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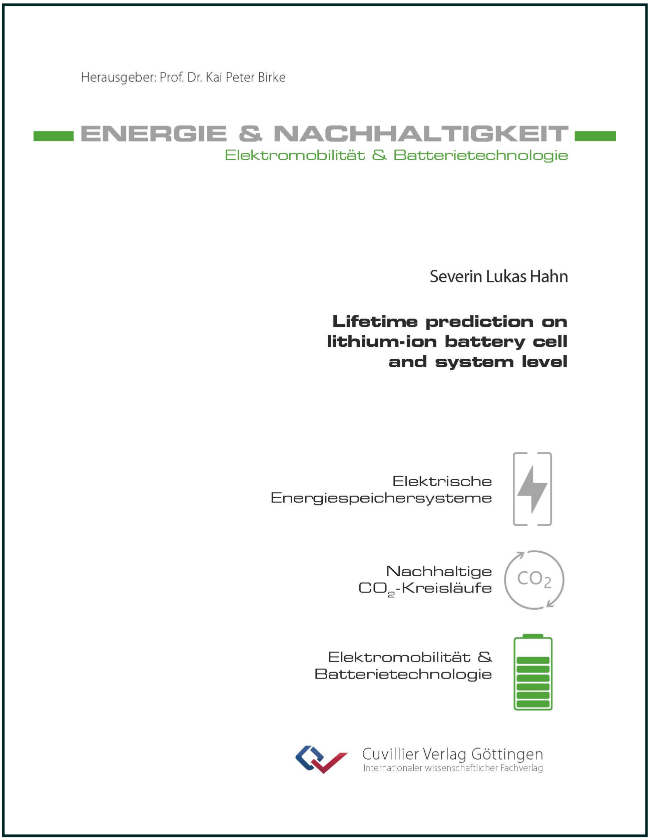
Lifetime prediction on lithium-ion battery cell and system level



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Chapter 1 Introduction

The transformation from a fossil fuel based to a sustainable, climate-neutral society is the greatest challenge of humanity in the 21st century. Failure will result in irreversible loss in biodiversity, sea level rise, droughts and more extreme weather phenomena on the entire planet.[9] Governments are already taking concrete climate action. However, if the pledged goal of the Paris Climate Agreement to limit global warming to 1.5 °C are to be met this will need to accelerate even further, soon. As one of the leaders in global per capita emissions, the European Union (EU) has set a target to be climate-neutral by 2050. Note that this entails cutting current emissions by a factor of more than sixteen[10] or offsetting them by carbon capture. In 2017, transportation accounted for 22 % of European climate forcing emissions.[11] Consequently, fossil-fueled mobility is clearly unsustainable and the EU set the CO_2 fleet emission target to 95 g km^{-1} by 2020 with targeted reductions to 68-75 g km^{-1} by 2025. Clearly, these numbers must tend toward zero in the following years and, indeed, the commission has put forward plans to end wide-spread use of internal combustion engines by 2035. For passenger cars, industry trends tend towards electric vehicles (EV) or plugin-hybrid electric vehicles (PHEV) to reach these targets. Other options such as fuel-cells, synthetic fuels or smaller cars are held back by high cost, low energy efficiency or consumer preference.

Lithium-ion battery (LIB) technology was the key factor to enable this new age of electric vehicles.[12] Their high energy-density enabling ranges of more than 400 km, low-self discharge and comparably long lifetime satisfy consumer needs even for luxury cars. With increasing industrialization, technological and material improvements cost for LIBs is dropping far enough to soon compete with internal combustion engines - regardless of regulation.[13] In such a mass market, battery lifetime must be guaranteed for customer satisfaction, warranty and leniency considerations. Due to the frontloading of energy consumption of electrified vehicles in production, some jurisdictions even impose regulatory requirements for lifetime to ensure sustainability.[14] Reliable lifetime prediction is thus imperative to assess and control risks of this new technology.

Lifetime of LIBs is not only affected by external environmental exposure such as corrosion or vibration, but also by complex mechanical and electrochemical effects originating from inside the cells.[15] For many external effects mitigation strategies and accelerated test for assurance are well known. Among them are thermomechanical stress[16–18], environmental corrosion[19] and vibration[20–23]. On the contrary, merely storing LIBs in so-called calendar aging causes electrochemical degradation that based on current theories cannot be avoided and does not stop. In addition, when cells are operated in cyclic aging multiple degradation phenomena can occur that differ on the applied loads and temperature. Literature[3,24,25] has even proven in multiple cases that aging mechanisms can interact. These effects can limit the system performance due to degraded capacity and increased resistance or even threaten the system safety due to cell opening or module deformation. A module usually consists of stacked cells to integrate cells to a mechanically stable system. Indeed, the lifetime limiting factor may be different in different cells due to differing geometry, housing, materials and chemistry. Due to this complexity, prediction models are often based on physical principles and generalizing assumptions in order to quantitatively predict degradation. Thankfully, many research groups[1,26–29] compete in an enormous effort to develop new and better models to reduce uncertainties.

