomposition products, spallation products and disintegrated carbon particles [104].

Fig.6.1. Electrochemistry-based electrical model [4].

The various parameters values in the ECBE model shown in Fig.6.1 are obtained from a discharging curve and best fitting via Simulated Annealing [88] to obtain an approximated global minima, followed by LMA to obtain the local minima, which is now the global minima as the search region is now narrowed and around the actual global minima. As ECBE can provide the values of the individual internal components of LiB in-situ and non-destructively, it will be used to investigate the evolution of the internal components degradation as LiB is cycled in this work.

6.2 Experiments

6.2.1 Selection of LiB Cells

Lithium ion battery coin-cells (LIR 2032) with nominal capacity of 44mAh are selected for the cyclic experiments in this work. The electrodes materials of these cells are graphite anode and lithium cobalt oxide (LCO) cathode. The specifications obtained from the manufacturer are shown in Table.6. 3. Fig.6.2 shows a photo of the cell used in this work.

Fig.6.2. Coin cell used in this work (Picture taken by K. Maher at the ERIAN – Nanyang Technological University).

Table.6. 3: LIR2032 LiB specification is provided to distributors by manufacturers

Battery	Characteristics
Series	LIR 2032
Chemical System	Lithium cobalt oxide (LCO)
Nominal voltage	3.6V
Capacity	44mAh Typical
Charging Condition	CCCV 4.2V max. 1/6 C-rate (7.33mA), 0.05mA cut-off 25 °C
Discharging Condition	CONSTANT CURRENT, 2.75V cut-off 25 °C
Max discharge current	88mA (25 °C)
Diameter(with tube)/Max.	20 (mm)
Height(with tube)/Max	3.2 (mm)
Approx.Weight	3.1 (g)

6.2.2 Test procedures

Arbin BT2000 with installed MITS Pro Software (Battery Cyclier) is used for the experiments. Fresh battery cells are first discharged to the cut-off voltage of 2.75V as specified in the battery specification which corresponds to 100% depth of discharge (DoD). A standard constant current/constant voltage (CCCV) charging protocol with a fixed current rate of C/6

until the voltage reach 4.2V, followed by maintaining the voltage at 4.2V until charging current dropped to below 0.05mA ($\sim C/900$), is used for all the cells under study. The cells are rested for 160 seconds after charging for stabilization of their terminal voltages.

For the discharging experiments, the cells are discharged at 20mA constant current (a galvanostatic regime $\sim C/2$ rate) to the cut-off voltage of 2.75V. The terminal voltages and currents of the cells are monitored on-line to ensure safety and recorded every 20 seconds. The charge/discharge cycles are repeated up to 1000 cycles and terminated when the cell reached $\sim 80\%$ of Q_m , which is considered as end of life (EoL) criteria for replacement [112]. Discharging curves at eleven cycle numbers, namely 1, 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 are selected for detail investigations. In particular, after each 100 cycles, cells are transferred to Electrochemical Thermodynamics Measurement System instrument (ETMS, Battery Analyzer BA-2000®, from KVI PTE LTD, Singapore) to determine cells' discharge capacity [52]. All the cyclic aging tests are conducted at constant laboratory ambient temperature of 25°C unless otherwise stated.

6.3 Characterization of cyclic degradation in LiB

Three principle effects of LiB cycle aging are identified in literatures, namely capacity fade, open circuit voltage (OCV) decrease, and cell impedance raise [22, 58, 113]. As Q_m is directly related to the OCV through Nernst Equation [81, 114], in this work, only capacity fade and cell impedance rise are considered, and the mechanisms underlying of these effects will be examined by investigating the variation of the internal components in LiB through ECBE model parameters.

6.3.1 Maximum charge storage capacity

The maximum charge storage capacity (Q_m) rated in ampere-hours(Ah) quantified the ability to deliver available electric charge stored in a fully charged battery, and it is also a leading health indicator for a battery where SoH is defined as Q_m (aged)/ Q_m (fresh). The SoH is one of the most important battery state parameters for BMS to estimate battery performance and remaining useful life (RUL). Thus, accurate estimation of Q_m is critical to in-situ SoH monitoring and battery diagnosis [16, 17, 32].

The most common determination method of Q_m is Coulomb counting method. The value obtained is termed as discharge capacity (Q_d), to differentiate it from the actual Q_m . According to recommendation of battery manufacturers, Q_m should be measured in such a way that the cell is first charged to 4.2V at a rate of 0.1C followed by a rest period of 24 hours

in a controlled environment, and a discharge of 0.1C to cut-off voltage (COV) of 2.75V [17, 37]. The long rest period is to ensure the battery stays at the equilibrium state completely, and low C-rate is aim to maintain at this equilibrium state and eliminate the effect of over-potential which can render energy loss and thus produces unreliable value [10, 37]. However, this recommended method is too time-consuming and it will take about two days to complete one cycle, making it impractical in many applications.

In order to provide fast measurement, higher discharging currents are experimented, and the discharge capacities (Q_d) of the coin cells with two discharging rates are shown in Fig.6.3. After the first cycle, the Q_d measured at C/2 rate is 36.58mAh and the Q_d measured at C/4 rate is 43.07mAh. The Q_m for the cell from manufacturer is 44mAh, and thus the accuracy of C/2 is lower as compared to C/4, and the discharge capacity measured using C/2 rate has a consistent lower value as compared to that in the case of C/4 as can be seen in Fig.6.3. This is attributed to the loss of energy to the cell internal impedance, resulting in lesser Q_m to flow out of the LiB for integration [37]. The loss of energy is in the form of $i^2 R$, where i is the discharging current and R is the total cell resistance.

The difference in Q_d between the cases of C/2 and C/4 increases as battery ages as seen in Fig.6.3. This is expected as the total cell resistance increases with cycles due to cell's internal components' degradation. It also indicates that the effect of total cell resistance on Q_d determination at C/4 is quite small. In other words, the discharging C-rate plays an important role in determining the discharge capacity (Q_d) of LiB. Hence capacity fade as reported in most literature may not be related to the degradation of Q_m . The capacity fade may appear to be more severe due to the degradation of the total cell resistance. Basically, the lower the discharging current, the more accurate the Q_d is in estimating Q_m , and the value will be higher [4, 7].

Fig.6.3. Discharge capacity vs. cycle number. Measured by ETMS at $\frac{1}{2}$ and $\frac{1}{4}$ discharging C-rate.

Although the Coulomb counting method is simple and easy to implement, the process is time consuming (as discharging current has to be small), and the cell needs to be disconnected from its services. Furthermore, full discharge of LiB cells can shorten their lifespans significantly.

As ECBE can provide estimation of Q_m from just one discharging curve, and it requires neither full discharge only up to 20% SoC (as shown in Chapter 3) of a cell nor a disconnection of the cell from its service [4, 32], it is useful for on-line monitoring of battery health condition for realistic applications. However, the accuracy of the Q_m estimation using ECBE must be established before it can be used for diagnosis.

The comparison of the measured Q_d at C/4 and Q_m estimated by ECBE is shown in Fig.6.4. After the first cycle, the Q_m estimated using ECBE is 43.955mAh, which is even closer to the manufacturer data. Note that the method of ECBE in estimating Q_m is not affected by the cell impedance [7]. Also, the difference in the cell capacity determination between Q_d measured at C/4 and Q_m estimated using ECBE does not increase with cyclic aging of the cell as can be seen in Fig.6.4, indicating that the effect of internal impedance on cell capacity determination is eliminated in both cases. The slightly lower value of Q_d measured at C/4 is believed to be due to the cut-off voltage of 2.75V. As the cell is not actually discharged completely yet at 2.75V, some charges remain in the cell, and hence the measured Q_d is slightly lower than the actual value [7]. On the other hand, lower the cut-off voltage could induce safety concern.

From the above discussion, C/4 is found to be good enough for the Coulomb counting method as measured by ETMS for this coin cell. The Q_m estimated from the ECBE method can be considered as the real Q_m of the cell without the effect due to internal components in LiB and their degradations. Thus, Q_m estimated from ECBE is useful to examine the degradation of cell capacity without compound effects from the degradation of the internal components in LiB.

Fig.6.4. Capacity profile vs. cycle number. Measured by ETMS at 1/4 discharging C-rate and estimated by ECBE model.

