Lithium-ion Battery Lifetime Prediction: Integrating Statistical Models with Physics-of-Failure Mechanisms

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Presented to

the Faculty of the Department of Industrial Engineering

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In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in Industrial Engineering

By

Shufeng Li

August 2016
Lithium-ion Battery Lifetime Prediction: Integrating Statistical Models with Physics-of-Failure Mechanisms

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Abstract

One of the critical concerns for lithium-ion batteries that have been widely used in the electronics and automotive industries is the evaluation and prediction of battery lifetime. Several approaches for lifetime prediction have been developed including electrochemical models, equivalent circuit based models, empirical models, and performance-based models. However, statistical models based on physics-of-failure of lithium-ion batteries have not been well established. This research begins with the analysis of the battery aging mechanisms using the Failure Mode and Effect Analysis (FMEA) method, and identifies major physical degradation models for lifetime prediction. Then a statistical method is developed to model the battery performance degradation that is induced by aging mechanisms. The nonhomogeneous Wiener process model integrated with physical degradation mechanisms, namely, capacity decay and power fading, is developed for battery degradation data analysis. The proposed model is first demonstrated through a simulation study, followed by the evaluation using real data of lithium-ion batteries. This effort shows the effectiveness of our proposed methodology of integrating statistical models with physics-of-failure mechanisms.
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Chapter 1 Introduction

1.1 Background and Motivation

Lithium-ion batteries have been commercialized in the past decade and widely used in the electronics and automotive industries. Battery life is a critical concern in these practical applications. Therefore, evaluation of battery lifetime is required and has been put forward as a technology that can guarantee the reliability and quality of batteries, and potentially determine the strategies of maintenance and warranty for customer usage. Traditional approaches of lifetime prediction focus on estimating the probability of failure using failure time data. However, research shows that degradation measures often provide more information than failure time data for assessing and predicting the reliability of systems [1], particularly for batteries whose performance degrades over the whole life cycle that severely limits their functionality. Meanwhile, the steady growth of battery technologies has resulted in significant changes that lead to potential failures, which demands the advancement of techniques for lifetime prediction. An effective approach for battery lifetime prediction relies on the understanding of potential failure mechanisms, or physics-of-failures, which can be integrated with statistical models considering uncertainties. The research conducted in this article explores these issues and provides a comprehensive assessment of battery lifetime.

Several approaches for lifetime prediction of lithium-ion batteries have been developed over the past few decades, which can be generally classified into five categories [2]: electrochemical models, analytical models with empirical fitting,
equivalent circuit based models, performances based models, and statistical models. The first four approaches take into account the aging processes of batteries (the physical processes and failure mechanisms), enabling physics-based lifetime prediction. Based on the well-characterized relationship for battery aging processes, these four approaches are widely used in analyzing the degradation of battery performance and predicting lifetime [2-4]. The fifth approach, statistical models, however, has not been well established for lithium-ion battery lifetime prediction.

The performance degradation of batteries degrades over time, leading to the potential failure of batteries. This degradation process is considered random and can be described using stochastic process models. In the literature of using statistical models for battery degradation, stochastic process models have not been well studied, although these models have been widely applied in other industrial fields, such as wind turbines and LED products. It motivates us to study the feasible stochastic processes to analyze the battery degradation processes and then predict the lifetime of lithium-ion batteries.

In general, an effective technique for lifetime prediction requires the knowledge of (a) the aging processes within a battery that lead to a loss of performance, (b) the stress factors that induce aging and influence the rate of aging, and (c) the relationships between the stress factors and the aging processes. To make an effective use of statistical models, it is helpful to integrate the physical degradation information of batteries into stochastic process modeling. The information underlying physical phenomena can be derived from physical models associated with the degradation processes. This motivates us to explore feasible physical models and then integrate physical models into statistical models for battery lifetime prediction.
There are various physical models related to different degradation mechanisms or failure mechanisms of batteries. In the literature, there is a lack of a general model to describe multiple degradation mechanisms of batteries, even with the simplified physical degradation processes. Exploration of physical degradation mechanisms of batteries reveals that multiple physical mechanisms can lead to the same performance degradation, whereas one degradation mechanisms can lead to different performance degradations. For example, the formation and growth of solid electrolyte interphase (SEI) lead to an impedance rise at the anode of a battery during storage, while the corrosion in the current collector can also result in an impedance rise. Therefore, it is imperative to identify the major degradation mechanisms that contribute to a specific performance degradation and aging process. The failure mode and effects analysis (FMEA) method is an effective tool to analyze the potential degradation mechanisms and then identify the critical degradation mechanisms related to battery aging processes.

This research is motivated to develop a methodology for battery lifetime prediction and degradation analysis by integrating statistical models with physical degradation mechanisms. The physical degradation mechanisms are analyzed by using FMEA methods, and the physical models related to critical degradation mechanisms are identified. The integrated statistical model with critical physical degradation mechanisms can provide an effective tool to analyze the degradation trend and predict the lifetime of lithium-ion batteries.

1.2 Literature Review

In this section, the five approaches for battery lifetime prediction are reviewed:
electrochemical models, analytical models with empirical fitting, equivalent circuit based models, performances based models, and statistical models.

Over the past few years, there have been substantial efforts focused on the first four approaches to predict lifetime of batteries [5-17, 52-54]. For example, Darling and Newman [10] developed a series of electrochemical models that establish the mathematical description for battery electrode fade during battery aging. Smith et al. [13] optimized the battery model in [10] and analyzed the degradation over the life of a cell based on degradation mechanisms in the electrodes, involving degradation mechanisms such as lithium deposition. Grolleau et al. [14] developed an empirical degradation model to predict capacity fade under time-dependent storage conditions, state of charge (SoC) and temperature. Eddahech et al. [15] focused on equivalent circuit based models for predicting battery life, and used the identified parameters from Electrochemical Impedance Spectroscopy (EIS) tests to predict the remaining useful life (RUL). For performance-based models, Ecker et al. [16] performed the accelerated calendar aging test by storing batteries at different combinations of temperature and SoC. An impedance-based electric-thermal model coupled with an aging model concerning capacity fade is obtained to predict the lifetime. Wang et al. [17] investigated the effects of parameters (time, temperature, depth of discharge (DoD), discharge rate) using the accelerated cycle life test, and established a cycle life model to describe the time and temperature dependence of capacity fade under different discharge rates. All the models in these four approaches take the physical processes and failure mechanisms into account properly, enabling physics-based lifetime prediction.

Researchers have started to engage in statistical analysis of battery fade data to
develop battery fade models that involve degradation processes [18-21, 46-51]. Thomas et al. [18] developed an empirical accelerated degradation model to reflect the battery power degradation in a static aging environment. Thomas et al. [19] later proposed an integrated empirical model (degradation and error models) to predict the battery calendar life based on the accelerated aging experiment data. Some researchers considered statistical data-driven approaches or integrated methods for battery lifetime prediction. Time series models are regarded as a simple approach for battery lifetime prediction, especially autoregressive (AR) / autoregressive moving average (ARMA) models. Kozlowski [20] developed an ARMA prediction model for SoC and discussed a combined data-driven approach. Liu et al. [21] used the optimized nonlinear autoregressive model for estimating the remaining useful life of lithium-ion batteries. The nonlinear feature of the battery capacity degradation was analyzed. AR/ARMA models are typically effective for short-time prediction; however, they are not reliable for long-term prediction [22].

On the other hand, stochastic processes can be used for battery lifetime prediction. Tang et al. [23] used a Wiener process to analyze the stochastic process of battery degradation, where a linear model is presented. Si [24] later proposed a nonlinear prognostic model to estimate the remaining useful life of batteries, and a Wiener process is used for modeling degradation. Considering the existing applications of degradation models in other engineering fields (e.g., power generators), stochastic processes are regarded as a powerful tool for the degradation analysis. Degradation phenomenon of lithium-ion batteries as a random process can be modeled by different stochastic processes.
1.3 Objectives and Contributions

This research aims to develop a methodology for lithium-ion battery lifetime prediction and degradation analysis by integrating statistical models with physical degradation mechanisms. Four specific objectives to be achieved are:

Objective 1: We begin with an investigation of the aging mechanisms of lithium-ion batteries based on their structures and materials. We analyze the battery aging mechanisms using the FMEA method and identify the critical physical degradation mechanisms according to failure modes categorized from FMEA results. These degradation mechanisms contribute to the major aging process of batteries and have the effects on the performance degradation, e.g., reduction of capacity and reduction of current density. (Chapter 2)

Objective 2: Based on the major aging processes of batteries, we identify the feasible physical models related to the critical degradation mechanisms. The lifetime prediction methods based on physical models are discussed. Monte Carlo simulation method is applied to analyze and predict the lifetime. Physical models based on capacity loss and resistance increase (the major effects by critical degradation mechanisms) are used in lifetime prediction. (Chapter 2)

Objective 3: Stochastic process models are developed to analyze the battery degradation that can capture the temporal variability, and unit-to-unit variability in degradation. A nonhomogeneous Wiener process model with random effects is used to describe the evolution of the degradation process. (Chapter 3)

Objective 4: Integrated statistical models with physical degradation mechanisms are developed based on stochastic process models. A nonlinear model is
developed to reflect the physical degradation mechanism. These integrated models are used for the battery lifetime distribution prediction and degradation data analysis. (Chapter 3)

To achieve these four objectives, several research areas need to be explored as part of this research. Lithium-ion battery aging mechanisms should be investigated, and the FMEA-based method for aging mechanism analysis needs to be developed and extended to study degradation mechanisms. Physical models describing degradation mechanisms need to be analyzed, and the major physical models corresponding to critical degradation mechanisms should be identified. The proposed work provides the capability to combine stochastic process models and physical models to predict the lifetime of batteries, which can handle the major physical degradation mechanisms of lithium-ion batteries.

1.4 Organization

The thesis is organized as follows. Chapter 2 investigates the aging mechanisms of lithium-ion batteries and provides the analysis based on the FMEA method. The identified major degradation mechanisms are used to link with the physical degradation models, and the appropriate methods for lifetime prediction are discussed. In Chapter 3, we provide a modeling procedure for the integrated method, including degradation models based on battery physical mechanisms, stochastic process models based on Wiener processes, and the development of integrated statistical models. The lifetime estimation is developed, and the maximum likelihood estimation (MLE) and expectation-maximization (EM) algorithm are used for parameter estimations. Moreover, numerical experiments, including a simulation-based numerical example and a case study, are
illustrated to demonstrate the effectiveness of the proposed approach by integrating statistical models with physical degradation mechanisms. The analyses for both numerical experiments use the lithium-ion battery degradation data under two different physical degradation mechanisms, respectively. The results show that the integrated method is well adapted. In Chapter 4, the concluding remarks and future research directions are given.
Chapter 2 Lithium-ion Battery Aging Mechanisms and Physical Degradation Models

2.1 Introduction

Battery aging processes take forms of the change in the structure of the components or the change in the materials used in batteries. These changes lead to deteriorations in the properties of batteries that are irreversible under the normal constraints of operation. As a result of these changes in the properties, battery lifetime is impacted by different aging processes. To predict the lifetime of batteries, therefore, it is critical to understand the aging mechanisms underlying the aging processes. It enables us to link the effects induced by aging mechanisms with physical models. Once the physical models for describing different aging mechanisms are established, the battery lifetime or the performance under a certain threshold can be calculated by considering aging factors, such as stress variables under aging conditions.

