Chapter 1

Introduction

Lithium-ion batteries play a key role for transforming the automotive sector into a greener and more sustainable industry [1, 2]. On the one hand, they are characterized by a high gravimetric and volumetric energy density [3], a high power and lifetime [4] whereby costs are steadily decreasing [5, 6]. On the other hand, global demand for lithium-ion batteries is expected to grow by more than 500% by 2030 due to new net-zero targets, great customer adaption rates and strategical shifts towards battery electric vehicles of the top OEMs [2].

For achieving full market penetration, consistent and save performance with moderate degradation over lifetime is mandatory. Therefore, lithium-ion cell operation is required to be within an ideal operating window [7–9]. As comprehensive state estimation by measurements is not possible, precise models and state prediction are required [10]. While electric parameters as cycling protocol, C-rate and the charge/discharge cut-off voltages play an important role [11], a key aspect is the adherence to thermal limits [12, 13].

1.1 Motivation

In order to prevent the battery from overheating and causing a thermal runaway, ensure a uniform temperature distribution among different cells and avoid degradation in extreme temperature regions, a thermal management system (TMS) needs to be carefully designed for lithium-ion batteries [14, 15]. By precisely predicting the cell temperature inside a battery pack, various contributing factors as the heat generation and heat accumulation, convection and conduction [13, 16] need to be understood in detail. However, since many different cooling and heating concepts and strategies exist [17–19] and their behavior is different for varying chemistries and cell formats [13, 20], thermal management is complex. Furthermore, the heat generation inside lithium-ion batteries is caused by reaction heat, ohmic heat, polarization heat and secondary reaction heat [21]. While a big variety of thermal, thermal-electric and thermal-electrical-electrochemical models exist for determining the heat generation inside the lithium-ion cell [13, 21], they also strongly differ in complexity. Either being a one-dimensional model, two-dimensional model, three-dimensional model or lumped parameter model, there always exists a tradeoff between complexity and accuracy [22].

Regardless of the model complexity, the accurate determination of thermal characteristics of the lithium-ion cell is of high importance [23, 24]. However, the thermal conductivity and specific heat capacity require a deep understanding of the cell's interior structure and materials. As this is often not provided by the manufacturer or is classified as confidential [14], model parametrization is troublesome. Many numerical models chose frequently used literature values without validation and physical correlation [25, 26]. Since the stacked assembly of lithium-ion electrodes is responsible for anisotropic material properties which lead to a heterogeneous heat flow along the in-plane and through-plane direction [27], the in-plane and through-plane thermal conductivity differ by more than a magnitude [28]. Hence, their precise determination and a full understanding of the thermal behavior is crucial. Furthermore, the specific heat capacity of lithium-ion cells is of high importance for predicting the thermal characteristics of lithium-ion cells [22]. Because the specific heat capacity defines the amount of heat required to increase the cell's temperature, it strongly quantifies the cell's thermal budget [23].

Even though the precise thermal characterization is of high importance, the values found in literature scatter strongly [29]. The in-plane thermal conductivity values range from 21 $\mathrm{Wm^{-1}K^{-1}}$ to 40 $\mathrm{Wm^{-1}K^{-1}}$ [30, 31]. The associated uncertainty of $\pm 31\%$ from the mean value is significant whereby no clear correlation between cell parameters and resulting in-plane thermal conductivity can be determined. Even though there exists a well-used analytical model for the prediction of the in-plane thermal conductivity, it lacks validation [29]. Furthermore, the through-plane thermal conductivity shows the strongest scattering with values between 0.15 $\mathrm{Wm^{-1}K^{-1}}$ to 1.4 $\mathrm{Wm^{-1}K^{-1}}$ [32, 33]. Despite a big amount of collected measurement data, cell chemistry, cell format, porosity, tortuosity, electrolyte and gas content as well as the thermal contact resistance seem to strongly influence the through-plane thermal conductivity [29]. Similar to the in-plane thermal conductivity, a model for the prediction of the through-plane thermal conductivity exists [34]. Though, experimental measurements strongly deviate from the calculated through-plane thermal conductivity values [35–38]. Finally, the specific heat capacity varies between 800 $\mathrm{Jkg^{-1}K^{-1}}$ and 1400 $\mathrm{Jkg^{-1}K^{-1}}$ [39, 40]. As there are many possible reasons fur such high deviations, explanations ranging from the cell format and cell chemistry over the cell housing and housing material to the difference between a high-power and high-energy design are presented. However, no precise correlation between mentioned factors exist [29] and analytical prediction methods exist but lack validation on a full cell level [34]. In summary, the prediction of the thermal characteristics still remains difficult and the selection of a distinct literature value for parametrizing a model is difficult.