6.3.2 Cyclic aging effect on Q_m

The degradation of Q_m of the LiB cells used in this work is shown in Fig.6.5. Approximately 20.56% reduction in Q_m from its initial capacity (43.955mAh) over 1000 cycles can be observed. A careful examination of Fig.6.5 shows that the degradation rate of Q_m is changing over the 1000 cycles, indicating a possibility of five different degradation mechanisms in LiB which denotes five different regions as shown in Fig.6.5.

Fig.6.5. Maximum charge storage capacity vs. cycle number. As the data points are obtained at 100 cycle interval, Region I degradation could also be according to the dashed line due to the explanation in the text. This dashed line is also consistent with the studies reported in several literatures [10, 22, 37, 55, 56].

To investigate these mechanisms in each region, the degradation of each internal component in the battery is examined by computing their values using ECBE model from their discharging curves over the 1000 cycles. The values are shown in Figures 6-11. **Error! Reference source not found.** summarizes the percentage changes of these components values in these five regions. All the internal components in LiB cell degrade over the charge-discharge cycling, and among the various internal components, graphite electrode and Warburg capacitance are relative stable within these 1000 cycles. On the other hand, LCO electrode and Warburg resistance degrade the most, especially during the first 200 cycles. In this work, the possible degradation in each of these five regions will be explored, using the known degradation mechanisms of the various internal components as reported in the literatures.

Fig.6.6. m_1 of cobalt-oxide electrode vs. cycle number. m_1 denotes the effectiveness of the LCO electrode in storing Li-ions [4, 7, 8].

Fig.6.7. Rate constant vs. cycle number. This is the charge transfer rate, and it shows the rate of Li^+ transport as it goes from electrode to electrolyte and vice versa [65].

Fig.6.8. Total cell resistance vs. cycle number. Total cell resistance is the sum of electrodes resistance (R_e) and electrode/electrolyte resistance (R_{CT}).

Fig.6.9. m_2 of graphite electrode vs. cycle number. m_2 denotes the effectiveness of the graphite electrode in providing its stored Li-ions[4, 7, 8].

Fig.6.10. Warburg element resistance vs. cycle number.

Fig.6.11. Warburg element capacitance vs. cycle number.

Table.6. 4: The percentage change of the model parameters in each region.

Region	I	II	III	IV	V	Total
Q_m (%)	10.5	1.8	3.18	3.37	1.71	20.56
m_1 (%)	3.45	5.27	3.84	0.57	2.29	15.4
m_2 (%)	0.30	0.16	0.24	0.10	0.41	1.21
k (%)	0.98	2.4	0.49	1.48	0.5	5.85
$R_e + R_{CT}$ (%)	9.94	10.63	0.21	6.88	2.46	30.12
R_n (%)	18.89	9.06	10	10.61	7.53	56.12
C_w (%)	0.667	2.77	0.78	0.57	1.18	5.967

6.3.2.1 Region I

In region I, Q_m drop significantly in the first 100 cycles, losing almost 10.5% of its initial Q_m .

The large decrease in Q_m can be attributed to the degradation of both electrodes. For the LCO electrode, Li-Ions are being extracted from and reintercalated into LiCoO_2 lattice during charge and discharge cycling, causing off-stoichiometric compositions of $\text{Li}_{1-x}\text{CoO}_2$. As a result, transformation of hexagonal structure to cubic spinel structure occurs via an intermediate phase of H1-3. This transformation nucleates at the interface of LCO electrode and the electrolyte, and continuous toward the interior of the electrode as shown by Gabrisch et al.[59]. As the spinel phase has lower electroactivity, a decrease in the m_1 value is observed as in Fig.6.6, and this layer of spinel phase is also known to affect the charge transfer coefficient [59], in consistent to the decrease in the k value as shown in Fig.6.7. Since such transformation is progressing via the intermediate phase, its impact on the decrease in Q_m and the increase in k value are gradually severe, being less impactful at the first few cycles.

A more dominate degradation in Region I, especially in the first few cycles, is attributed to the Solid Electrolyte Interphase (SEI) formation at the graphite electrode/electrolyte interface. It is known to occur at the first few charge/discharge cycles due to the side reaction through electrolyte decomposition [22, 52, 56, 58, 115]. Although all LiBs are subjected to 1-2 cycles before shipment where a thin layer of SEI is formed at the electrode/electrolyte interface, the steep Li^+ surface-bulk concentration gradients at the surface of graphite occur during the early stages of intercalation processes, and the inherent increase of the Li_xC d-spacing tend to induce local stresses at the edges of graphene layers, lead to the breakage of C-C bonds. The exposed graphite edge sites react with the electrolyte to (re)form the SEI layer, and thus SEI is still continue to grow [57]. This formation of the SEI consumes active Li material [22, 116], reducing the Q_m , follows possibly the dashed line in Fig.6.5.

In fact, the formation of SEI is a result of the surface structural disorder of the graphite electrode. This surface structural disorder is according to the Daumas-Herold model. Daumas and Herold [117] in 1969 proposed that Lithium-ion intercalation and deintercalation in graphite occurs via staging, *i.e.*, formation of metastable phases. The electrochemical intercalation of Li^+ in graphite proceeds from a dilute stage-4 to a concentrated stage-1 compound. Upon prolonged charge/discharge cycling, the staging proceeds from stage-4 to stage-1, and during this process, graphite crystallites are affected and the resulting structural disorder promotes the formation of SEI. As the staging proceeds, the formation of SEI slow

down, and when the graphite electrode reaches stage 1 compound, very little SEI growth will occur at the graphite electrode. This happens within the first several ten of cycles [57], depending on the quality of the graphite electrode. The above-mentioned phenomenon explains our findings in Region I where m_2 decreases (Fig.6.9). The growing SEI builds up significant mass-transfer and charge transfer barriers at the graphite electrode/electrolyte interface [57], leading to an increase in the total cell resistance (Fig.6.8) and a decrease in the rate constant k (Fig.6.7).

As the growth rate of SEI is slowing down after the first several ten of cycles, the consumption of Li Ion is also reduced, and then the degradation rate of Q_m after approximately 30 cycles is reduced (Fig.6.5). Since the increase in the thickness of the SEI film is now at a reduced rate, the rate of increase in the total cell resistance should also be reduced. Thus, the decrease in degradation rate of the total cell resistance between 100-200 cycles could indicate the slowing down of the SEI growth at the graphite electrode/electrolyte interface.

Therefore, the impact of SEI at graphite electrode/electrolyte interface is gradually weakening while the impact from the structural transformation of the LCO electrode is gradually dominating, resulting in a continuous decrease in the rate constant k as shown in Fig.6.7.

This sharp decrease in the actual Q_m increases the effective charge/discharge rate for the same charging and discharging profile. In other words, the charging voltage to 4.2V that is supposed to correspond to the 100 percent of SoC is indeed overcharged, and this leads to higher over-potentials at the electrodes that can initiate side reaction that consume cyclable lithium through electrolyte decomposition [70, 118]. The reaction product of this decomposition can begin to choke the small pores in the separator. Similar phenomena occur when the cut-off voltage is at 2.75V that is actually over-discharged to the LiB due to much smaller Q_m .

The large decrease in Q_m also renders a reduction in the active ionic species through the electrolyte, and thus an increase in the apparent diffusion resistance as reflected in the Warburg resistance as shown in Fig.6.10. Another factor for the increase in the Warburg resistance is because some pores in the separator are filled with the electrolyte decomposition products as mentioned earlier.

The decreasing number of ionic charge stored (due to the decrease in Q_m) in the two electrodes and the decrease of the effective areas for ionic movement (as some pores are

choked) during cyclic aging results in a decrease in the Warburg capacitance as shown in Fig.6.11, according to the capacitance equations $C = \varepsilon A / d$ and $CV = Q$ where ε is dielectric constant, A is the effective area for ionic movement, d is the thickness of separator, V is the voltage across the electrodes and Q is the total ionic charge stored. In the present case, A decreases and d hardly decreases as the thickness of the SEI layer on graphite electrode is very small, therefore C decreases. Also, Q decreases, and thus the apparent C decrease for the same voltage across the electrodes.

From the above analysis, the degradation of capacity of LiB in the early part of Region I should be mainly related to the losses of Li-ions as a result of the SEI formation at the graphite electrode, and the latter part of Region I is related to the structural transformation of the LCO electrode.