1.1 Motivation and goals of the thesis

The earliest lifetime prediction models for lithium-ion batteries have been introduced in the first few years of the new millennium.[30,31] These early models were based on theoretical considerations for calendaric aging of single cells. Specifically, they try to model the aging induced due to growth of the anodic solid passivation layer on commonly used graphite. In this chapter, these concepts themselves will not be elucidated in detail yet, but they will be properly introduced and discussed in **Chapter 2**. These theoretical models included hard-to-measure parameters that are simply fitted to measured aging behavior of cells. The models often consist of simple mathematical equations for the two main performance indicators for degradation, capacity and resistance. Furthermore, when theory could not explain certain behavior - famously the charging state dependence – empirical terms with additional fitting parameters were appended.[32] Additional simplifications made it possible to fit aging data sets globally instead to aging of single cells. This allows for interpolation and extrapolation to conditions not included in the aging data set. The resulting so-called semi-empirical models could fit given aging data well. Increasing the amount of fitting parameters, however, may critically favor models that merely fit well to given data, but make inaccurate predictions at other conditions, in a phenomenon generally referred to as overfitting. Importantly for calendaric aging, the behavior in rapidly degrading tests at high temperature could be used to extrapolate the slow aging behavior at lower temperature using an Arrhenius dependency.[27]

Cyclic aging has been similarly modeled with mostly purely empirical and rarely semi-empirical models. Especially the widely used empirical models have little extrapolative power. However, despite being exhaustive it is possible to test the entire estimated energy throughput and the corresponding aging making such models viable.[1] For comparison, testing for calendar aging over the years of vehicle lifetime is infeasible.[1] Despite recent doubts,[33,34] calendaric and cyclic aging are often calculated independently and cumulated additively to a total sum.[29,35,36] This includes the assumption, that aging is path independent.

With the proliferation of electric vehicle development in recent years, the above literature models have been adopted in industry. These modeling principles can be expanded to determine the aging state of the entire battery system made of multiple cells.[35] There are many use cases for aging models. Classically, battery lifetime due to estimated consumer behavior can be calculated and compared to consumer expectation of batteries retaining performance for 200-300'000 km and 10-15 years.[1,23] Often, consumer behavior distributions are used to estimate failed batteries in the entire fleet to assess risks, size reserves for warranty and leniency cases and comply with regulatory conditions.[1] In reverse, the models can be used to identify and rank consumer loads in terms of aging or even to optimize operating strategy to restrict critical loads. Succinctly, the models yield grand statements.

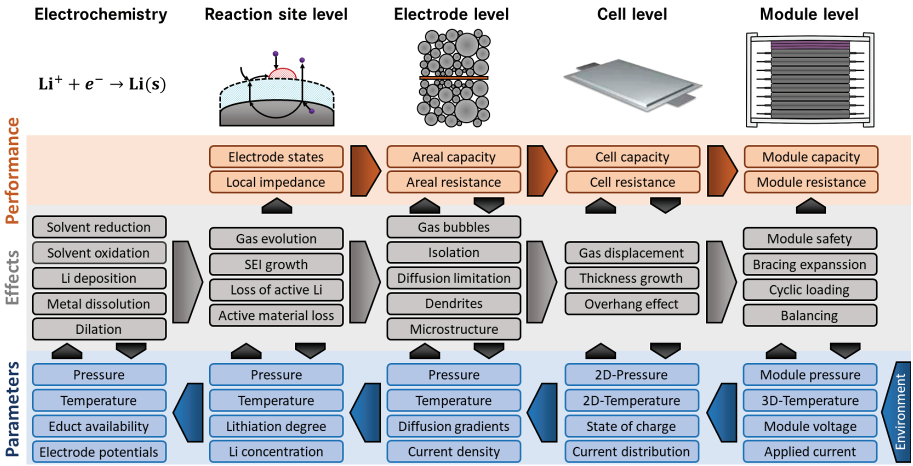

Figure 1.1 Complexity diagram for lithium-ion battery aging interacting on different scales. Effects can have backtracking effects by changing parameters and affect performance. Concept explanations will follow in this thesis.