Despite there exist many factors which influence the thermal characteristics as described in the paragraph above, thermal simulations of lithium-ion cells always select constant thermal conductivities and specific heat capacities over the full operating range [28, 41–47]. However, it is experimentally proven that factors as pressure [48], temperature [48, 49], state of charge (SOC) [50, 51] and state of health (SOH) [52–54] influence the thermal characteristics of lithium-ion cells. Furthermore, the significance of described parametric effects strongly varies and cannot be quantified in general [29]. Thus, the assumption of constant thermal characteristics in simulations is a simplification whereby the resulting inaccuracy has never been analyzed. Corresponding errors are unknown and the inclusion of operating point-dependent thermal characteristics could potentially increase precision and reliability.

In summary, the design of a TMS is crucial for ensuring a consistent, save and predictable performance of lithium-ion batteries. However, the thermal characteristics of lithium-ion cells are complex. While varying in terms of absolute value, they also show a dependance on parametric effects under varying operating conditions. However, thermal simulations always assume constant thermal characteristics that are not precisely determined. A full understanding of the thermal characteristics and their effect on the thermal behavior of the battery system does not yet exist. The assumption of constant thermal characteristics in thermal models of lithium-ion batteries leads to inaccuracies which have not been quantified yet.

1.2 Goals

The ultimate goal of thermal management for lithium-ion batteries is the exact prediction of the battery's thermal behavior. In detail, this means that the temperature of every element in every cell of the battery pack should be known at all operating points. Hence, the thermal management system should be designed such that the battery is always at the upper performance limit while no degradation occurs. Moreover, the boundaries of the existing trade-off between performance, cost, service life and security can be pushed altogether once a highly accurate operating window is determined. The environmental footprint can be reduced as a result of the degradation-free operation, too. Finally, the fatal consequences of a thermal runaway of the battery should not occur anymore whereby the impeding effects on the adoption rate as well as ecological impacts are minimized.

Even though the described objectives are ambitious and will not be achieved in the near future, the goal of this work is to contribute towards the vision of a precise prediction of the battery's thermal behavior. Especially with a focus on the thermal characterization, the importance of an accurate parametrization of thermal models is analyzed. Thereby, a thorough literature review on the existing measurement approaches and experimental data of the in-plane thermal conductivity, the through-plane thermal conductivity and the specific heat capacity should be performed. Based on that, suitable measurement approaches should be designed or employed in order to allow for a customized parameter tuning with a sufficient accuracy. Furthermore, parametric effects on the thermal characteristics of lithium-ion cells should be analyzed with the developed measurement setups. Although a broad range of parametric effects exists, this work focuses on temperature, SOC and SOH due to their high importance in literature. While this helps to gain a deep understanding of the cell's thermal behavior, it mainly gives important dependencies of thermal input parameters of simulations. Moreover, the experimental data should be used in order to find shortcomings of existing analytical approaches and validate methods for the determination of thermal characteristics. Utilizing the collected data and knowledge, the operating point-dependent thermal characteristics should be implemented into proven thermal models. Although these simulations require adaptions to include variable parameters, the focus should be set on the results of parameter studies and the consequences for parametrizing thermal models. Such numerical data can assist to find physical correlations to contribute towards a guideline for assessing the effect of variable thermal parameters on thermal simulations.

1.3 Outline

As illustrated in Figure 1.1, the following chapter will further elaborate on the theoretical basics of lithium-ion cells. In detail, the different lithium-ion cell formats and their inner structure are presented. The basic effects of the chemistry and layered structure on the thermal behavior are explained. A short introduction into heat generation and thermal simulation of lithium-ion cells is given. Following, chapter 3 to chapter 5 focus on the experimental part of this work. In each chapter, the in-plane thermal conductivity, the through-plane thermal conductivity or the specific heat capacity are comprehensively analyzed. Thereby, a detailed overview of the existing literature and the available measurement data is given. Measurement approaches are compared and a suitable setup is designed or selected to enable a high parameter variation with satisfying precision. In the next step, several sample cells are experimentally analyzed under varying parametric conditions. Corresponding effects of temperature, SOC and SOH are then assessed followed by a validation of an analytical model. Afterwards, chapter 6 analyzes the influence of the previously recorded effects on the thermal simulation. Therefore, an already validated model is adapted and extensive parameter studies are conducted. Finally, a conclusion is given and potential for future work is stated.