6.3.2.2 Region II

In region II, Q_m decreases at a smaller rate, losing only 1.8%.

The effective overcharging and discharging continue due to the decrease in Q_m , however, as the surface structural disorder of the graphite electrode is in stage 1, the growth of the SEI layer at graphite electrode is becoming very slow after Region I, hence a very small degradation rate of m_2 is observed.

On the other hand, structural change of the LCO electrode from a hexagonal phase (less stable, but active) to a cubic phase or spinel structure (less active) as described by Garbisch et al.[59] is becoming dominate at the latter part of Region I, and in this region, the spinel structural change grow into the interior of the LCO electrode. Garbisch et al.[59] found that near complete transformation occur between 300-400 charge/discharge cycles, which coincide with Region II where a large degradation in m_1 (Fig.6.6) and the corresponding large degradation in the rate constant (Fig.6.7) are observed. This transformation is also known to reduce the conductivity at the interface [59] and hence an increase in the charge transfer resistance (R_{CT}). The conductivity of the spinel structure also has lower value, resulting in an increase in R_e , and hence the total cell resistance as in Fig.6.7. The significant slowing down of the total cell resistance increase after 400 cycles could indicate that the spinel transformation is near to completion.

On the other hand, it is interesting to observe that such a large change in m_1 and rate constant are found to have insignificant impact on the degradation of Q_m . The underlying reason could

be similar to the work reported by Broussely [119] who showed that electrolyte reduction on the carbon anode is the most important contributor to capacity loss for cell calendar aging. Further investigation is needed for verification.

The smaller decrease in Q_m also results in a smaller degradation rate of the Warburg resistance as shown in Fig.6.10.

The structural transformation of the LCO electrode introduces the transformation stress in the electrode. The resulting internal strain might cause spallation of the surface layer [59], reducing the volume for active Li intercalation, and hence a reduction in Q_m . Given that the reduction of Q_m in our case is small, the spallation is believed to be not severe. However, with the slight reduction of the surface layer and the LCO particles from the spallation of the surface layer that fill in some of the pores in the separator, the thickness of the separator (d) will increase slightly. This slight increase results in a reduction of the Warburg capacitance as d is in the denominator of the capacitance formulae.

Therefore, the main degradation in Region II is the structure transformation of the LCO electrode.

6.3.2.3 Region III

In this region, the degradation rate of Q_m increases again, and 3.18% of Q_m is further lost.

This is believed to be due to the Joule heating at the electrodes as a result of the high total cell resistance which is now close to 20% increase from its initial value as shown in Fig.6.8. Since the total cell resistance is mainly due to the SEI film at the graphite electrode and at the interface of the spinel structure of LCO and the electrolyte, most heat will be generated at the electrodes, and the temperature at the electrodes will increase significantly as the heat generated cannot be easily dissipated from the battery to the outside environment.

With such high temperature, the reduction reaction on the surface of carbon electrode proceeds at a faster rate and more gaseous products from the higher reduction rate are formed in a short period of time as shown by Ning et al.[58]. This high temperature also causes evaporation of the electrolyte, and thus the pressure build up by these gases can stretch or damage the SEI film, renders Li^+ and electrolyte to go through the enlarged cracks or newly formed cracks and react with the internal lithiated carbon particles [58]. Hence, new electrodes surfaces are exposed, and the situation is similar to the very first few cycles. In fact, the pattern of the degradation rate of m_2 in region III is similar to that in Region I as can be

seen in Fig.6.10. However, the degradation rate of Q_m and k are lesser in Region III as compared to Region I because the total exposed electrodes surfaces without SEI are much smaller in this region as compared to Region I.

The transformation of the remaining hexagonal phase in LCO electrode to cubic phase continues under high temperature, resulting in a continue degradation of m_1 . The mismatch between the two phases that produces transformation stress is now higher due to the high temperature as differential thermal expansivities of the two phases also come into play.

On the other hand, the conductivity of the electrolyte increases at the LCO electrode due to high temperature, and thus the total cell resistance has only a small degradation rate.

After 500 cycles, the transformation is believed to have completed, with high stress in the spinel structure. This is because a change in the degradation rate in m_1 is observed after 500 cycles. The increase in the degradation rate of m_1 after 500 cycles is believed to be due to the higher stress in the spinel structure that results in surface spallation. This stress is further increased as the intercalation and deintercalation of Li Ion into LCO electrode are accelerated by the high temperature. As a result, the thickness of the LCO electrode decreases, leaving a gap between the electrode and separator. As LCO particles are spalled out from the electrode, they choke more pores in the separator, and hence the Warburg resistance increases. This is further enhanced by the viscoelastic creep that close up more pores [120]. The viscoelastic creep of the separator is enhanced by the high temperature in the cell, closing up more pores [119], increases the Warburg resistance. The reduction in the surface layer of LCO and the expansion of the separator due to more choked pores and high temperature increases its thickness d , and hence a decrease in the Warburg capacitance is observed (Fig.6.11).

Hence, the main degradation mechanism in this Region is the Joule heating and the cracking of the SEI films at the graphite electrode and the spallation of surface layer at the LCO electrode.

6.3.2.4 Region IV

In this region, the degradation rate of Q_m further increases, losing additional 3.37%.

The phenomena of the SEI formation at graphite electrode mentioned in Region III continues up to 700 cycles. Due to high temperature and thus high reaction rate, the formation of SEI will also be faster. Thus, the thickness of the SEI will be larger, and the graphite electrode is

now better protected, and hence its degradation rate reduces after 700 cycles as indicated by the degradation of m_2 .

With the reduction in the volume of LCO as a result of surface spallation, and together with the high temperature, the stress and strain in the LCO due to structural transformation are reduced significantly (as high temperature will also anneal out the stress), diminishes the driving force for spallation, and LCO electrode becomes stable, leading to small degradation in m_1 in this region as shown in Fig.6.6.

The thickness of the SEI at the graphite electrode results in an increase in the cell resistance as shown in Fig.6.8.

The evaporation of electrolyte in Region III continues at the temperature remain high, and this results in local electrolyte drying, and leads to non-uniform current density [56]. The closure of several pores in the separator can cause mechanical deformation of the separator that also results in non-uniform current density [120]. The gap between the LCO electrode and separator created in Region III also lead to non-uniform current density through the separator [103]. Consequently, the current density through the separator is highly non-uniform in this Region. In the presence of effective overcharge (as Q_m is now so much lower), this non-uniform current density will cause localized lithium plating as shown by Cannarella and Arnold [120]. Thus, at 700 cycles, an additional increase in the total cell resistance is observed in Fig.6.8, and a slight increase in the rate of degradation of Q_m in Fig.6.5.

The presence of Li plating lengthen the path of ionic diffusion as Li-Ions cannot penetrate through the plated Li layers, and thus the diffusion resistance given by the Warburg resistance increases. On the other hand, since the thicknesses of the plated Li layers are so thin, their impact on the Warburg capacitance is minimal.

As ionic exchange is not effective in the areas where there are Li plating, the area of Li-Ions exchange with electrodes reduces, and hence the rate constant k decreases continuously with an increase in the charge transfer resistance, causing an increase in R_{CT} , and thus the total cell resistance as shown in Fig.6.8. The sharp increase in the total cell resistance could indicate that the plating begin at 700 cycles and go up to 800 cycles.

Therefore, the main degradation mechanism in this region is the continuous cracking and formation of SEI film on graphite electrode and the degradation of the separator that leads to Li plating.

6.3.2.5 Region V

In this region, Q_m degradation rate reduced. However, electrodes degradation rates increase.

The continuous overcharge due to the degradation of Q_m that lead to structural change in the LCO electrode material, and the continuous insertion/extraction of lithium ions that leads to changes in the molar volume of the LCO electrode material. induce mechanical stress and strain to the electrode that are now accumulated to a sufficiently high value that can lead to degradation of inactive materials e.g. binder decomposition, oxidation of the conductive agent and corrosion of the current collector, all of which result in a partial loss of contact and thus an increase in the total cell resistance, as reported by Wohlfahrt-Mehrens et al.[60]. Thus a reduction in m_1 is observed. On other hand, such degradations of these inactive components are found to have no impact on the degradation of Q_m [60].