There are several approaches to analyze and identify degradation modes, potential failure modes, aging mechanisms, and their effects. A systematical method to analyze failure modes and mechanisms is the Failure Mode and Effects Analysis (FMEA) method. FMEA method is an effective tool to systematically evaluate potential ways in which a product or process can fail, to assess the risk of those potential failures, and finally to prioritize the areas where corrective actions are needed to mitigate the consequences of failures. By using FMEA, we can link the aging mechanisms with the physical models.

In this chapter, we begin with an investigation of the aging mechanisms of lithium-
ion batteries and provide the analysis of aging mechanisms using FMEA method. The critical degradation mechanisms are identified according to degradation modes or potential failure modes, and then prioritized by risk assessment criteria. These identified critical degradation mechanisms have the effects on the performance degradation of batteries that can be used to link with physical degradation models. Based on the physical models of critical degradation mechanisms that we propose to use, the lifetime prediction methods are discussed. Finally, Monte Carlo simulation-based method is applied to study a battery degradation data set for the lifetime prediction.

2.2 Battery Aging Mechanisms Analysis using FMEA

To obtain physical models of critical degradation mechanisms, we investigate the aging mechanisms of lithium-ion batteries focusing on structures and materials, followed by using the FMEA method to identify degradation modes and degradation mechanisms in Section 2.2.1. In Sections 2.2.2 and 2.2.3, we present a FMEA table and explain how it is derived, along with the prioritization of degradation mechanisms and potential failure mechanisms. Based on the prioritized results for degradation mechanisms, the effects induced by those mechanisms are evaluated and ranked. The physics-based models are identified based on the major effects of the combined critical degradation mechanisms to capture the physical degradation of batteries. These identified physics-based models will be used for the lifetime prediction of batteries.
2.2.1 Aging Mechanisms and Degradation

There are two different aging processes for different types of batteries: 1) the aging processes that lead to slow degradation and a gradual loss of performance, and 2) the aging processes that have no or virtually no impact on the performance until they suddenly lead to a major problem (sudden death). Lithium-ion batteries exhibit the gradual performance loss over their service life and generally do not suffer from sudden failure that can happen to other battery technologies, e.g., lead acid batteries. Therefore, the scope of this research is focused on the first type of aging processes, the gradual performance loss of batteries.

There are several terminologies in describing battery aging processes and degradation. *Battery performance* [4] (e.g., capacity, high rate discharge power at various SoC and temperatures, charge acceptance and self-discharge) can be measured and assessed using a scalar value such as ampere-hour (Ah) or time until a certain voltage limit has been reached. *Effect* of aging processes [4] is the impact of aging processes on the performance of batteries including capacity, high rate power capability, charge acceptance, etc. For example, reduction of capacity and increased charge transfer resistance are observed effects due to the degradation in the cathode. *Stress factors* [25] are parameters that can describe the operating conditions and the rate at which aging processes proceed (e.g., temperatures, mechanical loads, humidity). These factors affect the battery performance and influence the battery degradation.

Lithium-ion batteries are complex systems with different structures and materials, which makes their aging processes very complicated. Most aging processes interact with each other and cannot be studied separately. That makes it difficult to model aging
processes for battery performance degradation analysis. Aging mechanisms, which can account for aging processes, can lead to changes in the structure and composition of materials of the components, and then cause performance loss. By studying aging mechanisms, we can evaluate the battery degradation during aging processes. Thus, a prior knowledge on the aging mechanisms of battery degradation is crucial in predicting the lifetime.

Figure 1. Aging mechanisms within a lithium-ion cell [26][27]
We investigate the battery aging mechanisms on the cell level and the cell assembly level based on the work in [26-28]. The aging mechanisms are discussed according to the structure of battery cells. Figure 1 and Figure 2 show the cell internal structure and the cell assembly, respectively. In Figure 1, the aging mechanisms and effects marked in red are investigated in this section. Anodes and cathodes are main components whose aging mechanisms differ significantly. The aging of electrolytes mainly takes place at the electrodes and in the interaction with other components. Solid electrolyte interphase (SEI) is a protective layer and has a significant influence on the battery aging. Other internal components and materials such as separators and solvents have interactions with them and with other components during aging processes. External components also play an important role when they come to battery aging. We separately discuss the aging mechanisms of all these components of lithium-ion batteries.

A. Aging of Anodes

Changes at the electrode/electrolyte interface due to reactions of the anode with the electrolyte are considered to be the major source for aging of/at the anode [26].
graphite anodes, a defined SEI layer thickness is necessary to protect the particle surface. As shown in Figure 1, there are two main issues about this layer: the SEI decomposition and a stronger growth in layer thickness. If the SEI-layer grows, the transition of Li+-ions is retarded. After reaching a certain threshold, films become more and more resistive, which can be seen as an aging effect. In contrast, SEI decomposition is also a potential failure mechanism, as the protective function of the layer is a crucial requirement for proper battery functionality. Any defect in the protection layer results in lithium corrosion, and thus, in irreversible energy loss. Especially at high temperatures, the SEI-layer begins to decompose, causing the anode’s passivation to fail.

Electrode particle fracture can occur if the battery is charged too quickly or if the electrode particle size distribution is not well designed. Typically, electrode particles have reduced internal intercalation-induced stresses, allowing the battery's life to be prolonged. The modeling of intercalation stresses can help the design of battery electrodes to minimize mechanical stresses, and further influence on the degradation of lithium-ion batteries. The effects of particle fracture, capacity loss and power fade, can be evaluated and incorporated into lifetime prediction models that are based on a particle fracture failure mechanism. Volumetric changes in the electrode structure lead to electronic disconnect in the battery. These changes can cause isolation of electrode particles, resulting in a reduction in usable capacity. Reduced electrode porosity is the observed degradation mode in the electrode structure.

Lithium plating takes place as a result of lithium metal deposit on the surface of the anode when a battery is charged rapidly or at the low temperatures. The Li+-ions cannot intercalate fast enough into the anode material and Li deposits are formed on the graphite
surface. An ongoing growth of these deposits and the formation of dendrites can destruct the separator and finally cause an internal short circuit of the cell. Corrosion of current collectors may lead to the contact loss and thus to an increase in contact resistance. Studies have shown that the copper anode current collector is especially susceptible to environmentally assisted cracking.

**B. Aging of Cathodes**

Changes in the SEI layer, electrode particle fracture, and volumetric changes in the cathodes are similar to those occurred in the anodes. The aging mechanisms of these changes are the same. Gas generation and bloating of cell casing occur when overcharging of the cathode structure or short circuit. Under overcharging conditions, the electrolyte becomes unstable and reacts with cathode, resulting in temperature raise and gas release. Decomposition of the binder, especially after a lithium-ion battery is exposed under the accelerated cycling life test, is found to be more frequent in the inner parts of the cell.

Moisture intrusion is the common external effect to decrease the cell performance when internal reactions occur after battery exposures over time. The current collector corrosion of aluminum (Al) is based on the corrosion vulnerability of this material, particularly in combination with conducting salts. It leads to increase of resistance, reduction of power, and reduction of current density of battery.

**C. Aging of Electrolytes**

The electrolyte serves as an ionic conductor while guaranteeing electronic insulation. There are several groups of electrolytes: organic electrolytes, solid-state electrolytes and ionic liquid electrolytes. The electrolyte can contribute to side reactions with the
electrodes that reduce the available capacity of the battery and lead to wear-out failures. While the electrolyte most commonly used in lithium-ion batteries has beneficial properties for ion transport, it is highly flammable and unstable outside of a narrow voltage and temperature range. If a battery is operated under extreme temperature or voltage conditions, the electrolyte can decompose, cause gas generation, and lead to thermal runaway.

D. Aging of Separators

The separator in a lithium-ion battery is a porous polymer sheet that allows ion transport while preventing internal electrical short circuits between the electrodes [26]. Typically, electrode contact is due to thermal or mechanical damage to the separator. If metallic particles are present in the battery and puncture the separator, internal short-circuiting can occur. These particles may come from external contamination during assembly, lithium dendrite growth, and/or copper dissolution. Internal short circuit failure mechanisms are observed as an anode/cathode bridge by the particle accompanied by tearing of the separator. This thermal and mechanical damage to the separator can be observed through an inspection device. The pores of the separator are designed to prevent short-circuiting. However, if the battery continues to heat up, the separator can further melt and allow an internal short circuit. Thus, separator shrinkage when exposed to electrolytes or high temperatures can cause the electrode edges to touch, possibly initiating a thermal runaway.

E. Aging of Exterior Cell Components

Exterior cell components play an important role when it comes to battery aging. The structure of a cell with metal housing is shown in Figure 2. The respective aging effects
related to these components are discussed as follows.

The cell terminals are responsible for conducting current from the current collectors to the external electric circuit. The terminals are typically connected to the current collectors by spot welding a tab onto the current collector. Poor spot welding process or an insufficient number of spot welds may lead to the increased resistance to electrical current. Thermo-mechanical fatigue also can cause the connection between the cell terminals and the current collector to degrade and fail. Loss of connectivity or intermittent connectivity can cause the host device to malfunction or fail altogether. Corrosion is another way for failures of the terminals or internal performance degradation. Moisture surrounding the terminals on the exterior of the battery can cause short circuiting of the cell through corrosion reactions or through formed conductive pathways.

The thermal runaway can be induced through denting or crushing of the housing of battery or the cell casing, which causes stress to be transferred to the electrodes and possibly results in a short circuit. This potential failure mode is caused by damage under mechanical loads to the housing of battery or the cell casing.

2.2.2 FMEA Method Implemented for Lithium-ion Batteries

Developed in the 1950s, FMEA has been used to analyze the failures that arise in complex systems in various industries. Although the purposes and terminologies can vary in different types of industry, the principal objectives of the different FMEA processes are to anticipate problems early in the development process, and then either prevent them or minimize their consequences. FMEA is a systematic approach to identify failure or degradation mechanisms and models for all potential failure modes, and then to prioritize
them. In general, high-priority failure or degradation mechanisms can determine the operational stresses, and the environmental and operational parameters that need to be accounted for in the design or to be controlled. These highlighted failure or degradation mechanisms associated with potential failure or degradation are critical in assessing product reliability.

Developing FEMA begins with the understanding of product requirements, the physical characteristics of the product and their variation in the production process. Failure modes are defined as the effects by which failures are physically observed to occur or the ways that product can fail to meet or deliver the intended function. Failure causes are identified by finding the basic reasons that may lead to a failure during operation conditions. The underlying failure or degradation mechanisms driving the failure modes can be identified according to the knowledge of potential failure causes. Finally, these failure or degradation mechanisms are prioritized, and play a critical role to enable the modeling of the relationship between operational or environmental loads and time-to-failure.

Lithium-ion batteries are complex systems that can take many paths towards a failure. FMEA methodology can illustrate the possible causes of a failure and identify the potential failure or degradation mechanisms. Through the prioritization, the major failure mechanisms of batteries are identified and can be used to assist in the physics-of-failure (PoF) approach to account for the stresses experienced by lithium-ion batteries during their life cycles. Thus, the development of an FMEA is the first step in making a transition to physics-based models that can be used for battery lifetime analysis.

In the literature, there is a lack of study on using the FMEA method to analyze the
battery failure modes and mechanisms. Schlasza et al. [27] presented a review of existing literature on battery aging mechanisms and summarized the known aging mechanisms using the FMEA method in order to categorize mechanisms and establish the relationship between failure effects and causes. Hendricks et al. [28] presented an FMMEA of battery failures and described how to improve battery failure mitigation control strategies.