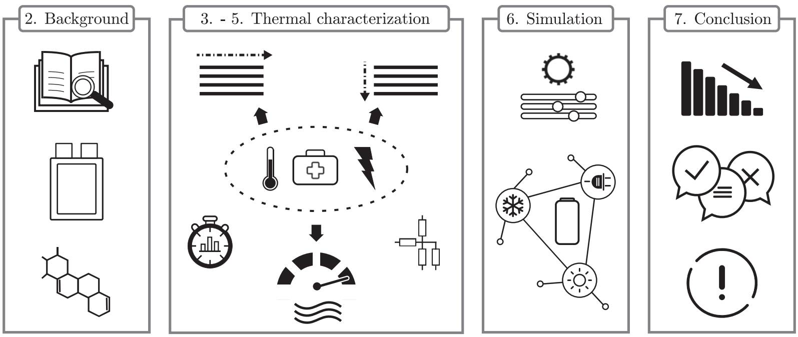

Figure 1.1: Schematic overview of the following chapters.

Chapter 2

Basics of lithium-ion cells

Lithium-ion cells gathered significantly increasing attention over the past decade [55]. Because of their high energy density, high efficiency and long service life [56], they are a versatile approach for energy storage. Ranging from stationary energy buffers over power tool batteries to electric vehicle batteries, lithium-ion batteries find application in many different industries and research clusters [57].

In the following sections, the basics of lithium-ion batteries are presented. With a special focus on the correlation between lithium-ion cells and their thermal behavior, a brief explanation of the charging and discharging process of lithium-ion cells is given. Then, the cell formats and different cell chemistries are described whereby the inner structure as well as the role of every component are analyzed in detail. Furthermore, the physical background of thermal conductivity and specific heat capacity is illustrated. Finally, the different heat generation mechanisms in lithium-ion cells are assessed followed by an overview of thermal simulations for lithium-ion cells.

2.1 Charging and discharging of lithium-ion cells

Lithium-ion cells store energy in chemical form which can be converted into electrical energy by ongoing chemical reactions [58]. Employing the principle of lithium-ion movement, those charge carriers move between the positive and negative electrode. Comprising an anode (negative electrode), cathode (positive electrode), separator and electrolyte as shown in Figure 2.1, the direction of lithium-ion movement depends on whether the cell is charged or discharged [59]. Illustrated in Figure 2.1, a potential difference at the anode and cathode leads to an ionic flow from the cathode to the anode. Thus, electric current flows from the cathode to the anode and the cell is charged [59]. Such ionic migration processes are performed by the electrolyte which is a fluid incorporating a conducting salt to carry the ions from one electrode to the other. Thereby, a separator needs to be passed. Being a porous polymer structure, it prevents the electrodes from shortening while still allowing ionic permeability [60]. When reversing the process displayed in Figure 2.1, the ionic and electric flows are reversed and the cell is discharged. Thus, an electric current is delivered by the cell and the electric energy can be consumed by a connected device [61].

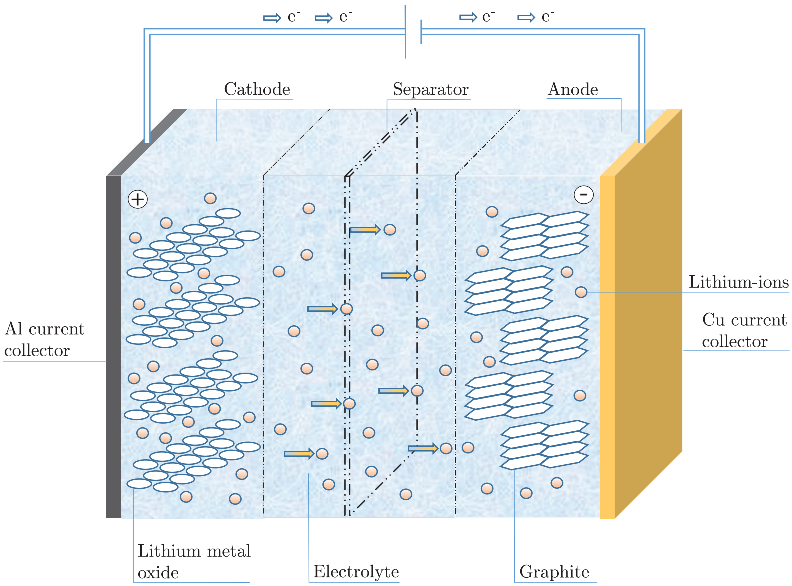

Figure 2.1: Schematic illustration of a charging process inside a lithium-ion cell [61].