As SEI films on graphite electrode by now are fully covering the carbon particles as shown by Ning et al.[58], the continuous growth of SEI films on graphite electrode increases the mechanical stress in the electrode. Ultimately, the mechanical stress is so high that mechanical disintegration on the graphite electrode occurs, including the contact loss between carbon particles; disintegration between current collector and carbon, between binder and carbon as well as between binder and current collector as reported by Vetter et al.[56]. Thus large degradation in m_2 for the graphite electrode after 900 cycles is observed in Fig.6.9, and the total cell resistance also increases at an increasing rate. Correspondingly, the rate constant will also decrease after 900 cycles as shown in Fig.6.7.

However, Q_m degradation does not seem to be severe in this region as in Fig.6.5 despite the disintegration of the graphite electrode. This is likely due to the high temperature in the cell in this region, and it is known that high temperature will increase Q_m as electrochemical reduction-oxidation (redox) reactions at anode and cathode are enhanced due to elevated temperature [10, 37]. Another plausible explanation is that the disintegrated carbon particles suspended in the electrolyte might release the Li-ions back to electrolyte at high temperature as they are now simply free suspension particles without biased in the electrolyte.

The disintegrated carbon particles in the electrolyte are now choking the pores of the separator, and hence the Warburg resistance continues to increase as more of the carbon particles are releasing into the electrolyte. Correspondingly, the active area of the separator is decreasing, and thus the Warburg capacitance is decreasing.

From the above discussions, the progression of the degradations of the internal components of a LiB can be summarized using the following diagram.

Fig.6.12. The main degradation mechanisms of cycle aging of LiB in different Regions.

6.4 Summary

This work attempt to put the various reported degradations of the various internal components in a LiB into a progression time sequence and identify their dominance in different charge/discharging cycles, so that the evolution of the degradation process can be imaged.

Five regions of degradation have been identified. Within five regions, the dominant mechanisms are changing with cycling. The rapid SEI formation at the graphite electrode is considered as initial degradation, and the LCO phase transformation thereafter, followed by the Joule heating that lead to the cracking and continues formation of SEI at the graphite electrode as well as surface spallation at the LCO electrode, and the degradation of the separator which results in non-uniform current density and hence Li plating. Further cycling

results in the disintegration of the graphite electrode and the degradation of the inactive materials of LCO electrode that lead to the degradation of the contact of the cathode.

Chapter 7. A Reliability-based Design Concept for Lithium-ion Battery Pack in Electric Vehicles

7.1 Introduction

As we discussed in Chapters 1 and 2, the reliability of battery pack is very important characteristic need to be taken into account for HEV/EV application as it is closely related to cost and reputation of the business. In order to improve the reliability and safety of a battery pack, one simple and direct method is to add redundant cells to the battery pack, but two associated questions should be investigated. Firstly, the configurations of the redundant cells in the battery pack; Secondly, the number of redundant cells for cost effectiveness. In this chapter, a design concept is developed to answer these two questions quantitatively.

For the first question, the effect of cells configuration in the pack on the pack's reliability is generally overlooked. However, the effect can be significant. Let us illustrate the effect with the following idealistic example.

Assuming perfect conversion such that the total power in the battery pack can be converted into the required voltages and currents at a given output power without any loss, Figures 7.1-7.3 show four possible configurations of 10 identical cells in a battery pack.

Fig.7.1. Structure a.

Fig.7.2 Structure b.

Fig.7.3. Structure c (left) and Structure d (right).

Assuming every cell has two states, namely the normal and abnormal, and the probability of a cell in the abnormal state is x . Given that the different battery packs are to supply the same power P , the current I through each cell in the 4 different configurations will be the same and equal to $= \frac{P}{10V_0}$, where V_0 is the voltage of a cell. If we assume that the battery packs are charged/discharged for the same number of cycles, and the degradation of the cells are identical, the probability of normal state for the battery packs with different configurations could be calculated as follows, and they are shown in Fig.7.4.

$$P_a = 1 - [1 - (1 - x)^5]^2 \quad (7.1a)$$

$$P_b = (1 - x^2)^5 \quad (7.1b)$$

$$P_c = 1 - [1 - (1 - x)^2]^5 \quad (7.1c)$$

$$P_d = (1 - x^5)^2 \quad (7.1d)$$

Fig.7.4. The probability for different structures.

From the above example, we can see that the reliabilities of the parallel-series structures, i.e. structures b and d are higher than the series-parallel configurations, i.e. structure a and c, with structure d being the best for the reliability. Therefore, if the redundant cell number and cost are not in consideration, adding more parallel branches in battery pack will be preferred, and its reliability can be greatly enhanced [121]. With cost consideration, trade-off between reliability and the number of the cells is inevitable, and this is the focus of this work.

SoH of the cells will be used here for analysis. SoH is defined as a variable which reflects the general health condition of a cell and its ability to deliver specified energy or charge as compared to its fresh state. The knowledge of SoH can be used to recognize ongoing or abrupt degradation of the cells and to prevent possible failure.

There have been many SoH methods in literatures [122-126], and none is considered as standard currently. To illustrate our design concept, any SoH method that models the effects of temperature, charge-discharge cycling and current on cell capacity fading, and its rate capability losses will be good enough for our purpose. In this chapter, we choose the model proposed in [126], which is also used by others [127, 128]. This model is based on the electrochemistry mechanisms of the cells. With this model, a capacity fade prediction that describes the degradation effects from the charge and discharge cycling number, temperature and the discharge rate is possible.

To calculate the reliability of a battery pack using the cell's SoH, multi-state systems (MSS) and universal generating function (UGF) techniques are employed in this work. Many real-world systems are composed of multi-state components, which have different performance levels and failure modes with various effects on the system's entire performance. Such systems are called multi-state systems [129]. For MSS, the system performance will be essentially different for components with different performance rates. In order to calculate the reliability of MSS, universal generating function technique is applied.

The UGF methodology is an essential tool to obtain the performance distribution of an overall system from the performance distributions of the individual elements in the system. UGF has been used to analyze the reliability and optimize the structures of MSS [130, 131], and it is found to be effective and can be applied to solve many problems of MSS. Tan et al. [132, 133] applied UGF to study the reliability of a repairable system under the various maintenance schemes, and demonstrate the significant benefit of predictive maintenance. UGF was also used to analyze the reliability of primary battery packs with defined required capacities and voltages in [134].

There have been many reliability-based design methodologies for different applications. A scheme is proposed to define optimum design domains of LED-based luminaires for a given light output requirement by considering their reliability in [135]. Another method is proposed for reliability-based design optimization on the basis of the concept of reliable design space, within which all design could satisfy the reliability requirements in [136]. In [137], an integrated algorithm system is proposed to implement the reliability-based design for offshore towers that enable them to perform well in complicated environment conditions. A mixed redundancy strategy is proposed by Ardakan et al.[138] to determine the component type, redundancy level, number of active and cold-standby units for system in order to maximize the system reliability. Zhang et al.[139] provided a design for a modular converter system with consideration of the trade-offs between reliability, cost and space consumption, and they provided insights and guidance for designers in their decision-making. However, none of them using MSS and UGF for the design assessment. As mentioned before, battery pack degradation is a complex multi-states process for each cell in the pack, and it depends on many factors, such as cell number, cell configuration, cycle number and SoH etc., hence MSS is needed for the modelling of the cells' reliability and UGF is required to combine the different states of the cells for the reliability evaluation of the entire pack. The above mentioned design methods are not applicable to battery pack for its design for reliability.

The usage of MSS and UGF combination have been used for the study of predictive maintenance which is reliability based [132, 133]. Li et al.[140] used UGF to develop a MSS model for reliability assessment of a distributed systems. Tian et al.[141] applied UGF for a MSS series-parallel system to determine the optimal component reliabilities and redundancy levels for each sub-system. Their optimization objective was cost, and different versions of the components with different performance rates were also considered.

In contrast to the work of Tian et al.[141], we consider only one version of battery cells, but their performances and health states are varying and governed by a statistical distribution. Also, the reliability of a battery pack is sensitive to the cells connection configuration as illustrated earlier, and such configuration is considered in the design for reliability. Furthermore, the purpose of this work is to provide a design for a given required reliability of the battery pack with minimum cost, and thus reliability curve of a battery pack is needed. Thus the method of Tian et al.[141] cannot be applied directly, and a new methodology is proposed in this chapter.