![Figure 3. The framework of FMEA-based battery lifetime prediction](image)

To facilitate the prediction of battery lifetime, we propose a new FMEA-based
framework to identify the physics-based models linked to major failure/degradation mechanisms, shown in Figure 3.

**Step 1:** Identify the items, including all components of lithium-ion batteries.

**Step 2:** Potential failure or degradation modes are investigated, according to the desired level of the depth in the analysis.

**Step 3 and Step 4:** For each failure or degradation modes, potential failure causes and failure/degradation mechanisms need to be identified. All of these are related to aging processes of lithium-ion batteries. For each failure mode, a severity \((S)\), occurrence \((O)\) and detection \((D)\) rating is defined according to subjectively-defined scales, which are based on available information and supported by expert opinions and evaluation. The combination of three ratings defines an overall risk measure, the risk priority number \((RPN)\), which indicates the relevance of each failure or degradation mechanism affecting the lithium-ion battery. The general RPN is calculated for each failure mode according to the following equation:

\[
RPN = S \times O \times D.
\]  

(1)

Generally, a high RPN is a critical indicator for the consideration of corrective actions on the identified components. In this research, a high RPN is a critical indicator for key aging mechanisms related to battery degradation.

**Step 5 and Step 6:** Identify the possible physics-based models, and prioritize failure or degradation mechanisms.

**Step 7 and Step 8:** According to the risk prioritization of failure or degradation mechanisms, we can rank the effects induced by critical failure or degradation mechanisms, and select the corresponding physics-based models to conduct lifetime
prediction.

The results of FMEA analysis for aging mechanisms of lithium-ion batteries are listed in Table A (in Appendix A) [26-28]. It summarizes the potential failure mechanisms or the possible degradation mechanisms leading to failures according to the previous analysis.

2.2.3 Risk Identification based on Aging Mechanisms

The RPN value for each failure mode provides an effective way to prioritize the risk levels. Generally, to quantify the influence of a single failure, Table A contains FMEA-typical columns, which express the occurrence probability of a failure, the severity of the failure effects, and the difficulty to detect the failure using numbers (e.g., 1 to 10). These values are then multiplied using (1), resulting in the RPN for each failure, which gives an indication for the importance of the failure mode and risk priority. As the principal aim of FMEA, this value will be mainly used to express the necessity of a diagnostic method for the respective aging mechanism.

In this research, we simplify the numbers of severity ($S$), occurrence ($O$) and detection ($D$). We consider the severity ($S$) of 3 levels: low, moderate, and high. The low level describes the minor failures or degradation processes that are hardly detectable or have no influence on the lithium-ion battery performance. The moderate level means that the failure or degradation can be detected by the plant owner/operator/user, and will cause dissatisfaction or deterioration of the component or system performance. The high level means that the failure or degradation will result in non-operation of the battery or severe loss of performance. Similarly, we consider the occurrence ($O$) of 3 ranking levels:
low, moderate and high. The low level describes the failure/degradation that is unlikely to occur and the failure rate per unit-hour is in the order of E-7. The moderate level means that the failure/degradation has an occasional probability to occur and the failure rate per unit-hour is in the order of E-5. The high level means that the failure/degradation has a high probability to occur and the failure rate per unit-hour is in the order of E-3 and E-2. For detection (D), we also have 3 levels: low, moderate, and high. The low level describes that almost failure/degradation will be detected with a chance of 71-100%. The moderate level means that the failure/degradation can be detected under a moderate probability of 31-70%. The high level means that none/minimal of probability that failure/degradation will be detected and the chance is 0-30%. Based on these ranking criteria, the evaluation for each failure/degradation mode is provided in Appendix A.

Since the purpose of using FMEA in this research is to find critical failure or degradation mechanisms of lithium-ion batteries, we use the multiplication of severity (S) and occurrence (O) to evaluate the risk level. The risk acceptability matrix is listed in Table 1.

<table>
<thead>
<tr>
<th>Severity</th>
<th>Likelihood of Occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>Low risk</td>
</tr>
<tr>
<td></td>
<td>Low risk</td>
</tr>
<tr>
<td>Moderate</td>
<td>Low risk</td>
</tr>
<tr>
<td></td>
<td>Moderate risk</td>
</tr>
<tr>
<td></td>
<td>High risk</td>
</tr>
<tr>
<td>High</td>
<td>Moderate risk</td>
</tr>
<tr>
<td></td>
<td>High risk</td>
</tr>
<tr>
<td></td>
<td>High risk</td>
</tr>
</tbody>
</table>

As shown in Table A in the Appendix, the battery failure mechanisms are identified and the corresponding risk evaluations are provided. According to these identified risks, we can summarize the major failure mechanisms related to performance degradation of
batteries. We first list all observed effects caused by each failure mode or failure mechanism. For example, there are two observed effects from thickening of SEI layer in the anode: increase in resistance (reduction of power), and reduction of capacity. Each failure effect related to this failure mechanism is assigned a moderate risk. Then we obtain the summary of all occurred failure effects as listed in Table 2. According to the values of the occurrence of observed effects, we can rank all effects based on the information in Table 2, and the histogram is provided in Figure 4. For example, there are a total of 13 occurrences for the increased resistance under different failure mechanisms, including 6 moderate risks and 7 low risks. These major effects are linked to physical degradation mechanisms.

Table 2. Occurrence of observed effects

<table>
<thead>
<tr>
<th>Potential failure mode(s)</th>
<th>Risk evaluation</th>
<th>Observed Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickening of SEI layer in the anode</td>
<td>Moderate</td>
<td>Increased 1</td>
</tr>
<tr>
<td>Particle fracture in the anode</td>
<td>Low</td>
<td>Reduction of 1</td>
</tr>
<tr>
<td>Reduced electrode porosity in the anode</td>
<td>Low</td>
<td>Current density 1</td>
</tr>
<tr>
<td>Lithium plating and dendrite growth on anode surface</td>
<td>Moderate</td>
<td>Heat rise 1</td>
</tr>
<tr>
<td>Free copper particles or copper plating on anode collector</td>
<td>Moderate</td>
<td>Reduction of 1</td>
</tr>
</tbody>
</table>

23
## Table 2. Occurrence of observed effects (Continued)

<table>
<thead>
<tr>
<th>Effect Description</th>
<th>Severity</th>
<th>Occurrence</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickening of SEI layer in the cathode</td>
<td>Moderate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle fracture in the cathode</td>
<td>Low</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Reduced electrode porosity in the cathode</td>
<td>Low</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Gas generation and bloating of cell casing in the cathode</td>
<td>Moderate</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decomposition of binder in the cathode</td>
<td>Low</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture intrusion in the cathode</td>
<td>Low</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pitting corrosion of aluminum on the cathode collector</td>
<td>Low</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Hole in separator</td>
<td>Moderate</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Closing of separator pores</td>
<td>Moderate</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Reduction in lithium ions, thickening of SEI layer</td>
<td>Moderate</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decomposition of electrolyte</td>
<td>Moderate</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Decrease in lithium salt concentration</td>
<td>Moderate</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas generation and bloating of cell casing in the organic solvents</td>
<td>Moderate</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Thickening of SEI layer in the organic solvents</td>
<td>Moderate</td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

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Table 2. Occurrence of observed effects (Continued)

<table>
<thead>
<tr>
<th>External corrosive path between positive and negative leads in the terminals</th>
<th>Moderate</th>
<th>1</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solder cracking</td>
<td>Low</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Internal short circuit between anode and cathode</td>
<td>Moderate</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 4. Risk ranking based on failure/degradation effects

From Figure 4, we can see that the increased resistance and the capacity reduction (or capacity loss) are the two significant effects impacted by aging mechanisms during battery aging processes. The heat increase and the voltage reduction are also major effects caused by battery aging mechanisms. Critical aging mechanisms, such as the thickness growth of solid electrolyte interphase (SEI) layer and the copper plating in the current collector of anode, can contribute to the degradation effects, and thus the
corresponding power fade mechanism can be used to model the performance degradation of batteries under these aging mechanisms. Similarly, identified critical aging mechanisms with the moderate risk level, such as the reduction in lithium-ions and the gas generation and bloating of cell casing, can cause the reduction of capacity. The physical degradation model describing this mechanism can be used for lifetime prediction of lithium-ion batteries.

Using FMEA, we identify the two most critical degradation mechanisms and their physical degradation models: the capacity fading and power fading mechanisms. They will be used for predicting the onset of degradation of lithium-ion batteries and degradation data analysis.

2.3 Physical Models of Battery Degradation

The effects of battery performance degradation are identified using the FMEA method. Based on critical aging mechanisms, the critical physical models related to aging mechanisms can be identified, which is covered in this section before evaluating the lifetime of lithium-ion batteries.

2.3.1 Physical Degradation Models based on Aging Mechanisms

Physical models can well describe the degradation mechanisms of battery performance, which depend on many factors, such as material properties, stress conditions, and usage history. One of the important factors affecting on the life degradation is the stress conditions, e.g., temperature, humidity, voltage. Under a severe
stress condition (e.g., higher temperature), the decrease of battery life will be accelerated. The life-stress relationship follows different laws according to stress variables and degradation mechanisms, e.g., Arrhenius law for temperature, Eyring law for temperature or humidity, and power law for mechanical stress (e.g., cyclic loading) or electrical stress (e.g., voltage). In this research, we consider the Arrhenius law for the relationship between the performance degradation and temperature stress.

We define the degradation of battery performance at time $t$ as $Y(t)$. For the $i$th battery, the degradation is denoted as $Y_i(t)$. The mean performance of batteries, or the expectation of performance level of batteries over time, is defined as $\mu(t) = E(Y_i(t))$. The Arrhenius rate based model for describing physical degradation mechanisms of lithium-ion batteries is given as

$$
\mu(S; t) = a_0 + a_1 \cdot e^{\beta_0 + \beta_1 S} \cdot t^\rho,
$$

where $\mu(S; t)$ is the mean value for the battery performance degradation under a certain physical mechanism related to the temperature effect, $S$ is the temperature stress variable, $t$ is the time variable of the degradation process, and $a_0$, $a_1$, $\beta_0$, $\beta_1$, and $\rho$ are model parameters determined by degradation data. The relationship between the performance degradation and the stress variable in (2) is nonlinear.

Depending on physical degradation mechanisms, there are several metrics to express the degradation performance of lithium-ion batteries, such as measured impedance, charge acceptance, and self-discharge. Internal resistance increase and capacity decrease are primarily the results of lithium-ion battery degradation, which are associated with power fade mechanism and capacity fade mechanism, either as individual physical
mechanisms or with multiple mechanisms occurred in aging processes [17]. In this research, we consider these two battery degradation mechanisms, power fade and capacity fade. Accordingly, the measure of battery performance degradation in (2) is the relative resistance (the resistance at time \( t \) divided by the initial resistance), or the relative capacity (the capacity at time \( t \) divided by the initial capacity), while using temperature as a single stress factor. Thus, the degradation models for two physical mechanisms, power fade and capacity fade, are given as

\[
\mu_R(S;t) = 1 + e^{\beta_{0R} + \beta_{1R}/S} \cdot t^\rho_R \quad \text{and} \\
\mu_C(S;t) = 1 - e^{\beta_{0C} + \beta_{1C}/S} \cdot t^\rho_C,
\]

where \( \mu_R(S;t) \) is the expected relative resistance of batteries, \( \mu_C(S;t) \) is the expected relative capacity of batteries, \( S \) is the absolute temperature in Kelvins, \( \beta_{0R} \), \( \beta_{1R} \), and \( \rho_R \) are parameters of the degradation model for power fade and \( \beta_{0C} \), \( \beta_{1C} \), and \( \rho_C \) for capacity fade, obtained from physical degradation data or results of a semi-empirical model [17-19], [29, 30].