Still, current methods to estimate lithium-ion battery lifetime are relatively simple, especially when compared to the complexity and plethora of aging mechanisms.[15] Indeed, there are multiple effects that can theoretically limit cell operation just on cell level as will be discussed in **Chapter 2**. Further limitation appears with higher system integration that are influenced by underlying aging mechanisms. In order to meet customer requirements for the battery system, module performance in terms of capacity and resistance as well as integrity and safety must be assured. In order to illustrate the complexity[37], **Figure 1.1** shows select aging effects and their generalized interactions on different scales. An illustration offering all singleton interactions separately would be unclear. To reiterate, the effects will be properly introduced in **Chapter 2**. For now, **Figure 1.1** shows that aging effects can directly affect larger scales, performance, such as available capacity or resistance, and general parameters, such as temperature and pressure. Especially the effect on these parameters can cause a backpropagation to smaller scales. Recognizing the interplay of mechanisms on different scales was crucial in literature to understand and explain, to merely name a few, plating behavior in gassed cells[24], pressure induced plating in flat wound cells[38] or electrode crosstalk reducing gassing.[25] All these chains of effects can be redrawn within **Figure 1.1**. While **Figure 1.1** does not account for the degree of influence, it does illustrate that all aging effects are coupled. This means that aging models must identify and focus on the most important degradation modes in order to be practical to parameterize and use. This is the general area of conflict and tradeoff in LIB aging modeling. Simplifications are necessary[37], but must be carefully argued for given the complexity. Indeed, the previously discussed overfitting is another example of this tradeoff.

The pathway to better, more accurate models is to include more physiochemical effects[37] and modeled parameters that do not increase complexity unnecessarily. These are best derived by theoretical considerations in order to constrain model degrees of freedom and prevent overfitting. The application of this concept has already resulted in powerful predictive tools in literature in the last years expanding and improving existing semi-empirical models.[29,39]

The goal of this work is to use this strategy in order to improve battery life-time predictions for two very important phenomena. The first focus lies on the highly impactful anodic solid passivating layer.[40] It grows to substantial thicknesses[5] and can affect the system by consumption of cyclable lithium[41], impedance of efficient charge transport[27], gas evolution[42] and changes to the microstructure and thus even cell thickness expansion[43]. In fact, the layer grows inevitably[31] both due to calendar[1] as well as cyclic aging[39] and is – in many cases – dominating cell aging as a whole.[44]

The second focus lies on the prediction of pressure development on the module scale due to cell thickness growth as this can critically limit system lifetime and pose safety risks.[2,3] The understanding of pressure evolution can pave the way for informed module design decisions that extend the system lifetime.[3]

1.2 Contributions and structure of the thesis

In order to put the contributions of this thesis into context and a structure, the published scientific contributions are listed here first. This thesis produced several full-length articles[1–4] with the candidate as fully contributing main author:

- Reference [1] published in the *Journal of Power Sources* in 2018:

  S. Hahn, M. Storch, R. Swaminathan, B. Obry, J. Bandlow and K.P. Birke
  Quantitative validation of calendar aging models for lithium-ion batteries

- Reference [2] published in the *Journal of Energy Storage* in 2020. Both first and second author listed in alphabetical order contributed equally:

  T. Deich, S. Hahn, S. Both, K.P. Birke and A. Bund
  Validation of an actively-controlled pneumatic press to simulate automotive module Stiffness for mechanically representative lithium-ion cell aging

- Reference [3] published in the *Journal of Energy Storage* in 2021:

  S. Hahn, S. Theil, J. Kroggel and K.P. Birke
  Pressure Prediction Modeling and Validation for Lithium-Ion Pouch Cells in Buffered Module Assemblies

- Reference [4] published in the book *Modern Battery Engineering* in 2019. This article did not undergo a standard peer-review process.

  S. Hahn and K.P. Birke
  Every Day a New Battery: Aging Dependence of Internal States in Lithium-ion Cells

Furthermore, several articles[5–8] including contributions of this thesis were or are being published:

- Reference [5] pushlished in the *Journal of Power Sources* in 2019:

  M. Storch, S. Hahn, J. Stadler, R. Swaminathan, D.Vrankovic, C. Krupp and R. Riedel
  Post-mortem analysis of calendar aged large-format lithium-ion cells: Investigation of the solid electrolyte interphase

- Reference [6] published in the *Journal of Energy Storage* in 2019:

  J.P. Fath, D. Dragicevic, L. Bittel, A. Nuhic, J. Sieg, S. Hahn, L. Alsheimer, B. Spier, T. Wetzel
  Quantification of aging mechanisms and inhomogeneity in cycled lithium-ion cells by differential voltage analysis

- Reference [7] published in the *Journal of Energy Storage* in 2019:

  J.P. Fath, L. Alsheimer, M. Storch, J. Stadler, J. Bandlow, S. Hahn, R. Riedel, T. Wetzel
  The influence of the anode overhang effect on the capacity of lithium-ion cells – a 0D-modeling approach

- Reference [8] published in the *Journal of Power Sources* in 2021:

  O. Kessel, T. Deich, S. Hahn, F. Brauchles, D. Vrankovic, T. Soczka-Guth and K.P. Birke
  Mechanical impedance as a tool for electromechanical investigation and equivalent modeling of lithium-ion batteries