Using the combination of MSS and UGF, we propose a reliability-based design concept for Lithium-ion battery packs, considering the trade-off between the number of the redundant

battery cells, the configuration of the redundant cells, and their reliability. This concept provides a solution for the battery pack designers.

According to the capacity fade model of Li-ion cells [126], we first calculate the SoH of the cells. By assuming the SoH of all the cells following normal distribution, UGF technique is applied to calculate the reliability of a battery pack. We will show the reliability change by adding redundant cells to the battery pack with different configurations, and the battery pack design with the highest reliability and minimum number of redundant cells.

The remaining paper is organized as follows. The capacity fade model of the Li-ion cells is given in Section 7.2, and the MSS for describing the SoH of a battery pack and the UGF technique for calculating its reliability are shown in Section 7.3. In Section 7.4, the reliability of a battery pack is first calculated based on the MSS and UGF techniques, and the effects from the cycling number, temperature and the discharge rate are simulated. The reliabilities of the battery pack by adding redundant cells with different structures at different temperatures are then calculated. Section 7.5 shows our experimental plan for the verification of our design concept and the associated challenges. Conclusions and future works are given in Section 7.6.

7.2 The Capacity Fade Model of Lithium-ion Battery Cell

The SoH of a LiB cell is defined as [142, 143],

$$SoH = \frac{Q_{max}(aged)}{Q_{max}(new)} \quad (7.2)$$

$$Q_{max}(aged) = Q_{max}(new) - Q_{max}(fade) \quad (7.3)$$

where $Q_{max}(aged)$ and $Q_{max}(new)$ are the maximum amount of charge that can be drawn from the aged and new batteries, respectively. $Q_{max}(fade)$ represents the capacity faded due to temperature, cycle number and the discharge rate.

According to the analysis in [126], the faded capacity consists of three parts. The first part is the loss in capacity due to an increase in resistance at both electrodes. The second part is the loss of lithiation capacity at both electrodes. The third part is due to loss of active material Li^+ in the cell. These three parts of a cell are affected by the cell temperature, the number of its charging and discharging cycles and its discharging rate (also known as C-rate). A semi-empirical capacity fading model, which considers the effects of cell temperature and the number of charging/discharging cycles are given below [126]

$$Q_{lost}(T, N) = SOC_{lost} \times Q_{max}(new) \quad (7.4a)$$

$$\frac{dSOC_{lost}}{dN} = k_1 N + k_2 \quad (7.4b)$$

where $Q_{lost}(T, N)$ represents the capacity fading due to the charge/discharge cycle number N and temperature. The parameter k_1 accounts for the capacity losses that increase rapidly during the conditions such as cycling at high temperature, and k_2 is a factor to account for capacity losses under the normal conditions of cycling. Due to the increase in film resistance during cycling, the rate capability of the cells decreases. However, Eq.(7.4) can only be used at very low discharge rates, and it is necessary to update the above model for the capacity fade by considering the C-rate. According to the experiment in [126], the discharge capacity loss is linear with respect to the C-rate,

$$Q_{lost}(i) = k_3 i \quad (7.5)$$

With the capacity analysis [126] and Equations (7.4) and (7.5), we therefore have $Q_{max}(fade) = Q_{lost}(T, N) + Q_{lost}(i)$, and the SoH of a battery cell can be calculated as follows,

$$\begin{aligned} SoH &= \frac{Q_{max}(aged)}{Q_{max}(new)} = \frac{Q_{max}(new) - Q_{max}(fade)}{Q_{max}(new)} \\ &= 1 - \frac{Q_{lost}(T, N) + Q_{lost}(i)}{Q_{max}(new)} = 1 - \frac{Q_{max}(new) \left(\frac{1}{2} k_1 N^2 + k_2 N \right)}{Q_{max}(new)} - \frac{k_3 i}{Q_{max}(new)} \\ &= 1 - \left(\frac{1}{2} k_1 N^2 + k_2 N \right) - \frac{k_3 i}{Q_{max}(new)} \\ SoH &= 1 - \left(\frac{1}{2} k_1 N^2 + k_2 N \right) - \frac{k_3}{Q_{max}(new)} i \end{aligned} \quad (7.6)$$

where i is the discharge rate. The values of the coefficients in Eq.(7.6) are shown in Table 7.1, where “ ≤ 300 ” represents the cycle number of the cell is less than 300, and similarly for others.

Table 7.1: Values of the parameters in Eq.(7.6) at different temperatures [126].

Cycling Temperature (°C)	k_1 [cycle ⁻²]	k_2 [cycle ⁻¹]	k_3 [A ⁻¹]
25	8.5×10^{-8}	2.5×10^{-4}	$2.68 \times 10^{-2} (\leq 300)$
			$7.26 \times 10^{-2} (\leq 800)$
50	1.6×10^{-6}	2.9×10^{-4}	$5.20 \times 10^{-2} (\leq 300)$
			$6.82 \times 10^{-2} (\leq 500)$

7.3 Multi-State Battery Pack Systems

Consider the configuration of a battery pack as shown in Fig.7.5. The position of each cell in the battery pack is referenced by (i, j) , where $i = 1, 2, \dots, m, m+1, \dots, m+\Delta m; j = 1, 2, \dots, n, n+1, \dots, n+\Delta n$. The cells in the box enclosed by the red dashed lines are the redundant cells. For ease of discussion, the battery pack that contains $m \times n$ cells is denoted as battery pack I, and the battery pack with active redundant cells added, i.e. having $(m + \Delta m) \times (n + \Delta n)$ cells, is denoted as battery pack II.

Fig.7.5. The configuration of the battery pack with redundant cells.

In order to calculate the reliability of the battery pack using the SoH of all the cells in the battery pack, the SoH is assumed to be a normal distribution $N(\mu, \sigma^2)$ at any instant of time. This means that Eq.(7.6) provides only the mean SoH of the cells in a battery pack, and the individual cell's SoH is different from each others due to material variations of the fresh cells, the different degree of damages and their susceptibility to these damages during the charge/discharge cycles and the cell balancing method in the BMS. As the number of cells is usually large in a battery pack (> 100), the cells' SoH in the battery pack can be considered as a normal distribution, according to the Central Limit Theorem. Explanation of the Central Limit Theorem can be found in [144].

For a given electric vehicle with $m \times n$ cells in a battery pack, assuming that the pack's energy capacity can supply the required power up to N charge/discharge cycle, then with the addition of $(m + \Delta m) \times (n + \Delta n) - m \times n$ redundant cells in the new battery pack, the maximum charge/discharge cycle N_{new} , which the new battery pack needs to supply the same required power, will be given as follows,

$$N_{new} = \frac{mnN}{(m+\Delta m)(n+\Delta n)} \quad (7.7)$$

As the EV needs the same power P for driving on the road regardless of battery pack I or II, the discharging rates of the cells for both battery packs are related as follows, if new Δm parallel branches are added to battery pack II,

$$i = \frac{m}{m+\Delta m} \times I \quad (7.8)$$

where I is the individual discharging current in the $m \times n$ battery pack I. Similarly, with new Δn series branches, the cell discharging rates' relationship is

$$i = \frac{n}{n+\Delta n} \times I \quad (7.9)$$

So if Δm parallel and Δn series branches are added to the battery pack, the discharging rate becomes

$$i = \frac{mn}{(m+\Delta m)(n+\Delta n)} \times I \quad (7.10)$$

7.3.1 Universal Generating Function

To apply UGF for the reliability computation of the battery pack, the cell's SoH degradation is divided into different levels so as to convert it into a MSS model. Each level is defined by a range of SoH values, such as 100% – 90%, 90% – 80%, etc. In other words, we categorize the SoH of every cell in the battery pack into $\geq 90\%$, 90% – 80%, 80% – 70%, 70% – 60% and $\leq 60\%$ levels, and the MSS model for a battery pack has 5 levels.