**2.3.2 Lifetime Prediction based on Physical Degradation Models**

With physical models established based on degradation mechanisms, we can do the lifetime prediction according to the relationship of performance degradation over time under certain conditions. Methods of lifetime prediction by using physical models generally follow two steps: 1) determining the parameters in the physical models, and 2) using statistical methods or data-driven methods to do lifetime prediction. The determination of the model parameters usually requires specifically designed experiments.
and extensive empirical data. In the lifetime prediction, statistical methods such as regression are often used to analyze degradation data to update the model parameters. In prognostics, data driven methods are directly used to analyze the lifetime distribution.

In order to estimate the lifetime, we need to derive the closed-form reliability function from physical degradation models, and then to use empirical data to update parameters of physical models. A battery is considered failed when the performance of battery degrades to a critical threshold $D$. Based on the mean degradation model in (2), the time when the battery degradation reaches to the threshold $D$, $t_D$, is derived to be

$$t_D = \left( \frac{\mu_D - a_0}{a_1} \cdot e^{\beta_2/S} \right)^{1/\rho} = e^{(\log(\mu_D - a_0)/a_1 + \beta_2/S)\rho}, \quad (5)$$

where $\mu_D$ is the mean degradation reaches to $D$. By using (5), the mean lifetime of battery degradation can be calculated. According to the properties of physical models, the parameters in the models can be obtained from the empirical results based on experiments or field data analysis, or can be determined from the derived result for each failure mechanism. The lifetime of battery exposed under certain operation conditions can be obtained once the parameters of physical models, the stress variables and degradation values are available.

In this section, we use the Arrhenius rate based model with power fading degradation mechanism to do lifetime prediction for lithium-ion batteries. We select the temperature as a single stress factor and the relative resistance (resistance at time $t$ divided by the initial resistance) as the measure of battery performance. Thus, according to (3) and (5), the end of life time $t_{EOL}$ of battery can be expressed in (6) if the relative resistance is 0.3, as the threshold used in an end of life:
\[ t_{EOL} = e^{(\log(0.3) - \beta_0 R + \beta_1 R S) / \rho_R}, \]

where \( S \) is the absolute temperature in Kelvins, and \( \beta_0 R \), \( \beta_1 R \), and \( \rho_R \) are parameters of physical degradation model for power fade, obtained from physical degradation data or results of a semi-empirical model.

To consider the variability in the actual observed data from experiments or fields, including unit-to-unit variability and the measurement error, we need to add an error term to the mean degradation function. Let \( Y(t) \) denote the degradation characteristic of the battery performance at time \( t \), representing the actual observed performance of batteries. For the \( i \)th battery, the degradation is \( Y_i(t) \). The general degradation model including the mean model and an error term is

\[ Y(t) = \mu(S; t) + \varepsilon(S; t), \]

where \( \varepsilon(S; t) \) is an error item, representing the effects of unit-to-unit variability and measurement errors, and \( \mu(S; t) \) is the mean performance of batteries, \( \mu(t) = \text{mean}(Y_i(t)) \). The error model \( \varepsilon(S; t) \) is given by

\[ \varepsilon_i(S; t) = \kappa_i (\mu(S; t) - 1) + \pi_i(t), \]

where \( \kappa_i \) represents a random battery individual effect and \( \pi_i(t) \) represents the effects of measurement errors. Therefore, \( \kappa_i (\mu(S; t) - 1) \) expresses the unique effect on the performance of individual battery after degradation. In this paper, we assume the measurement error \( \pi_i(t) \) is only affected by the measurement system and is independent to the state of battery.
We assume the \( \kappa_i \) is a normal random variable with a mean of zero and a variance of \( \sigma_{\kappa_i}^2 \), and the measurement errors \( \pi_i \) are independent and identically distributed (iid) normal random variables with a mean of zero and a variance of \( \sigma_{\pi_i}^2 \). Then we can obtain the mean and variance of \( Y(t) \) using (7) and (8):

mean\((Y(t)) = \mu(S;t) \) and

\[
\text{var}(Y(t)) = \text{var}(\varepsilon_i(S;t)) = \sigma_{\kappa_i}^2 (\mu(S;t) - 1)^2 + \sigma_{\pi_i}^2.
\]

(9)

(10)

### 2.4 Lifetime Prediction using Monte Carlo Simulation

When there is no existing lifetime function, we can use statistical methods to find the possible distribution function of lifetime, such as Monte Carlo simulation. Even when the closed-form formulae of lifetime for some simple cases are available but the degradation data is limited, the lifetime prediction can be accomplished using numerical schemes such as Monte Carlo methods. It provides benefits to assess the uncertainty of the result.

The estimate of the end of life time \( t_{EOL} \) of a battery can be obtained if the parameters \( \beta_{0R}, \beta_{IR}, \) and \( \rho_R \) in (6) are estimated, i.e.,

\[
t_{EOL} = e^{\log(0.3) - \hat{\beta}_{0R} - \hat{\beta}_{IR} - \frac{1}{3} \hat{\rho}_R},
\]

(11)

where \( \hat{t}_{EOL}, \hat{\beta}_{0R}, \hat{\beta}_{IR}, \) and \( \hat{\rho}_R \) are the estimates of \( t_{EOL}, \beta_{0R}, \beta_{IR}, \) and \( \rho_R \), respectively.

The lifetime distribution can be estimated using Monte Carlo simulation. It can be done by generating a sufficiently large number of random sample paths from the
degradation paths with the estimated parameters. The steps in the algorithm of Monte Carlo simulation are:

**Step 1.** Use the empirical values of $\beta_{0R}$, $\beta_{1R}$, and $\rho_R$ to calculate the mean battery performance $\mu_R(S;t)$ based on the physical model (3).

**Step 2.** Generate the random samples of $\kappa_i$ and $\pi_i$, where $\kappa_i$ is sampled independently from a normal distribution with a mean of zero and a variance of $\sigma_{\kappa_i}^2$, and $\pi_i$ is sampled independently from a normal distribution with a mean of zero and a variance of $\sigma_{\pi_i}^2$.

**Step 3.** Compute the error data $\varepsilon_i(S;t)$ by substituting the sampled $\kappa_i$ and $\pi_i$ in (8). Then use (7) to combine the mean battery performance calculated in Step 1 and the error data to obtain the sampled paths.

**Step 4.** Conduct a regression analysis for the sampled paths to estimate parameters of the degradation model, $\beta_{0R}$, $\beta_{1R}$, $\rho_R$, $\sigma_{\kappa_i}^2$, and $\sigma_{\pi_i}^2$. Substitute these estimated parameters into (11) to compute $\hat{EOL}_t$.

**Step 5.** Repeat Step 2 to 4 $N$ times (e.g., $N = 1000$) to obtain the estimates of $\hat{t}_{EOL}$.

**Step 6.** Sort the estimates of battery life $\hat{t}^{(1)}_{EOL}$, $\hat{t}^{(2)}_{EOL}$, ..., $\hat{t}^{(1000)}_{EOL}$ to compute statistics, and obtain the distribution of $\hat{t}_{EOL}$.

In the numerical study, the degradation data of lithium-ion batteries is collected from the experiment of 9 batteries. Experimental conditions involved three levels of temperature, $30^\circ C$, $47.5^\circ C$, and $55^\circ C$, with 3 batteries at each level. The batteries are measured every 31.5 days for 7 cycles. Based on the simulation result described in [19],
we use $\beta_{0R} = 18.11$, $\beta_{1R} = -6236$, $\rho_R = 0.50$, $\sigma_{k_i}^2 = 0.0032$, and $\sigma_{\pi_i}^2 = 0.0012$ to construct the simulation data. By using Monte Carlo simulation, the new 9 sample paths are generated by substituting the parameters $\beta_{0R}$, $\beta_{1R}$, $\rho_R$, $\kappa_i$, and $\pi_i$ into (7) and (8). The random samples $\kappa_i$ and $\pi_i$ are obtained from Monte Carlo sampling, where $\kappa_i$ is sampled independently from a normal distribution with a mean of zero and a variance of $\sigma_{k_i}^2 = 0.0032$, and $\pi_i$ is sampled independently from a normal distribution with a mean of zero and a variance of $\sigma_{\pi_i}^2 = 0.0012$. From each trial, we can obtain the new estimates of the parameters $\hat{\Theta} = \{\hat{\beta}_{0R}, \hat{\beta}_{1R}, \hat{\rho}_R, \hat{\sigma}_{k_i}^2, \hat{\sigma}_{\pi_i}^2\}$ by implementing regression analysis. For example, after one trial, the estimated parameters are $\hat{\beta}_{0R} = 17.28$, $\hat{\beta}_{1R} = -5984$, $\hat{\rho}_R = 0.5019$, $\hat{\sigma}_{k_i}^2 = 0.0152$, and $\hat{\sigma}_{\pi_i}^2 = 0.0049$. Using (11), the estimated end of life time of battery $\hat{t}_{EOL}$ is 12.35 years. The detailed regression analysis and algorithm are provided in Appendix B.

Based on the Monte Carlo simulation, $N$ simulated paths $\tilde{Y}(t)$ generate the corresponding $N$ estimates of $\hat{\Theta}$, where $N$ is a large number (e.g., $N = 1000$). The corresponding $N$ simulated $\hat{t}_{EOL}$ is obtained by substituting $\hat{\Theta}$ into (11). Then the empirical distribution of $\hat{t}_{EOL}$ is determined. In our case, we choose $N = 1000$ for simulation. Figure 5 plots the estimated lifetime distribution for 1000 simulation trials. Figure 6 plots the cumulative distribution function of lifetime based on simulation trials.
Figure 5. Histogram of lifetime (1000 simulation trials)

Figure 6. Cumulative distribution function of lifetime

2.5 Discussions

Aging mechanisms provide the important information in analyzing physical degradation of batteries and predicting their lifetime. In this chapter, we investigate the aging mechanisms of lithium-ion batteries based on the structures and materials. Then we conduct FMEA for analyzing aging mechanisms and identify the critical physical degradation mechanisms, failure modes and failure effects through the prioritization of all
the potential failure or degradation mechanisms. Based on FMEA method, the physical
degradation mechanisms with high priority have the effects on the performance
degradation of batteries and are linked with physical degradation models. Two physical
models for identified critical degradation mechanisms are used in the lifetime prediction
and degradation data analysis for lithium-ion batteries. The general method for lifetime
prediction using physical models is discussed, and Monte Carlo simulation based method
is used in assessing the end of life of battery. Our work provides a framework for
physical degradation process analysis of batteries, including identification of battery
aging mechanisms and establishment of physical models. Finally, the numerical study in
lifetime prediction indicates the effectiveness of implementing the identified physical
models in practice.