2.2 Cell formats of lithium-ion cells

Lithium-ion cells can be found in different shapes. As illustrated in Figure 2.2, there exist three different cell formats which are commonly used. While all of them consist of a metal(-polymer) housing, they mainly differ in size, production cost, stored energy and power output [58, 62].

On the one hand, there is the cylindrical cell which resembles regular consumer battery cells. It has typical dimensions of 18 mm in diameter and 65 mm in height (18650), whereby 26650 and 21700 are common designs, too [63, 64]. The electrodes are produced by coating thin aluminum and copper foils with the active material slurry. Following, the electrodes are calendared, stacked and then wound. In the next step, the so called jelly roll is inserted into the cylindrical metal battery case and then the electrolyte is injected. Finally, the battery case is welded to the current collectors and the cell is closed and sealed. Noteworthy, the cylindrical cell does not have two terminals but one electrode is typically connected to the case which then acts as either the positive or negative terminal [65]. Furthermore, cylindrical cells have a customized pressure relief vent at the top for releasing gas at high pressures to contribute towards a controlled gas ejection [66].

On the other hand, prismatic cells have a rectangular shape with a thick battery casing made out of aluminum. Because the overall dimensions are bigger than for cylindrical cells, a single prismatic cell contains more energy as a regular cylindrical cell [45]. However, the electrode production steps are similar whereby the jelly roll is wound into a flat winding. The jelly roll is then inserted into the deep-drawn cell housing and electrolyte is injected. In contrast to cylindrical cells, prismatic cells have an individual terminal for the positive and negative electrode as shown in Figure 2.2 [57]. Prismatic cells also have a pressure relief vent at the top of the cell to release gas at high pressures [66].

Lastly, pouch cells also have a rectangular shape whereby the casing is a multi-layer foil composite with an aluminum core [57]. Although the electrodes are coated and calendared as well, they are then cut and stacked upon each other. Thereby, a regular stack as well as a z-folded separator stack exists. Moreover, pouch cells have a positive and negative tab in rectangular shape which are either one-sided or two-sided [68]. The electrode stack is assembled into the pouch foil followed by the electrolyte injection. As a final step, the pouch foil is sealed [65].

While the production of all three cell formats is followed by a formation to activate the active material and form the solid electrolyte interface (SEI) [65], each cell format

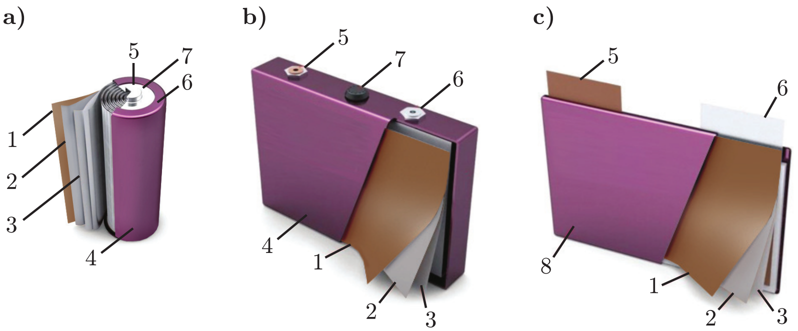

Figure 2.2: Schematic Illustration of the three different cell formats with major components as published in [67]. (a) Cylindrical cell. (b) Prismatic cell. (c) Pouch cell. 1: Anode. 2: Separator. 3: Cathode. 4: Metal case. 5. Negative tab. 6: Positive tab. 7: Pressure relief vent. 8: Metallised pouch foil. ©2012 Johnson Mattey Plc

has its own advantages. First, cylindrical cells can be produced in high quantities and are more likely to provide high currents. Due to their lower energy content per cell, a thermal runaway of a single cell is less dangerous compared to other cell formats. Second, prismatic cells have a more efficient space usage and can be cooled more easily due to the planar surfaces. Finally, pouch cells are characterized by a very high energy density as only a small amount of the cell's volume and weight are non-active. However, they are mechanically unstable and can be easily damaged by sharp objects [57, 58, 69].

2.3 Overview of lithium-ion cell components

The following section presents commonly used cathode and anode chemistries of lithium-ion cells. However, the chemical structure on molecular level is not discussed as it exceeds the scope of this work. Only important correlations which influence the thermal behavior are explained if necessary. The focus is rather set on the main characteristics of each anode and cathode material with regards to industrial application and thermal behavior. Following, the commonly employed separators and electrolytes are briefly presented.