With reference to Fig.7.5, we define $k_{(i,j)}$ ($= 4, 3, 2, 1, 0$) as the SoH level of the cell (i, j) in the battery pack, and $P_{(i,j)}(k_{(i,j)})$ as the probability of cell (i, j) at level $k_{(i,j)}$. Using the methodology of UGF [127], the u- function of the cell (i, j) is

$$u_{(i,j)}(z) = \sum P_{(i,j)}(k_{(i,j)}) z^{k_{(i,j)}} \quad (7.11)$$

and the UGF of the battery pack is

$$U(z) = \prod_{i=1}^m \prod_{j=1}^n u_{(i,j)}(z) \quad (7.12)$$

With the parallel-series structure of the battery pack, the performance G_s of the system takes the form [127],

$$G_s = \min_{j=1, \dots, n+\Delta n} \max_{i=1, \dots, m+\Delta m} g_{(i,j)}(k_{(i,j)}) \quad (7.13)$$

where $g_{(i,j)}(k_{(i,j)})$ represents the SoH of the cell (i, j) at level $k_{i,j}$. Let $\bar{s} = \inf\{s : G_s \geq W\}$, where W is the minimum user-set threshold demand value, the system can be divided into two disjoint subsets of acceptable states $\{\bar{s}, \bar{s} + 1, \dots, 4\}$ and unacceptable states $\{0, 1, \dots, \bar{s} - 1\}$. The reliability function R for a given user demand W can then be written as,

$$R = P(G_s \geq W) = \sum_{k=\bar{s}}^4 P(k) \quad (7.14)$$

where $P(k)$ is the state probability of the battery pack at k level.

7.4 Computational Method

The mean SoH of all the cells can be given by Eq.(7.6), i.e. $\mu = SoH$ during the operation of the cells. As each cell will degrade differently, the standard deviation of the SoH distribution will increase with the cycle number. Fig.7.6 depicts the cell's SoH distribution in the battery pack with respect to the charge/discharge cycle number, and the dotted line is described by Eq.(7.6).

Fig.7.6. The cell's SoH distribution in the battery pack. Figure no units

Unfortunately, the dependence of σ on the temperature, cycle number and C-rate is not available. On the other hand, the SoH distribution must be normal distribution by virtue of the central limit theorem. Since SoH cannot be more than 1, this will mean that the standard deviation σ at the start will have to be zero (this is possible due to our definition of SoH in Eq.(7.2)). As SoH degrades, σ will start to increase, but the increase must be such that its 6σ is at 1, thus we have,

$$\sigma = \frac{1-\mu}{6} = \frac{1}{6} \left[\left(\frac{1}{2} k_1 N^2 + k_2 N \right) + \frac{k_3}{Q_{max}(new)} i \right] \quad (7.15)$$

7.4.1 Reliability of the Battery Pack I

Sony 18650 with the capacity of 1.75Ah is used in this work, so that the data in [126] can be employed. For illustration, the structure of the battery pack I is assumed to be 2×5 parallel-series configuration. Using Equations (6) and (15), the probability density function of the cells' SoH is shown in Fig.7.7, and Table 7.2 gives the probability of the cell's SoH levels at 0.5C rate and 25°C. Fig.7.8 shows the similar probability density function, and Table 7.3 gives the probability for the cell's SoH levels at 0.5C rate and 50°C. As the safe operating temperature range for LiB operation is less than 60°C as reported [137], only two temperatures, 25°C and 50°C with 10°C allowance for self-generated heat during operation, are considered.

Fig.7.7. The probability density function at 0.5C rate and 25°C.

Table 7.2: Probability for the cell's SoH levels at 0.5C and 25°C.

Cycle Number	$\geq 90\%$	80%-90%	70%-80%	60%-70%	$\leq 60\%$
100	1	0	0	0	0
200	0.9994	0.0006	0	0	0
300	0.6935	0.3065	0	0	0
400	0.0354	0.9561	0.0085	0	0
500	0.0060	0.8304	0.1636	0	0
600	0.0012	0.4798	0.5137	0.0017	0
700	0.0003	0.2028	0.7572	0.0397	0
800	0.0001	0.0740	0.7229	0.2020	0.0009

Fig.7.8. The probability density function at 0.5C rate and 50°C.

Table 7.3: Probability for the cell's SoH levels at 0.5C rate and 50°C.

Cycle Number	$\geq 90\%$	80%-90%	70%-80%	60%-70%	$\leq 60\%$
100	0.9998	0.0002	0	0	0
200	0.2040	0.7960	0	0	0
300	0.0029	0.6838	0.3132	0.0001	0
400	0.0001	0.0459	0.6357	0.3140	0.0043
500	0	0.0023	0.1030	0.5243	0.3704

To calculate the reliability of the battery pack, let us set the failure threshold as $W = 80\%$, as it is a common practice for Li-ion battery pack in EV applications [15, 142]. To illustrate the computation of reliability, let us consider the u -function of the cells (i, j) in battery pack I after 600 charge/discharge cycle number at 0.5C rate and 25°C as follows

$$u_{(i,j)} = 0.0012z^4 + 0.4798z^3 + 0.5173z^2 + 0.0017z^1 + 0z^0, \forall i = 1,2; j = 1,2,3,4,5 \quad (7.16)$$

and thus

$$U(z) = 0z^4 + 0.2082z^3 + 0.7918z^2 + 0z^1 + 0z^0 \quad (7.17)$$

Using Equations (7.13) and (7.14), where $g_{(i,j)}$ is from Eq.(7.13), we have

$$R(G_s \geq 80\%) = 0 + 0.2082 = 0.2082 \quad (7.18)$$

Similar calculations can be performed for different cycle numbers, temperature and C-rate, and the reliability of the battery pack I are shown in Table 6 and Table 7 at 25°C and 50°C, respectively.

Table 6: The reliability $R(G_s \geq 80\%)$ of the battery pack at 25°C.

Cycle Number	0.5C	1C	1.5C	2C
100	1	1	1	1
200	1	1	1	1
300	1	1	1	1
400	0.9996	0.7330	0.0516	0.0004
500	0.8732	0.1139	0.0011	0
600	0.2082	0.0029	0	0
700	0.0065	0	0	0
800	0.0001	0	0	0

Table 7: The reliability $R(G_s \geq 80\%)$ of the battery pack at 50°C.

Cycle Number	0.5C	1C	1.5C	2C
100	1	1	1	0.9998
200	1	0.9997	0.9225	0.3667
300	0.5965	0.0860	0.0033	0.0001
400	0	0	0	0
500	0	0	0	0

7.4.2 Reliability of the Battery Pack II

To investigate the relationship between the battery pack reliability and the active redundant cell number and configuration, we consider two operating conditions for battery pack II. One

is charged/discharged for 800 cycles at 25°C, and another one is charged/discharged 500 cycles at 50°C. In both conditions, the discharge rate is 1C in every parallel branch. The reason of choosing the two operating conditions is that their reliabilities could be improved significantly with active cells redundancy.

We first calculate the cells' SoH of the battery pack according to Eq.(7.6) for additional cells with different configurations. For example, when $\Delta m = 1$ and $\Delta n = 1$, the mean SoH value after charging/discharging for 800 cycles, at 25°C and 1C discharge rate can be calculated as follows,

$$\begin{aligned}
 SoH &= 1 - \left[\frac{1}{2} \times 8.5 \times 10^{-8} \times \left(\frac{2 \times 5 \times 800}{(2+1) \times (5+1)} \right)^2 + 2.5 \times 10^{-4} \times \frac{2 \times 5 \times 800}{(2+1) \times (5+1)} \right] \\
 &\quad - 7.26 \times 10^{-2} \times \frac{2 \times 5 \times 1.75}{1.75 \times (2+1)(5+1)} \\
 &= 0.8402
 \end{aligned} \tag{7.19}$$

Similar calculations can be done for different Δm and Δn as shown in Table and Table . The percentage represents the SoH of each cell in the pack, and the integer above the percentage is the number of redundant cells. For example, for the case of $\Delta m = 1$, $\Delta n = 1$, “8” means that eight cells are added to the battery pack, and the configuration becomes 3×6 parallel-series.

Table 7.6: The SoH value after 800 cycles, at 25°C and 1C discharge rate.

SoH	$\Delta n = 0$	$\Delta n = 1$	$\Delta n = 2$	$\Delta n = 3$	$\Delta n = 4$	$\Delta n = 5$
$\Delta m = 0$	0	2	4	6	8	10
	70.02%	75.39%	79.14%	81.90%	84.02%	85.69%
$\Delta m = 1$	5	8	11	14	17	20
	80.62%	84.02%	86.40%	88.17%	91.23%	92.14%
$\Delta m = 2$	10	14	18	22	26	30
	85.69%	88.17%	91.55%	92.65%	93.49%	94.16%

Table 7.7: The SoH value after 500 cycles, at 50°C and 1C discharge rate.