However, most physical models related to failure mechanisms are damage models
that provide the relationships between stress variables and failure mechanisms. It is
difficult to extend these models to the time-dependent probability models for lifetime
distribution. This limitation motivates us to explore the way to establish the time-
dependent models by integrating the physical degradation or failure mechanisms.
Stochastic process models can characterize the evolution of degradation processes. It is a
powerful tool to analyze the battery aging processes. Stochastic process models can
capture the effects of unit-to-unit variability on performance degradation of batteries.
Monte Carlo simulation can estimate the lifetime when no time-dependent probability
function is available. It can also be used in the stochastic processes analysis since the
closed-forms of time-dependent probability functions are not often available from
degradation processes. In Chapter 3, we propose to develop the integrated model to
integrate physical degradation mechanisms with stochastic processes for battery lifetime prediction.
Chapter 3 Physics-of-Failure based Statistical Degradation

Models for Lithium-ion Battery Lifetime Prediction

3.1 Introduction

The objective of this chapter is to integrate physical mechanisms of battery degradation into the stochastic process modeling to conduct lifetime prediction. Physical degradation models are used to represent the degradation behaviors induced by battery aging (performance loss), such as power fade and capacity fade. The models also describe the stress factors that attribute to battery performance changes. Stochastic degradation models are used to characterize the evolution of degradation processes and compute the lifetime distribution of batteries. Specifically, we use the nonhomogeneous Wiener process to capture the temporal variability of battery aging. Nonlinear mean models are developed to reflect the physical degradation mechanisms for power fade and capacity fade, respectively.

Section 3.2 integrates the physical degradation model into a Wiener process, and the lifetime distribution function is provided. Parameter estimation of the integrated statistical model is performed in Section 3.3. The framework of battery lifetime prediction using the integrated method is discussed in Section 3.4. Section 3.5 provides case studies using simulated-based and real degradation data to illustrate the integrated statistical model and the proposed procedure for estimating battery lifetime distributions.
3.2 Physics-of-Failure based Statistical Models

3.2.1 Stochastic Models Using Wiener Process

Stochastic process models have been widely used for analyzing the degradation data. A Wiener process $W(\cdot)$ can describe the degradation process with a non-monotonic trend. Approaches based on Wiener processes have been used and extended to analyze degradation data [31-44, 55-61]. For example, Whitmore [31] described a Wiener diffusion process model for the measured degradation data that take into account randomness of degradation and measurement errors. Whitmore and Schenkelberg [32] extended the model in [31] with a time scale transformation and incorporated the Arrhenius extrapolation for the accelerated testing. Park and Padgett [33] provided an accelerated degradation model based on the geometric Brownian motion, and the corresponding statistical inference was given. Ye et al. [34, 35] proposed a new inference procedure for a Wiener process with measurement errors based on EM algorithm. Peng and Tseng [36] investigated a random-effect Wiener process with measurement errors and provided the MLE method for estimation. Lim and Yum [37] developed the optimal design of accelerated degradation tests based on Wiener process models and took into account test stress levels and the proportion of test units. Wang [38] introduced a random-effect model by assuming that the drift and diffusion parameters follow a normal-gamma mixture distribution. Ye and Xie [39] provided a comprehensive review on the Wiener process and its various extensions.

Let $Y(t)$ denote the degradation characteristic of the performance at time $t$. The general degradation model using a Wiener process is [40]
where \( \Lambda(t;\phi) \) and \( \tau(t;\eta) \) are continuous non-decreasing functions of time \( t \), the drift parameter \( \nu \) and the diffusion parameter \( \sigma \) can be constants or random variables, and \( W(\cdot) \) is a standard Brownian motion or Wiener process.

The model in (12) can be simplified to a linear model when \( \Lambda(t;\phi) = t \) and \( \tau(t;\eta) = t \):

\[
Y(t) = \nu t + \sigma W(t),
\]

(13)

Tsai et al. [41], Peng and Tseng [36], and Jin et al. [42] used this model in their degradation data analysis.

When \( \Lambda(t;\phi) \neq t \) and \( \tau(t;\eta) = t \), the general model in (12) becomes

\[
Y(t) = \nu \Lambda(t;\phi) + \sigma W(t),
\]

(14)

which is a nonlinear model due to the form of the drift function \( \Lambda(t;\phi) \). Si et al. [43, 44] and Wang et al. [40] used this model to analyze degradation data and provided statistical inference.

When \( \tau(t;\eta) = \Lambda(t;\phi) \) in (12), the degradation model in (12) becomes

\[
Y(t) = \nu \Lambda(t;\phi) + \sigma W(\Lambda(t;\phi)),
\]

(15)

which can describe a time-transformed Wiener process. The drift and diffusion parameters can be assumed to take different forms. This model can handle different sources of variabilities in degradation modeling such as unit-to-unit variability (Wang [38] and Whitmore [32]). In this research, we consider the degradation model in (15) to analyze the battery degradation data. For convenience, we consider the simplified form given by

\[
Y(t) = \nu \Lambda(t) + \sigma W(\Lambda(t)).
\]

(16)
The form of $\Lambda(t)$ can be inferred from the degradation information such as physical degradation mechanisms. $\Lambda(t)$ is typically an increasing function with $\Lambda(0) = 0$ and $\Delta \Lambda = \Lambda(t + \Delta t) - \Lambda(t)$ as a time increment. A Wiener process $W(\cdot)$ can describe the evolution of the degradation with temporal variability. The unit-specific random effects can be incorporated to represent the heterogeneity due to substantial unit-to-unit variabilities. In this research, we define $\omega = \sigma^{-2} \sim Gamma(\delta, r^{-1})$, and $\nu|\omega \sim N(1, \theta / \omega)$ [38]. The resulting Wiener process with normal-gamma mixtures can be used to characterize battery degradation with both temporal and unit-to-unit variabilities.

### 3.2.2 Lifetime Distribution Using Integrated Statistical Models

We integrate the physical mechanisms of battery degradation in Section 2.3.1 into the stochastic process modeling in Section 3.2.1 to analyze the lifetime distribution. By transforming $\mu(S;t)$ in (2) to $\Lambda(t) = (\mu(S;t) - a_0)/a_1 = e^{\beta_0 + \beta_1 S} t^\rho$, and inserting $\Lambda(t)$ in (16), the integrated stochastic model by considering the temporal and unit-to-unit variabilities is given as

$$Y(t) = \nu(e^{\beta_0 + \beta_1 S} t^\rho) + \sigma W(e^{\beta_0 + \beta_1 S} t^\rho).$$

Then, according to (3) and (4), $\Lambda(t)$ can be expressed to $\Lambda(t) = \mu_k(S;t) - 1$ for the relative resistance and $\Lambda(t) = 1 - \mu_c(S;t)$ for the relative capacity, respectively. The parameters in (17) are assumed to follow the normal-gamma mixture distribution as in (16), and as a result, the increment of $Y(t)$ has $\Delta Y(\nu, \sigma) \sim N(\nu \Delta \Lambda, \sigma^2 \Delta \Lambda)$. 

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The battery lifetime \( T \) is defined as the time the degradation reaches the threshold value, \( D \), or the first passage time, \( T = \inf\{t|Y(t) \geq D\} \). It follows the inverse Gaussian distribution with the density function [38]

\[
f(t|\nu, \omega) = \frac{D}{\sqrt{2\pi\sigma^2}\Lambda(t)^3} \exp\left\{-\frac{(\nu\Lambda(t) - D)^2}{2\sigma^2\Lambda(t)}\right\}.
\]

If the joint density function of the parameters \( \omega \) and \( \nu \) is denoted as \( h(\nu, \omega) = f(\nu|\omega)f(\omega) \), the marginal density function of lifetime \( T \) with the normal-gamma mixtures is

\[
f(t) = \int_{-\infty}^{\infty} f(t|\nu, \omega) h(\nu, \omega) \, d\omega \, d\nu = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(t|\nu, \omega)f(\nu|\omega)f(\omega) \, d\omega \, d\nu
\]

\[
= \frac{\Gamma\left(\delta + \frac{1}{2}\right)}{\Gamma(\delta)\sqrt{2\pi r\Lambda(t)^3}(\theta\Lambda(t) + 1)} \left(1 + \frac{(\Lambda(t) - D)^2}{2r\Lambda(t)(\theta\Lambda(t) + 1)}\right)^{-\delta - 1}.
\]

If the degradation paths are monotonic, the cumulative distribution function of \( T \) has an explicit form given by

\[
F(t) = P(T \leq t) = P(Y(t) > D) = \tau_{2\delta}\left(\sqrt{\frac{\delta}{r}} \frac{\Lambda(t) - D}{\sqrt{\Lambda(t)(\theta\Lambda(t) + 1)}}\right),
\]

where \( \tau_{2\delta} \) is the \( t \) distribution function with degrees of freedom \( 2\delta \).

The degradation data \( Y(t) \) at time \( t_1, ..., t_k \) is denoted as \( Y(t_1), ..., Y(t_k) \). We denote \( y(t_k) = Y(t_k) - Y(t_{k-1}) \) and \( \lambda(t_k) = \Lambda(t_k) - \Lambda(t_{k-1}) \) with \( Y(0) = 0 \) and \( \Lambda(0) = 0 \). Similar to (18), \( y(t_k) \) has the density function of

\[
f(y_1, ..., y_k) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(y_1, ..., y_k|\nu, \omega)f(\nu|\omega)f(\omega) \, d\omega \, d\nu
\]
\[
\Gamma\left(\frac{\delta + k}{2}\right) \Gamma\left(\frac{\delta}{2}\right)^{-1} \left(1 + \frac{(y - \lambda)' M^{-1} (y - \lambda)}{2r}\right)^{-\frac{\delta - k}{2}},
\]

where \( y = (y_1, \ldots, y_k)' \), \( \lambda = (\lambda_1, \ldots, \lambda_k)' \), and \( M \) is the matrix obtained by \( M = \lambda(t) (\theta \lambda(t) + 1) \) at time \( t_1, \ldots, t_k \). (21) is used to obtain the maximum likelihood estimation (MLE) of the parameters in Section 3.3.

### 3.3 Parameter Estimation of Integrated Statistical Models

This section discusses the estimation of parameters in (21) using degradation data. We use the maximum likelihood estimator (MLE) to estimate the unknown parameters of degradation model. Expectation Maximization (EM) algorithm is a natural choice to obtain the estimates of unknown parameters using degradation data. The estimation method is also adapted to the applications when the observation times differ from unit to unit.

#### 3.3.1 Maximum Likelihood Estimator

Based on (16) and (21), the likelihood function of parameters \((\lambda, r, \delta, \theta)\) can be written as [38]

\[
L(\lambda, r, \delta, \theta) = L_1(\lambda) + L_2(r, \delta, \theta),
\]

where

\[
L_1(\lambda) = \sum_{i=1}^{m} \left( \frac{N}{2} \log \omega_i - \frac{1}{2} \sum_{k=1}^{N} \lambda_k - \frac{1}{2} \sum_{k=1}^{N} \left( y_i - \lambda_k \right)^2 \right),
\]

(23)
\[ L_2(r, \delta, \theta) = \sum_{i=1}^{m} \left( \delta - \frac{1}{2} \log \omega_i - \frac{1}{2} \log \theta - \frac{\omega_i (v_i - 1)^2}{2\theta} + \delta \log r - r \omega_i - \log \Gamma(\delta) \right), \] (24)

where \( k = 1, \ldots, N \) and \( i = 1, \ldots, m \). \( N \) is the number of observation time points, and \( m \) is the number of batteries. \( \lambda_k = \lambda(t_k) - \Lambda(t_{k-1}) \) is computed based on degradation data.

The MLE of \((r, \delta, \theta)\) can be obtained using the likelihood function in (22):

\[
r = \frac{1}{m} \sum_{i=1}^{m} \omega_i, \tag{25}
\]

\[
\hat{\theta} = \frac{1}{m} \sum_{i=1}^{m} \omega_i (v_i - 1)^2 = \frac{1}{m} \sum_{i=1}^{m} (\omega_i v_i^2 - 2 \omega_i v_i + \omega_i), \text{ and} \tag{26}
\]

\[
\psi(\hat{\delta}) - \log \hat{\delta} = \frac{1}{m} \sum_{i=1}^{m} \log \omega_i - \log \left( \frac{1}{m} \sum_{i=1}^{m} \omega_i \right), \tag{27}
\]

where \( \psi \) is the digamma function.