- Paper to be submitted to *Nature Energy* in 2021:

  K. Schofer, F. Laufer, J.Stadler, S. Hahn, G. Gaiselmann and K.P. Birke
  Machine learning based lifetime prediction of lithium-ion cells

In the following, an overview of the structure of this work is presented. Within, the contributions of this thesis to each of the published articles in Ref. [1–8] are put into context. Both Ref. [1] and [4] encompass the first focus of the thesis on the solid surface layer on the anode while Ref. [2] and [3] embody the second focus on the pressure evolution of aging modules. Given the complexity of aging displayed in **Figure 1.1**, however, it is unsurprising that the two topics are all but separate. Indeed, as shown in Ref. [3] cell growth is attributed to the surface layer growth on the anode. The structure of the thesis reflects this dependency.

Starting in **Chapter 2**, the fundamentals of lithium-ion technology that build the basis for this thesis are introduced based on a detailed literature review. Starting with electrode potentials, the discussion is based on the half-cell framework developed in the theoretical work of Ref. [4]. Changes to electrode states due to different reactions are tracked based on charge flow. Within the framework, simple operation principles as well as the complex aging mechanisms such as the important anode passivating layer are discussed in detail. Understanding aging reactions on this level yields two key insights heavily relied on in this work. The first is the principle of limitation between the main degradation modes of a cell. The second is the readout of these main degradation modes from merely features of non-destructively obtained discharge curves using so-called differential voltage analysis. In Ref. [6] this feature based deduction was automated and optimized in order to quantify aging modes even in highly degraded cells. This method also detected planar aging mode inhomogeneities which lead to the modeling of the overhang effect in Ref. [7]. The overhang effect is also discussed in detail in this chapter.

Chapter 3 presents the overarching experimental details of the different investigations. The automotive cells investigated in this work as well as the cycling conditions and parameter tests used to characterize them are presented. Disassembly and post-mortem procedures detailed here can validate model assumptions and reveal aging modes.

In the following three chapters, the results of this thesis are presented. The beginning of each is structured similarly. A chapter summary places the topic within the context of the entire thesis and gives an overview of the content. In the following, the chapter topic is introduced and motivated as well as relevant insights from literature are presented.

In **Chapter 4,** theoretical considerations of the solid surface layer on the anode in Ref. [1] show that many widely-used time dependencies in literature models are wrongly applied to data and suggest a model correction. This novel semi-empirical model is parameterized experimentally using two matching methods and does not introduce additional degrees of freedom. In order to properly compare the performance to competing literature models, the dataset was split into varying portions for training and validation inspired by machine learning. Based on this, the reduced predictive error and superior performance of the developed model is quantitatively validated. This approach also reveals downfalls of overfitting models previously proposed in literature. The work contributed the idea to directly train machine learning models for lifetime prediction using the predictive error as a fitness function. Indeed, Schofer *et al.* will soon publish an evolutionary symbolic regression algorithm that surpasses the model of Ref. [1] in some aspects. Still, the algorithm model suffers from extrapolative limitations. This is a common challenge in the current push towards machine learning lifetime prediction in literature. Furthermore, the extensive aging matrix published in Ref. [1] with 54 automotive cells has been used for analysis with depth-resolving spectroscopy in Ref. [5]. This article was able to reveal layered structures of the very thin anode passivation layer for the different aging conditions.

Chapter 5 moves toward understanding the cell expansion that causes pressure evolution in aging modules. Based on force equilibrium considerations, an expanding cell stack on one hand put the surrounding module under tension which, on the other, puts the stack under pressure. The pneumatic cell press published in Ref. [2] is introduced that may simulate this mechanical environment for the cells during their operation. An active feedback control loop was developed that may not only control forces accurately, but also reenact the tensile stiffness of a module surrounding the cell in a system. The exact regulation to forces also enables the measurement of mechanical impedances which has been exploited in Ref. [8]. Furthermore, the setup builds the basis for parameterization and validation experiments needed in the modeling effort in the following chapter.

Chapter 6 endeavors to measure, model and validate the evolution of pressure in aging modules. A literature review on cell growth mechanisms causing the pressure is contrasted to experimental results of the investigated cell. Both detailed post-mortem and microscopy image analysis reveal cell growth to correlate to the anodic passivation layer thickness disproving some literature theories. Based on this and force equilibrium considerations, a module model is developed that resolves the pressure evolution due to aging. The model is successfully validated with the measured pressure development of 22 aging modules with different designs. Industry has introduced buffer layers to modules to retain medium pressures over aging which can now be understood on a model basis. In fact, with the model these buffer layers as well as the entire module can be optimized for an improved lifetime.

Chapter 7 summarizes and puts the work into perspective. The results are discussed critically in light of future trends in terms of cell formats and developments in literature.