SoH	$\Delta n = 0$	$\Delta n = 1$	$\Delta n = 2$	$\Delta n = 3$	$\Delta n = 4$	$\Delta n = 5$
$\Delta m = 0$	0	2	4	6	8	10
	58.68%	68.34%	74.57%	78.86%	82.88%	85.15%
$\Delta m = 1$	5	8	11	14	17	20
	76.90%	82.88%	86.08%	88.32%	89.96%	91.21%
$\Delta m = 2$	10	14	18	22	26	30
	85.15%	88.32%	90.41%	91.89%	92.98%	93.83%

From Table and Table , we can see that increasing the cells in the battery pack can improve the mean SoH of each cell in the battery pack regardless of the configuration. For example, considering the case of $\Delta m = 0, \Delta n = 4$, the SoH value is equal to the case of $\Delta m = 1, \Delta n = 1$, as the total number of the added cells in both configurations is 8. Therefore, we can conclude that when the number of the added cells is the same, the SoH of the battery pack will remain the same. We use red colour to show the SoH at the same redundant cell number. Fig.7.9 shows the relationship between the cell mean SoH and the cell redundancy number.

Fig.7.9. The mean SoH of the battery pack w.r.t. the cell redundancy number.

The reliability of the battery pack at the two different operating conditions is given in Table and Table , which are computed similarly as in the case of battery pack I. From Table and Table , we can see that the reliability of the battery pack can be improved by using cell redundancy as expected. We can also see that the amount of improvement in reliability is higher if we increase the parallel branch for a given number of redundant cells. For example, at 25°C, the reliability by adding 8 cells in series configuration (i.e. 2×9) is 0.9617, while the reliability by adding 8 cells in parallel-series configuration (i.e. 3×6) is 0.9983. We also find

that the reliability can be improved significantly by adding just 1 new parallel and 1 new series branches, and total number of added cell is only 8.

Table 7.8: The Reliability by discharging 800 cycles, at 25°C and 1C discharge rate.

$R(G_s \geq 80\%)$	$\Delta n = 0$	$\Delta n = 1$	$\Delta n = 2$	$\Delta n = 3$	$\Delta n = 4$	$\Delta n = 5$
$\Delta m = 0$	0	2	4	6	8	10
	0	0.0002	0.0454	0.5600	0.9617	0.9993
$\Delta m = 1$	5	8	11	14	17	20
	0.6724	0.9983	1	1	1	1
$\Delta m = 2$	10	14	18	22	26	30
	1	1	1	1	1	1

Table 7.9: The Reliability by discharging 500 cycles, at 50°C and 1C discharge rate.

$R(G_s \geq 80\%)$	$\Delta n = 0$	$\Delta n = 1$	$\Delta n = 2$	$\Delta n = 3$	$\Delta n = 4$	$\Delta n = 5$
$\Delta m = 0$	0	2	4	6	8	10
	0	0	0	0.0185	0.8008	0.9965
$\Delta m = 1$	5	8	11	14	17	20
	0.0336	0.9774	1	1	1	1
$\Delta m = 2$	10	14	18	22	26	30
	1	1	1	1	1	1

As adding more cells to the battery pack increases the cost of the battery pack, trade-off between the additional cell number and the reliability must be considered for battery manufacturers. Fig.7.10 shows the reliability improvement with respect to the cell redundancy number, and higher reliability values are chosen when the number of redundant cells is the same. For example, we choose 0.9983 as the reliability value for 8 redundant cells.

Fig.7.10. The reliability with respect to the cell redundancy number.

From Fig.7.10, for 2×5 battery pack, it is very clear that adding 8 cells can obviously improve the reliability, from 0 to 0.9983 at 25°C , and 0 to 0.9774 at 50°C . However, we can also see in Fig.7.10 that when the added cell number is 6, the reliability of the battery pack is lower than adding 5 cells due to the different configurations. The same issues could also be found in Fig.7.11, which shows the reliability with respect to the cycle number for different configurations.

Fig.7.11. The reliability of different configurations at 25°C . a): 2×5 Configuration; b): 2×8 Configuration; c): 3×5 Configuration; d): 2×9 Configuration; e): 3×6 Configuration; f): 2×10 Configuration; g): 4×5 Configuration.

Fig.7.12. The reliability of different configurations at 50°C. a):2×5 Configuration; b): 2×8 Configuration; c): 3×5 Configuration; d): 2×9 Configuration; e): 3×6 Configuration; f): 2×10 Configuration; g): 4×5 Configuration.

In Fig.7.11 and Fig.7.12, we can see that for the same charge/discharge cycle number, using cells redundancy could improve the reliability, but the configuration also has an effect on the reliability. For example, in Fig.7.11, 2×10 configuration and 4×5 configuration have the same 10 redundant cells, but the 4×5 configuration has higher reliability. 3 × 5 configuration has smaller redundant cells than 2 × 8 configuration, but its reliability is higher.

We can also find the battery pack configuration with minimum cells for a desired reliability at a given cycle number from Fig.7.11 and Fig.7.12. For example, when we need to design a battery pack, if the battery pack is to be reliable ($R \geq 80\%$) after being charged/discharged 800 times, we can select 3×6 configuration, which demands a minimum cost.

Therefore, during the design of high reliability Li-ion battery pack, we should consider both the configuration and the cell redundancy number, as the relationship between the reliability, the cell number and the configuration of the battery pack is non-trivial.

7.5 Experimental challenges

To verify our proposed design concept, a small scale battery pack will be constructed, and the test experiments will be done. However, there are still some practical challenges in the experiments, so the experiment results cannot be shown in the paper now. Firstly, the experiments will take a long time. For example, if we test some Li-ion battery packs (with 18650 cells) in safety operation range, it will take at least a few months to degrade the cells to

its 80% capacity. Secondly, the experimental verification of the design concept proposed in the paper requires a lot of cells. It will take about 10 thousand dollars. Thirdly, there are also some problems in the integration of the cells into the battery pack. The construction of the battery packs requires a thermal management system and a BMS. The reliability of the battery pack is related to the temperature, SoC and SoH of the batteries, charging/discharging rate, depth of discharge and so on. So, according to these challenges, experimental verification of the design concept is a huge project, and industrial collaboration will be needed.

7.6 Summary

In this chapter, a concept for design-in reliability for Li-ion battery pack in EVs applications using cells redundancy is proposed, and the analysis is based on the SoH of the cells in the battery pack. The reliability of the battery packs with different configurations has been calculated through UGF technique. In addition, the reliability of battery packs operated at different temperatures has been analysed. From our analysis, it can be concluded that the reliability of battery pack can be improved by adding redundant cells as reported in literatures. Meanwhile, its reliability is significantly influenced by the configuration of the redundant cells. The proposed design concept provides a way to choose the best redundant cells configuration for higher pack reliability, while considering the total cost through the optimal number of the redundant cells.

Chapter 8. Conclusions and Future Works

8.1 Conclusions

With the fast development of EVs, the reliability of the LiB pack received lots of attentions, and it is mainly determined by reliability of the LiB cell. The gradual degradations in battery functionality with time are mainly resulted from battery aging, abuse conditions as well as the environmental impact. The discussion in Chapter 1 and 2 demonstrated the importance of reliability and safety of LiB cell and pack in the EVs. Reliability of a battery pack depends on the reliability of the battery cell, including the number of redundant cells and their configurations. The reliability of the battery cell is mainly determined by the continuous functionality which will gradually degrade over time mainly due to battery cyclic aging and abusive operations (e.g. overcharge, high temperature). These abuses will cause the battery cell lack of safety, and the Battery safety is one of the main concerns for many EVs as various abusive operations can occur in a LiB cell during its operation, and these abusive operations can cause the severe degradation, shortening the lifetimes of the battery cell and even catastrophic hazardous in a single battery cell that may influence other battery cells within the battery pack. Moreover, the cycle life of LiB cell is another important characteristic for its use in EVs as long life cycle can help the battery pack to last for the lifetime of the EVs so as to save cost. In an effort to prolong the battery cycle life and to prevent those failures from occurring in a LiB cell, a systematic detection of the underlying degradation mechanisms is necessary, so that safety and reliability improvement of LiB cell can be designed and produced. In addition, the effect of temperature on the cyclic aging of LiB cell also needs to be taken into account as the underlying aging processes will be accelerated differently and even trigger some new aging mechanisms engender different problems at elevated temperature. The performance of LiB cell determines safety, reliability and operation efficiency of battery pack as the accurate estimation of SoC and SoH which are implemented in the BMS can help to ensure the safe and reliable battery operations, extending its life, and optimizing the power management of the battery pack in EVs.