### 3.3.2 EM Algorithm

The estimators of parameters \((r, \delta, \theta)\) cannot be computed directly by using (25) to (27). Therefore, we use an EM algorithm to estimate the parameters \((r, \delta, \theta)\). The EM algorithm iteratively applies two steps, an E-step (Estimation step) and an M-step (Maximization step).

**E-Step**

Denote \( \Omega^{(t)} = \{ \hat{\lambda}^{(t)}, \hat{r}^{(t)}, \hat{\delta}^{(t)}, \hat{\theta}^{(t)} \} \) to be the estimates at the \( t \)th EM iteration, where \( t \) is the iterative number. The expectation of the unknown parameters after the \( t \)th EM
iteration is \( Q(\lambda, r, \delta, \theta; \lambda^{(t)}, r^{(t)}, \delta^{(t)}, \theta^{(t)}) = E_{\xi^{(t)}}[L(\lambda, r, \delta, \theta; y_{ik}) \mid y_{ik}] \), or the \( Q \) function. The values of \( \lambda^{(t)} \), \( r^{(t)} \), \( \delta^{(t)} \), and \( \theta^{(t)} \) are obtained from the updated \( Q \) function.

The expectations of the sufficient statistics at the \((t+1)^{th}\) \( E \)-step are

\[
E(\omega_i) = \left( \delta + \frac{N}{2} \right) \left( -\frac{\theta^{-1} + \sum_{k=1}^{N} y_{ik}}{2} + \frac{\sum_{k=1}^{N} y_{ik}^2 + \frac{1}{2 \theta} + r}{\theta^{-1} + \sum_{k=1}^{N} \lambda_k} \right)^{-1}, \tag{28}
\]

\[
E(\log \omega_i) = \psi \left( \delta + \frac{N}{2} \right) - \log \left( -\frac{\theta^{-1} + \sum_{k=1}^{N} y_{ik}}{2} + \frac{\sum_{k=1}^{N} y_{ik}^2 + \frac{1}{2 \theta} + r}{\theta^{-1} + \sum_{k=1}^{N} \lambda_k} \right), \tag{29}
\]

\[
E(\omega_i \nu_i) = E(\omega_i) \frac{\theta^{-1} + \sum_{k=1}^{N} y_{ik}}{\theta^{-1} + \sum_{k=1}^{N} \lambda_k}, \text{ and} \tag{30}
\]

\[
E(\omega_i \nu_i^2) = E(\omega_i) \left( \frac{\theta^{-1} + \sum_{k=1}^{N} y_{ik}}{\theta^{-1} + \sum_{k=1}^{N} \lambda_k} \right)^2 + \frac{1}{\theta^{-1} + \sum_{k=1}^{N} \lambda_k}. \tag{31}
\]

**M-Step**

The objective of this step is to find \( \Omega^{(t)} \) that maximizes \( Q(\lambda, r, \delta, \theta; \lambda^{(t)}, r^{(t)}, \delta^{(t)}, \theta^{(t)}) \) over \( \Omega \). \( \Omega^{(t+1)} \) at the \((t+1)^{th}\) iteration can be obtained following the \( E \)-step method. The iteration stops at the \((t+1)^{th}\) iteration when the maximums of (28) to (31) are obtained.

The corresponding estimators at the \( t^{th} \) iteration are updated in (25) to (27) as follows:
\[ \hat{r} = \frac{\hat{\delta}}{\sum_{i=1}^{m} E(\omega_i)} , \]

\[ \hat{\theta} = \frac{1}{m} \sum_{i=1}^{m} E(\omega_i (\nu_i - 1)^2) = \frac{1}{m} \sum_{i=1}^{m} E(\omega_i \nu_i^2 - 2 \omega_i \nu_i + \omega_i) \]

\[ = \frac{1}{m} \sum_{i=1}^{m} \left( E(\omega_i \nu_i^2) - 2 E(\omega_i \nu_i) + E(\omega_i) \right), \] and

\[ \psi(\hat{\delta}) - \log \hat{\delta} = \frac{1}{m} \sum_{i=1}^{m} E(\log \omega_i) - \log \left( \frac{1}{m} \sum_{i=1}^{m} E(\omega_i) \right), \]

where \( \psi \) is the digamma function.

The steps of M-step are as follows:

a) Find \( \Omega^{(t+1)} \) in \( \Omega \) such that

\[ Q(\lambda^{(t+1)}, r^{(t+1)}, \delta^{(t+1)}, \theta^{(t+1)}; \lambda^{(t)}, r^{(0)}, \delta^{(t)}, \theta^{(t)}) \geq Q(\lambda, r, \delta, \theta; \lambda^{(t)}, r^{(0)}, \delta^{(0)}, \theta^{(0)}) . \]

b) The E-step and M-step are repeated alternately until the difference

\[ l(\lambda^{(t+1)}, r^{(t+1)}, \delta^{(t+1)}, \theta^{(t+1)}) - l(\lambda^{(0)}, r^{(0)}, \delta^{(0)}, \theta^{(0)}) \] is less than a prescribed small quantity, or the result converges.

Summary of the EM Algorithm

We summarize the proposed procedure for the EM algorithm as the following algorithm:

**Algorithm 1 (EM Algorithm):**

- Initialize the model parameters by setting the initial values of \( (\lambda^{(0)}, r^{(0)}, \delta^{(0)}, \theta^{(0)}) \).
- E-step: Compute (28) to (31) under current estimators of the parameters.
- M-step: Update \( (\lambda^{(1)}, r^{(1)}, \delta^{(1)}, \theta^{(1)}) \) by using (25) to (27).
• Repeat iteration to E-step for the maximized expectation and obtain the new estimators \((\hat{\lambda}^{(i+1)}, r^{(i+1)}, \hat{\delta}^{(i+1)}, \theta^{(i+1)})\) from each M-step.

• Check \(l(\hat{\lambda}^{(i+1)}, r^{(i+1)}, \hat{\delta}^{(i+1)}, \theta^{(i+1)}) - l(\hat{\lambda}^{(i)}, r^{(i)}, \hat{\delta}^{(i)}, \theta^{(i)})\) until the result is convergent.

### Uncertainty Analysis

Bootstrap method is used to assess the uncertainties of the estimators. In this research, Hall’s percentile bootstrap method is used to estimate the confidence intervals of the estimators \((\hat{r}, \hat{\delta}, \hat{\theta})\). Using \(q\) (e.g., \(q = 1000\)) degradation paths from simulation, the bootstrap algorithm is given as follows:

**Algorithm 2 (Hall’s Percentile Bootstrap Algorithm):**

**Step 1:** Obtain the original estimate of \((r, \delta, \theta)\) from the degradation data through the EM algorithm. Denote \(\hat{\Omega} = (\hat{r}, \hat{\delta}, \hat{\theta})\) as the original estimate.

**Step 2:** Generate the bootstrap degradation paths \(Y_{i}^{(1)}, \ldots, Y_{i}^{(q)}\) from the degradation paths of \(Y_{i}\), where \(q = 1, \ldots, 1000\), i.e., 1000 bootstrap samples are available.

**Step 3:** For each bootstrap sample \(q\), compute the sample estimate \(\hat{\Omega}^{(q)} = (\hat{r}^{(q)}, \hat{\delta}^{(q)}, \hat{\theta}^{(q)})\) by using the same EM algorithm in **Step 1**.

**Step 4:** Sort the \(\hat{\Omega}^{(q)}\) and compute the \(\alpha^{th}\) and \((1 - \alpha)^{th}\) quantiles for \(\hat{\Omega}^{(q)}\).

**Step 5:** Compute \(\eta = \hat{\Omega} - \hat{\Omega}\). Denote \((\eta^{(1)}, \ldots, \eta^{(q)})\) for \(q\) bootstrap replications of \(\hat{\Omega}^{(q)}\).

After sorting, the new bootstrap values \((\eta^{1}, \ldots, \eta^{q})\) are obtained. Then the lower
and upper percentile bootstrap confidence intervals of $\eta$ at $1-2\alpha$ would be $\eta^{a_0}$ and $\eta^{(1-\alpha)q}$.

Finally, the percentile bootstrap confidence interval is obtained, $(\hat{\Omega} - \eta^{(1-\alpha)q}, \hat{\Omega} - \eta^{a_0})$.

Based on the discussion in the previous sections, Figure 7 shows the procedure for the estimation of the lifetime distribution using the integrated statistical model.

**Figure 7. Procedure for the estimation of lifetime distribution**

**Step 1**: Initial data analysis is conducted to obtain battery degradation data $Y(t)$. For instance, battery capacity fade data is extracted from battery performance degradation data (raw measurement data). Then the relative capacity degradation data is obtained by the ratio between the capacity at time $t$ and the initial capacity. In (17), $\Lambda(t)$ is obtained according to the selected physical degradation model. For example, we propose to use the Arrhenius rate model for describing physical
degradation mechanisms of lithium-ion batteries in this research. In (2), the mean performance of batteries is obtained, $\mu(t) = mean(Y_i(t))$.

**Step 2:** Initialize the model parameters $(\lambda, r, \delta, \theta)$ in (20) or (21) by setting the initial values, e.g., the initial values of $(\lambda, r, \delta, \theta)$ is $(1, 1, 1, 1)$.

**Step 3:** Use *EM algorithm* to compute the MLEs of the unknown parameters $(r, \delta, \theta)$.

**Step 4:** Insert the estimates $(\hat{r}, \hat{\delta}, \hat{\theta})$ in (20) to obtain the lifetime distribution function $F(t)$.

**Step 5:** Use *Hall’s Percentile Bootstrap Algorithm* to assess the uncertainties of the estimates.

### 3.4 Framework of Battery Lifetime Prediction

Based on the discussions in Chapter 2 and Chapter 3, Figure 8 displays the framework for battery lifetime prediction using physics-of-failure based statistical degradation models. The proposed methodology for battery lifetime prediction follows three major steps, degradation data collection and initial analysis, identification for physics-of-failure models, and lifetime prediction using integrated statistical models. The first aspect of this three-part framework is data collection and analysis. To explore the degradation of batteries under different operation conditions, the effective data collection should consider these aspects, the metrics of battery performance degradation, the stress factors, the effects of battery aging processes, etc. Then the initial data analysis is conducted to obtain the appropriate transformation of degradation data. For example, we calculate the mean performance of batteries in (2) to transform degradation data.
The second aspect is the identification for physics-of-failure models, which is discussed in Chapter 2. If the physics-of-failure mechanisms are not understood for battery degradation, we propose to use the FEMA-based method to identify potential failure mechanisms. The major failure mechanisms can be linked with physical degradation models. These physical models with PoF mechanisms will be integrated into statistical models to do lifetime prediction for lithium-ion batteries. The lifetime prediction aspect of this framework is based on previous discussions in Chapter 3. Integrating statistical models with physics-of-failure mechanisms provides the feasible solution to predict lifetime of batteries when the degradation mechanisms and characteristics are important for battery life. A key aspect of this framework for lifetime prediction is the integrated statistical models. In this research, we propose to use the nonhomogeneous Wiener process combined with PoF mechanisms to complete lifetime prediction. Other stochastic models integrated with PoF mechanisms can follow the same framework for battery lifetime prediction.
Figure 8. Framework of battery lifetime prediction
3.5 Numerical Examples

In this section, the physics-of-failure based statistical model and the proposed procedure for estimating battery lifetime distributions are illustrated using simulated and real degradation data. In each case, the estimated parameters are obtained by conducting the EM algorithm for the initial parameters of degradation model, and those estimates are used to compute the expected lifetime distribution of batteries. The results of these case studies for lithium-ion batteries can demonstrate the effectiveness of our proposed methodology of integrating statistical models with physics-of-failure mechanisms.

3.5.1 Simulation-based Numerical Study

We consider the power fading process of a certain type of lithium-ion batteries. In this simulation, we generate a sample set containing 20 battery degradation paths. For the physical degradation model in (3), or the degradation of the relative resistance, the empirical values of the parameters are \( \beta_{0R} = 18.11 \), \( \beta_{1R} = -6236 \), and \( \rho_R = 0.50 \), and the temperature stress is \( S = 30^\circ C \)[19].

By using Monte Carlo simulation (the parametric bootstrap method), 20 battery degradation paths, \( Y_i, i = 1, 2, \ldots, 20 \), are generated, where \( Y_i \) is the relative resistance as the measured degradation performance during power fade (or calendar fade). Figure 9 shows the increasing relative resistances of 20 simulated degradation paths.
Given the degradation paths $Y_i$, the estimates of unknown parameters $(r, \delta, \theta)$ in (20) are calculated using (28) to (31). The maximum likelihood estimates of $(r, \delta, \theta)$ are obtained through the EM algorithm. After 116 iterations as shown in Figure 10, the estimates of these unknown parameters are obtained, $(\hat{r}, \hat{\delta}, \hat{\theta}) = (0.1002, 12.8694, 0.0123)$.

Figure 9. Simulated battery degradation paths, $Y_i$

Figure 10. Iteration result of the MLE of $(r, \delta, \theta)$
The cumulative distribution function of the lifetime $T$ is estimated by inserting the estimates $(\hat{r}, \hat{\delta}, \hat{\theta})$ in (20). Consequently, the probability density function (PDF) and the cumulative distribution function (CDF) of the lifetime are shown in Figure 11.

![PDF and CDF of lifetime](image)

Figure 11. PDF and CDF of lifetime

Using the procedure of the bootstrap method discussed in Section 3.3.2, the confidence intervals of the MLEs of $(r, \delta, \theta)$ are obtained as follows, $\hat{r} = 0.1002([0, 0.1387])$, $\hat{\delta} = 12.8694([0, 17.9022])$, and $\hat{\theta} = 0.0123([0.0089, 0.0172])$. Figure 12 displays the histograms of estimated parameters for 1000 bootstrap samples.
Based on the simulated battery degradation data, the CDF (the red solid line) of the lifetime $T$ with the 95% pointwise confidence band (red dashed lines) computed by the bootstrap method is given in Figure 13. The plot also provides the Kaplan-Meier estimates, the empirical distribution (the blue solid line) with the 95% confidence band (blue dashed lines), computed from the follow-up of each unit until it crosses the failure threshold. The blue dash lines are the limits estimates for the lifetime. As shown in Figure 13, the estimated lifetime distribution based on the integrated statistical model well agrees with the empirical distribution. To conclude, this simulation example illustrates the effective estimation of the lifetime for batteries.
3.5.2 Case Study

To demonstrate the proposed physical-based statistical method, the general framework shown in Figure 8 is applied to the real lithium-ion battery degradation data from NASA Ames research center [45]. We selected four sets of capacity degradation data from NASA Randomized Battery Usage Data Set. The configuration of these battery sets is listed in Table 3. Among these four sets of data, three sets (#2, #3, and #4) are used for estimating the empirical parameters of the physical degradation model through the regression method, and one set (#1) is used for degradation process analysis through the proposed method in this research.
Table 3. Configuration of battery sets used for case study

<table>
<thead>
<tr>
<th>Battery set #</th>
<th>Battery number</th>
<th>Environmental temperature</th>
<th>Loading condition</th>
<th>Use for degradation data analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RW13, RW14, RW15, RW16</td>
<td>20°C</td>
<td>Low current</td>
<td>Degradation process analysis</td>
</tr>
<tr>
<td>2</td>
<td>RW17, RW18, RW19, RW20</td>
<td>30°C</td>
<td>Higher current</td>
<td>Physical model parameters estimation</td>
</tr>
<tr>
<td>3</td>
<td>RW21, RW22, RW23, RW24</td>
<td>38°C</td>
<td>Low current</td>
<td>Physical model parameters estimation</td>
</tr>
<tr>
<td>4</td>
<td>RW25, RW26, RW27, RW28</td>
<td>40°C</td>
<td>Higher current</td>
<td>Physical model parameters estimation</td>
</tr>
</tbody>
</table>

Figure 14. Degradation of relative capacity for set #2, #3, and #4

The degradation paths of battery set #2, #3 and #4 are shown in Figure 14. We used the robust linear regression method to obtain the estimates $\hat{\beta}_c$ and $\hat{\rho}_c$ in (4):

$$
\hat{\beta}_c = -5.0306, \quad \hat{\beta}_c = -1683, \quad \text{and} \quad \hat{\rho}_c = 1.192.
$$

Thus, the physical degradation model for capacity fade is

$$
\mu_c(S; t) = 1 - e^{-5.0306 - 1683/S \cdot t^{1.192}}.
$$
Figure 15 displays the degradation paths of four batteries, $Y_i, (i = 1, 2, 3, 4)$ in set #1 with the temperature stress $20^\circ C$. Given these degradation paths, the maximum likelihood estimates of $(r, \delta, \theta)$ in (20) are estimated through the EM algorithm. After 545 iterations, the estimates are obtained, $(\hat{r}, \hat{\delta}, \hat{\theta}) = (20.777, 2309.5, 0.0055)$.

The cumulative distribution function of $T$ is estimated by inserting the estimates $(\hat{r}, \hat{\delta}, \hat{\theta})$ in (20). Hall’s percentile bootstrap method is used to estimate confidence intervals of $(\hat{r}, \hat{\delta}, \hat{\theta})$. Based on 1000 degradation paths from simulation, corresponding confidence intervals of the estimated parameters $(\hat{r}, \hat{\delta}, \hat{\theta})$ are given as follows, $\hat{r} = 20.777([7.9927, 1024.6]), \hat{\delta} = 2309.5([1066.8, 10140]),$ and $\hat{\theta} = 0.0055([0.0046, 0.0326])$.

The PDF of the lifetime $T$ using the estimated parameters are displayed in Figure 16. The solid line is the result using the initial estimates of $(r, \delta, \theta)$ and the dashed lines are
the results using the lower and upper endpoints of 95% confidence intervals for the estimates of \((r, \delta, \theta)\). In Figure 17, the CDF (the solid line) of the lifetime \(T\) with the 95% pointwise confidence band (dashed lines) are plotted. The plots indicate that the procedure can provide reasonable estimates of lifetime in battery degradation analysis.

Figure 16. PDF of lifetime

Figure 17. CDF of lifetime with 95% CI
Chapter 4 Conclusions and Future Extensions

4.1 Summary and Contributions

In this thesis, we developed a methodology for lithium-ion battery lifetime prediction and degradation analysis by integrating statistical models with physical degradation mechanisms. Within the existing literature on lithium-ion battery lifetime prediction, there is a lack of research efforts that utilize statistical models in analyzing the degradation of battery performance and predicting lifetime, not to mention integrating statistical models with physical degradation mechanisms. The contributions of this research can be categorized into the following items:

1: Investigating the aging mechanisms of lithium-ion batteries based on their structures and materials, analyzing the battery aging mechanisms using the FMEA method, and identifying the critical physical degradation mechanisms according to failure modes categorized from FMEA results. These identified degradation mechanisms contribute to the major aging process of batteries and have two effects on the performance degradation, reduction of capacity and reduction of current density.

2: Identifying two physical models based on capacity loss and resistance increase. The lifetime prediction methods using two physical models are provided. Monte Carlo simulation method is applied to analyze and predict the lifetime.

3: Developing stochastic process models to analyze the battery degradation that can capture the temporal variability, and unit-to-unit variability in degradation. A
nonhomogeneous Wiener process model with random effects is used to describe the evolution of the degradation process.

4: Developing integrated statistical models with physical degradation mechanisms based on stochastic process models. A nonlinear model is developed to reflect the physical degradation mechanism. These integrated models are used for the battery lifetime distribution prediction and degradation data analysis.

5: Developing a systematic framework for lithium-ion battery lifetime prediction and degradation analysis based on the method that integrates stochastic process models with physical degradation mechanisms. This framework can be applied for battery lifetime prediction, not only using the nonhomogeneous Wiener process combined with PoF mechanisms proposed in this research, but also using other stochastic models integrated with PoF mechanisms.

Validation results show that using our proposed model can successfully predict the lifetime of batteries and that the effectiveness of the framework for lithium-ion battery lifetime prediction and degradation analysis adopted to real data application.

4.2 Directions for Future Research

The approaches presented in this research have raised a few important questions that require further study from the research communities in reliability, statistics and battery management.

We used the Wiener process for degradation path modeling in the proposed physics-based statistical method for lithium-ion battery lifetime modeling and prediction. However, there are some limitations of using this stochastic process. It does not handle
degradation processes when intermittent failures and random jumps exist in non-monotonic increments. The current proposed model does not capture the measurement error, which is an important effect on the degradation analysis of batteries. Error models in existing research are often assumed to follow a normal distribution, although the error terms are influenced by more complicate environmental conditions in actual cases. More accurate error models should be used to estimate the lifetime distribution.

The integrated models can be extended to cover more stochastic processes and physical degradation mechanisms, under the framework for battery lifetime prediction and degradation data analysis. More physical degradation mechanisms should be considered to reflect the complex battery aging processes, specifically in the assembly level.

Our numerical study used the battery degradation data mostly focusing on battery calendar life. However, the cycling life is another type of time scales suitable for lifetime prediction. The effect of battery cycling process for degradation analysis cannot be ignored, and it should be considered in the future research for degradation modeling.
Reference