In Chapter 3, the maximum charge capacity of a battery at the beginning of each discharge cycle is an important parameter for accurate estimation of SoC using Coulomb counting method. Its value can also be used as an indication of state-of-health (SoH) of a battery. In this work, a practical electrical framework is developed for in-situ online battery parameters estimation, based on the electrochemistry principle in the battery during discharging. This model is in contrast to many other electrical models where are derived by intelligent electronic components selection and connection so as to resemble the particular experimental

discharge curve but without the connection to its electrochemistry processes. The latter suffers from its lack of generality while the model developed is applicable to all LiB cells. The model developed is able to provide the maximum charge capacity online after each discharge cycle without the need to fully discharge a cell which can shorten the lifespan of a cell.

Experimental verification of the model developed shows good agreement, both in temporal as well as frequency space in the form of EIS spectrum. Its application to time varying current during discharging is also shown through step current change with slightly different model parameters as they are affected by the discharging currents. Application to actual time varying current is possible through a database or calibration curves of the model parameters values at different discharging currents.

The model developed allows the internal parameters of a cell to be determined which can be useful to determine the degraded components in the cell when the cell is aged or damaged. It can also be a useful tool to evaluate the quality of LiB cells non-destructively.

In Chapter 4, We have successful identify the seeming gain of LiB cell by having it to charge with high COV, and reveal the hidden issues associated with charging the cell with high COV, with the use of the ECBE model. Therefore the misconception of higher COV to enhance the runtime is clarified. With our method, we are able to provide real time on-line non-destructive assessment of the internal components in a Li Ion cell to evaluate its reliability and safety with respect to this overcharging abuse. We are able to characterize the degradation level of each internal electrochemical component in LiB and consequently identify the weakest material that is most vulnerable to the excessive COV. This will be beneficial for battery manufacturers to design and produce more robust cells against overcharging. Our method can also be incorporated into existing BMS so that a more advanced safety technology to ensure safe operation of the battery pack with enhanced system reliability can be possible.

Temperature is important factors critically affect the health and safe operation of LiB cell. In this study, the performance of each component inside LiB has been determined at different temperature. It is shown that the phase transition after 45 °C was identified as the main course of changes for each component in the investigated battery cells. Through this approach, we also can study the possible root causes of thermal runaway from the performance of each component. It is possible provide early warning of the battery thermal runaway and hence enhance the safe operation of the cells.

In Chapter 5, Temperature is an important factor that affects aging rate of LiB cell and ultimately its reliability and safety. In this chapter, we used a non-destructive in-situ approach through ECBE model to detect and characterize the effect of temperature on cycling aging rate in LiB. The performance degradation rate of each component inside the LiB due to cycling aging at different temperatures was determined. From our analysis, we can see that increasing the operating temperature increases the degradation rates of all components in the LiB which include maximum charge storage capacity, the effectiveness of the LCO electrode in storing Li-ions, charge transfer rate constant, effectiveness of the graphite electrode in providing its stored Li-ions, total resistance of electrode resistance and electrode/electrolyte resistance, Warburg element resistance, Warburg element capacitance and Warburg RC time constant. The increase in the degradation rates of the Warburg element and cell impedance are particularly sensitive to the operating temperature. We also showed that the increase in the degradation rate of irreversible capacity loss of LiB (i.e. SoH) with temperature is due mainly to the formation and modification of the surface films on the electrode and to the structural/phase changes of the LCO electrode.

ECBE model is capable of comprehensively identify the various aging causes through in-situ real time characterization. With this information given to BMS, online monitor the current health status of battery is possible, and one can then reduce the battery loads, namely the voltage, current and temperature according to its health, preventing it from overloading, and ensuring the safety and extend the life of a battery pack.

As we discussed in Chapter 6, the applications of LiB are extending to more areas, and the requirement on their cycle life and calendar life are also increasing. Hence, irreversible capacity loss mechanisms and their preventions are becoming crucial. This work is attempt to put the various reported degradations of the various internal components in a LiB into a progression sequence and identify their dominance in different charge/discharging cycles, so that the evolution of the degradation process can be imaged.

There are five regions of degradation within which the dominant mechanisms vary as the charge/discharge cycle continuous. The degradation begins with the rapid SEI formation at the graphite electrode, then the LCO phase transformation, followed by the Joule heating that result in the cracking and formation of SEI at the graphite electrode and surface spallation at the LCO electrode, and the degradation of the separator which results in non-uniform current density and hence Li plating. Further cycling results in the disintegration of the graphite electrode and the degradation of the inactive materials of LCO electrode that lead to the degradation of the contact of the cathode.

In the Chapter 7, a concept for design-in reliability for Li-ion battery pack in EVs applications using cells redundancy is introduced, and the analysis is based on the SoH of the cells in the battery pack. We calculate the reliability of the battery packs with different configurations using UGF technique. Comparing the reliability of two battery packs at different temperatures, we conclude that the reliability could be improved by adding redundant cells as expected, and the configuration of the redundant cells has significant effect on its reliability. The proposed design concept provides a way to select the best redundant cells configuration for good pack reliability, while considering the total cost through the optimal number of the redundant cells.

While the proposed design concept is promising, there remain a few open issues such as its experimental validation which is also discussed, and reliability of thermal management and cell-to-cell interconnects in the battery packs, which are yet to be studied. The latters are assumed to be perfect in this work.

8.2 Future Works

8.2.1 Implement the ECBE model to real operating conditions

We are going to implement the ECBE model to various discharging profiles based on the different applications e.g. digital signal, analog signal and EV current profile etc to show the robustness of the ECBE applied to the real operating conditions, demonstrating and extracting of useful information from the these experiments other than constant-current discharging over several hours

8.2.2 The effect of low temperatures (e.g. 0 to 25 °C) on the aging rate Li Ion battery

As low temperature operation below 25°C can also be important, investigation on the low temperature on the aging rate will also shed light on the good design of LiB for low temperature operation. We are going to purchase the test facilities and perform such work.

8.2.3 Experimental identifications of cyclic aging mechanisms in different regions

The range of the cycle number where each region belongs is expected to vary with the cell chemistry, cell design, cell manufacturer and even for the same type of cells, making the experimental identification of the regions challenging. Therefore, experimental verifications of these detail mechanisms will requires large resources and can only be possible with large team. We are going to collaborate with Chang Gung University, Center of Reliability Science and Technologies on this work to explore the time evolving nature of the degradation in LiB during charge-discharge cycling, so that the reliability of LiB can be improved, and even build in.

8.2.4 Experimental validations of the concept for design-in reliability for Li-ion battery pack in EVs applications

The experiments are on the stage of set-up, and we are going to find the funding to purchase the battery testers to real time register the voltage during operation, current and temperature of individual cell in the battery pack. Furthermore, we will plan enough time for the cycling test on the electrodes materials of lithium-ion batteries based on graphite anode and Lithium Nickel Manganese Cobalt Oxide (NMC) cathode used in this project will take as it will take 6 months in order to degrade the cell capacity to 60% so-called dead of LiB. Meanwhile we will buy a BMS to realize cell equalization that is required for experimental validation. And the cell interconnects configuration and redundancy number in the battery pack and experimentally verified the proposed model will be performed and uses it to further improve the design of battery pack with increased system reliability.

8.2.5 An Imbedded Chip for Battery Application

We are going to implement our ECBE into a Chip imbedded into a battery which enables us to online monitoring the degradation of the internal components of the cell in-situ and non-destructively. It allows us to determine the cell degradation characteristics in real time. ECBE model is able to comprehensively investigate the on-going degradation processes of electrodes, electrolyte and electrode/electrolyte interface during battery utilization simultaneously, making it ideal for battery in-situ prognosis and diagnosis.

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