## Appendix

### Appendix A:

### Table A. Table of FMEA

<table>
<thead>
<tr>
<th>Battery component</th>
<th>Potential failure mode(s)</th>
<th>Potential failure mechanism(s)</th>
<th>Mechanism type(s)</th>
<th>Observed effect(s)</th>
<th>Potential failure cause(s)</th>
<th>Likelihood of occurrence</th>
<th>Severity of occurrence</th>
<th>Ease of detection</th>
<th>Risk evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode (Active Material)</td>
<td>Thickening of solid electrolyte interphase (SEI) layer</td>
<td>Chemical reduction reaction and deposition</td>
<td>Wearout</td>
<td>Increased charge transfer resistance, reduction of capacity, reduction of power</td>
<td>Chemical side reactions between lithium, electrode, and solvent</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Particle fracture</td>
<td>Mechanical stress</td>
<td>Overstress</td>
<td>Reduction of capacity, reduction of power</td>
<td>Intercalation stress</td>
<td>Moderate</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Reduced electrode porosity</td>
<td>Mechanical degradation</td>
<td>Wearout</td>
<td>Increased diffusion resistance, reduction of capacity, reduction of power</td>
<td>Dimensional changes in electrode</td>
<td>Moderate</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Lithium plating and dendrite growth on anode surface</td>
<td>Chemical reaction</td>
<td>Wearout</td>
<td>Can cause short circuit if dendrites puncture separator</td>
<td>Charging the battery at low temperatures or high rates</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>Moderate</td>
<td></td>
</tr>
<tr>
<td>Battery component</td>
<td>Potential failure mode(s)</td>
<td>Potential failure mechanism(s)</td>
<td>Mechanism type(s)</td>
<td>Observed effect(s)</td>
<td>Potential failure cause(s)</td>
<td>Likelihood of occurrence</td>
<td>Severity of occurrence</td>
<td>Ease of detection</td>
<td>Risk evaluation</td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------------</td>
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<td>-------------------</td>
<td>---------------------------</td>
<td>--------------------------</td>
<td>----------------------</td>
<td>-------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Anode (Current Collector)</td>
<td>Free copper particles or copper plating</td>
<td>Chemical corrosion reaction and dissolution, environmentally assisted cracking</td>
<td>Wearout</td>
<td>Increased resistance, reduction of power, reduction of current density</td>
<td>Overdischarge of the battery</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>Moderate</td>
</tr>
<tr>
<td>Cathode (Active Material)</td>
<td>Thickening of solid electrolyte interphase (SEI) layer</td>
<td>Chemical reduction reaction and deposition</td>
<td>Wearout</td>
<td>Increased charge transfer resistance, reduction of capacity, reduction of power</td>
<td>Chemical side reactions between lithium, electrode, and solvent</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Particle fracture</td>
<td>Mechanical stress</td>
<td>Overstress</td>
<td>Reduction of capacity, reduction of power</td>
<td>Intercalation stress</td>
<td>Moderate</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Reduced electrode porosity</td>
<td>Mechanical degradation</td>
<td>Wearout</td>
<td>Increased diffusion resistance, reduction of capacity, reduction of power</td>
<td>Dimensional changes in electrode</td>
<td>Moderate</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Gas generation and bloating of cell casing</td>
<td>Thermally driven electrode decomposition</td>
<td>Overstress</td>
<td>Reduction of capacity</td>
<td>Overcharge of the battery or short circuit</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>Moderate</td>
<td></td>
</tr>
</tbody>
</table>
**Table A. Table of FMEA (Continued)**

<table>
<thead>
<tr>
<th>Battery component</th>
<th>Potential failure mode(s)</th>
<th>Potential failure mechanism(s)</th>
<th>Mechanism type(s)</th>
<th>Observed effect(s)</th>
<th>Potential failure cause(s)</th>
<th>Likelihood of occurrence</th>
<th>Severity of occurrence</th>
<th>Ease of detection</th>
<th>Risk evaluation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode (Active Material)</td>
<td>Decomposition of binder</td>
<td>Binder dissolution</td>
<td>Overstress</td>
<td>Increased resistance, reduction of power</td>
<td>High internal or external temperature, overcharging of the cell</td>
<td>Low</td>
<td>Moderate</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Moisture intrusion</td>
<td>Chemical reaction</td>
<td>Wearout</td>
<td>Increased resistance, reduction of power</td>
<td>Chemical side reactions between cathode material, water</td>
<td>Moderate</td>
<td>Low</td>
<td>Low</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Cathode (Current Collector)</td>
<td>Pitting corrosion of aluminum</td>
<td>Chemical corrosion reaction</td>
<td>Wearout</td>
<td>Increased resistance, reduction of power, reduction of current density</td>
<td>Overcharge of the battery</td>
<td>Low</td>
<td>Moderate</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Separator</td>
<td>Hole in separator</td>
<td>Mechanical damage</td>
<td>Overstress</td>
<td>High heat generation due to joule heating, bloating of cell casing, drastic voltage reduction</td>
<td>Dendrite formation, external crushing of cell</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Closing of separator pores</td>
<td>Thermally induced melting of separator</td>
<td>Overstress</td>
<td>Inability to charge or discharge battery</td>
<td>High internal cell temperature</td>
<td>Low</td>
<td>High</td>
<td>High</td>
<td>Moderate</td>
<td></td>
</tr>
<tr>
<td>Battery component</td>
<td>Potential failure mode(s)</td>
<td>Potential failure mechanism(s)</td>
<td>Mechanism type(s)</td>
<td>Observed effect(s)</td>
<td>Potential failure cause(s)</td>
<td>Likelihood of occurrence</td>
<td>Severity of occurrence</td>
<td>Ease of detection</td>
<td>Risk evaluation</td>
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<tr>
<td>Lithium ions</td>
<td>Reduction in lithium-ions, thickening of solid electrolyte interphase layer</td>
<td>Electrolyte reduction and solid product formation</td>
<td>Wearout</td>
<td>Reduction of capacity</td>
<td>Chemical side reactions between lithium, electrodes, and solvent</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Electrolyte Salt</td>
<td>Decomposition of electrolyte</td>
<td>Chemical reduction reaction and deposition</td>
<td>Wearout</td>
<td>Increased diffusion resistance</td>
<td>Chemical side reactions between electrolyte, conduction salt</td>
<td>High</td>
<td>Low</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Electrolyte Salt</td>
<td>Decrease in lithium salt concentration</td>
<td>Chemical reduction reaction and deposition</td>
<td>Wearout</td>
<td>Increased diffusion resistance</td>
<td>Chemical side reactions between lithium, electrodes, and solvent</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Organic Solvents</td>
<td>Gas generation and bloating of cell casing</td>
<td>Chemical decomposition of solvent</td>
<td>Overstress</td>
<td>Increased diffusion resistance, and may lead to thermal runaway</td>
<td>High external temperature, overcharging of the cell</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>Moderate</td>
</tr>
<tr>
<td>Battery component</td>
<td>Potential failure mode(s)</td>
<td>Potential failure mechanism(s)</td>
<td>Mechanism type(s)</td>
<td>Observed effect(s)</td>
<td>Potential failure cause(s)</td>
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</tr>
<tr>
<td>Organic Solvents</td>
<td>Thickening of solid electrolyte interphase layer</td>
<td>Chemical reduction reaction and deposition</td>
<td>Wearout</td>
<td>Increased charge transfer resistance, reduction of capacity, reduction of power</td>
<td>Chemical side reactions between lithium, electrodes, and solvent</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td>Terminals</td>
<td>External corrosive path between positive and negative leads</td>
<td>Chemical corrosion reaction</td>
<td>Wearout</td>
<td>High heat generation due to joule heating, bloating of cell casing, drastic voltage reduction</td>
<td>Inadvertent shorting of the terminals</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Solder cracking</td>
<td>Thermal fatigue</td>
<td>Wearout</td>
<td>Loss of conductivity between battery and host device</td>
<td>Circuit disconnect</td>
<td>Low</td>
<td>Moderate</td>
<td>High</td>
<td>Low</td>
<td></td>
</tr>
<tr>
<td>Casing</td>
<td>Internal short circuit between anode and cathode</td>
<td>Mechanical stress</td>
<td>Overstress</td>
<td>High heat generation due to joule heating, bloating of cell casing, drastic voltage reduction</td>
<td>External load on cell</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
<td>Moderate</td>
</tr>
</tbody>
</table>
Appendix B:

Regression Analysis for Physical Model and Algorithm for Monte Carlo Simulation

Regression Analysis for the Estimated Parameters of Physical Models

The parameters in (3) and (8) are estimated using one M-estimation approach \([62-66]\), iteratively reweighted least-squares (IRLS) estimation for linear regression model.

The logarithm form of (3) is given as

\[
\log (\mu (S; t) - 1) = \beta_0 + \beta_1 / S + \rho \log(t).
\] (35)

Thus, the degradation model has the linearized form:

\[
Z = \log (\mu (S; t) - 1),
\] (36)

\[
P_1 = 1 / S,
\] (37)

\[
P_2 = \log(t), \text{ and}
\] (38)

\[
\beta_{2R} = \rho_R.
\] (39)

The degradation model is transformed to be

\[
Z = \beta_{0R} + \beta_{1R}P_1 + \beta_{2R}P_2 = P_i \beta_R,
\] (40)

where \(P_i = [1, P_1, P_2]\), \(i = 1, \ldots, m\), and \(\beta_R = [\beta_{0R}, \beta_{1R}, \beta_{2R}]^t\).

The residuals are given by

\[
e_i = Z_i - \hat{Z}_i = Z_i - P_i b,
\] (41)

where \(b\) is the estimates of \(\beta_{0R}, \beta_{1R}, \text{ and } \rho_R\).
With M-estimation, the estimates $b$ are determined by minimizing a particular objective function over all $b$,

$$
\sum_{i=1}^{n} Q(e_i) = \sum_{i=1}^{n} Q(Z_i - P_i'b) ,
$$

(42)

where the function $Q$ gives the contribution of each residual to the objection function.

Let $\psi = \frac{\partial Q}{\partial e_i}$ be the derivative of $Q$. Differentiating the objective function with respect to the coefficients $b$ and setting the partial derivatives to 0, it produces a system of (2+1) estimating equations for the coefficients.

$$
\sum_{i=1}^{n} \psi(Z_i - P_i'b)P'_i = 0.
$$

(43)

Define the weight function $W_i(e_i) = \psi(e_i) / e_i$, then (44) is transformed to be

$$
\sum_{i=1}^{n} W_i(Z_i - P_i'b)P'_i = 0.
$$

(44)

An iterative solution (iteratively reweighted least-squares, IRLS) is performed as following:

Step 1: Select the initial estimate $b^{(0)}$, such as the least squares estimate,

$Q(e_i) = (Z_i - P_i'b)^2$ is the least squares $Q$-function.

Step 2: At each iteration $t$, calculate residuals $e_i^{(t-1)}$ and associated weights

$W_i^{(t-1)} = W(e_i^{(t-1)})$ from the previous iteration.

Step 3: Solve for new weighted least squares estimate

$$
b^{(t)} = (P'W^{(t-1)}P)^{-1} P'W^{(t-1)}Z ,
$$

(45)
where $W^{(r-1)}$ is diagonal matrix of biweight function with diagonal elements $W_i^{(r-1)}$.

**Step 4**: Repeat Step 2 and 3 until the estimated coefficients converge. The asymptotic covariance matrix of $b$ is

$$v(b) = \frac{E(\psi^2)}{(E(\psi'))^2} (P'P)^{-1},$$  \hspace{1cm} (46)

where $E(\psi^2)$ is estimated by using $\sum_{i=1}^n (\psi(e_i))^2$, and $(E(\psi'))^2$ is estimated by using

$$\left( \sum_{i=1}^n \psi'(e_i / n) \right)^2.$$

In an application, we use Tukey bisquare function as objection function $Q(e_i)$

$$Q(e_i) = \begin{cases} \frac{c^2}{6} \left[ 1 - \left( \frac{e_i}{c} \right)^2 \right]^3, & |e_i| \leq c \\ \frac{c^2}{6}, & |e_i| \geq c \end{cases},$$  \hspace{1cm} (47)

where $c = 4.685$ as a tuning constant.

Similarly, the parameters of the error model are estimated using the same method.

From (10), the variance of the error model is

$$\text{var}(Y_i(S;t)) = \text{var}(e_i(S;t)) = \sigma_y^2 \left( \mu(S;t) - 1 \right)^2 + \sigma_i^2$$

Set

$$Z = \text{var}(Y_i(S;t)),$$  \hspace{1cm} (48)

$$P_i = \left( \mu(S;t) - 1 \right)^2,$$  \hspace{1cm} (49)
\[
\beta_3 = \sigma_{\pi_i}^2, \quad \text{and} \quad (50)
\]
\[
\beta_4 = \sigma_{\kappa_i}^2. \quad (51)
\]
Corresponding transformation is \( Z = \beta_3 + \beta_4 P_4 \). The rest procedure for estimation refers to previous part.