Abstract

Lithium ion batteries have outperformed other battery technologies for decades. Further improvement requires enhancement of the materials, as well as optimization of electrode composition and processing. To enable application of electrochemical models in design optimization and battery production, this dissertation addresses the challenges and applications of battery models. Therefor, an electrochemical pseudo-2D battery model is parameterized assessing its practical model identifiability. Applying this model an uncertainty quantification is carried out to reveal relevant processes. Further, a 3D micro structure model is developed to address the influence of spatial effects, for instance due to the distribution of electron conducting additives. Eventually, the electrochemical and the micro structure model are coupled applying empirical surrogate models. The feasibility of the extended model to simulate the calendering influence is shown. The results show a need for three-electrode measurements with static and dynamic electrochemical tests to enable model identifiability. Further, the uncertainty quantification revealed the nonlinearity and C-rate dependency of the uncertainty propagation. Eventually, micro structure simulations revealed optimization potentials of all-solid-state electrodes through knowledge-based design of mixing routines to maximize electrical and ionic conductivity. The introduced models and the derived results contribute to the simulations-based optimization of battery production and the enhancement of battery performance.

Kurzfassung

Lithiumionen-Batterien finden Verwendung in einer Vielzahl technischer Anwendungen von Mobiltelefonen hin zu Elektrofahrzeugen und stationären Energiespeichern zur Netzstabilisierung. Mit der Verbreitung der Lithiumionen-Batterie steigen Anforderungen an Leistung und Qualität der Batterien. Zudem müssen Produktionskosten und der Einfluss der Batterieproduktion auf die Umwelt reduziert werden. Angesichts dieser Herausforderungen rückt die Batterieproduktion selbst in den Fokus der Wissenschaft und auch der Einsatz von elektrochemischen Modellen in der Produktion wird verstärkt diskutiert.

Entsprechend dieser Ausgangslage ist das Ziel dieser Dissertation Möglichkeiten und Limitierungen der elektrochemischen Modellierung im Kontext der Produktion von Lithium-basierten Batterien aufzuzeigen. Anschließend sollen die Modelle weiterentwickelt werden, um ihre Einsatzmöglichkeiten in der Forschung, aber auch in der Produktion zu erweitern.

Neben den Modellgleichungen sind die Parameter ein essentieller Bestandteil eines Modells, wobei die Parametrierung nicht trivial ist, da ein Teil der Parameter nicht, oder nur schwer experimentell bestimmt werden kann. Daher wurde zu Beginn dieser Arbeit das weitverbreitete pseudo-zweidimensionale Doyle-Newman-Modell auf eine Identifizierbarkeit anhand von Standardexperimenten untersucht. Ergebnis war eine weitgehende Unidentifizierbarkeit an C-Raten-Tests, wobei diese Limitierung mit zusätzlichen Impedanzdaten und der Erfassung von Halbzellpotentialen überwunden werden konnte. Das parametrierte Modell wurde verwendet, um die Fortpflanzung von Unsicherheiten zwischen Zwischenproduktеigenschaften und Produkteigenschaften in der Batterieproduktion zu quantifizieren. Dies ermöglichte die Identifikation relevanterer Prozesse in der Zelle, sowie in der Produktion.

Um den Gültigkeitsbereich des Batteriemodells zu erweitern und so z.B. eine Optimierung des Kalandriergrades in der Produktion zu ermöglichen, wurde ein dreidimensionales Mikrostrukturmodell entwickelt, dass die drei Hauptbestandteile der Elektroden (Aktivmaterial, Elektrolyt, Leitadditive/Binder) und deren räumliche Verteilung berücksichtigt. Dieses Modell wurde einerseits dazu genutzt, Ansätze zur Optimierung der Prozessierung von Festelektrolyt-Elektroden zu identifizieren und zu bewerten, andererseits wurden empirische Surrogatmodelle entwickelt, die das bestehende elektrochemische Batteriemodell um die komplexen Mikrostruktureinflüsse aus dem Mikrostrukturmodell erweitern. Diese Modellerweiterung steigert den Gültigkeitsbereich des Modells hinsichtlich der Elektrodenzusammensetzung signifikant, ohne die Rechenzeit nennenswert zu erhöhen.

Zusammenfassend tragen die Ergebnisse dieser Dissertation dazu bei, elektrochemische Modelle in der Batterieproduktion zu etablieren. Hinsichtlich der Identifizierbarkeit von Modellen wurden Handlungsempfehlungen für zukünftige Parametrierungen abgeleitet, und in der elektrochemischen Modellierung, wie auch in der Mikrostrukturmodellierung wurde der Einfluss der festen Leitadditive erstmals detailliert modelbasiert quantifiziert. Diese Modelle, sowie das gewonnene physikalische Verständnis über interne Prozesse der Batterie können perspektivisch dazu dienen, Batterien weiter zu optimieren und den Einfluss der Produktion auf die Umwelt, sowie die Kosten durch Vermeidung von Ausschuss zu reduzieren.

Chapter 1

Introduction

In this thesis, the battery cell production of lithium-based batteries is investigated. The dissertation addresses physics-based modeling in the context of electrode production. Electrochemical modeling is combined with three-dimensional micro structure modeling to quantify the influence of different aspects of electrode production on the cell performance.

1.1 Motivation

Nowadays, electricity generation from renewable sources and development of large-scale energy storage is growing rapidly. They are driven by environmental and ecological phenomena like an increased frequency of extreme weather conditions and air pollution due to human-induced emissions effecting billions of people. To reduce emissions, e.g. of CO_2, and thus global warming and air pollution, use of fossil fuels has to be substituted to a large extent. Further, increase of electricity production from time-variant wind and solar plants and the breakthrough of electric vehicles require storage of electrical energy. For applications with high requirements regarding energy and power density, the lithium-ion battery (LIB) has outperformed most other electrochemical storage technologies for about two decades now [1, 2].

For further increase of energy density, lithium foil anodes are aimed for as they have a high specific capacity and a low potential [3]. But due to safety and degradation issues of lithium foil anodes caused by dendrite growth, graphite intercalation anodes are commonly used. Today, different solid-state electrolytes are investigated as a possible candidate to reduce dendrite growth and enable the breakthrough of lithium foil anodes. With $600\,\mathrm{W\,h\,L^{-1}}$ and even more, all-solid-state batteries are believed to be a possible intermediate step to batteries with even higher theoretical energy densities [4]. Next-generation candidates are e.g. Li-air or Li-sulfur, which both are still subject of fundamental research but would allow energy densities beyond classical lithium-based intercalation batteries [3].

Current lithium-ion batteries with liquid electrolytes and graphite anodes can reach energy densities of up to $400\,\mathrm{W\,h\,L^{-1}}$ [4]. Till next-generation batteries potentially enable a steep increase of energy density, a steady enhancement of battery components and an optimization of battery production can increase the energy density and reduce waste and rejection rates and thereby contribute to reducing human-induced effects on the environment. Electrochemical battery modeling and process modeling can play an important role for optimization and understanding of cell performance and production. Beside mathematical optimization of cell design and production steps to reduce battery costs [5], an uncertainty quantification can reveal sensitive parameters and help to derive knowledge-based process bounds to reduce waste, rejection rates and cost. This application of models, electrochemical ones and others, in the production of lithium-based batteries lead to increased requirements regarding model accuracy. For instance, prediction of the calendering influence requires novel models to widen the range of validity of electrochemical models [6].

1.2 Scientific Question

Based on the global and societal importance of battery production and the development of modeling, the following hypothesis is stated: Mathematical modeling enables knowledge-based design of the battery cell production. This hypothesis leads to the need to assess the following question: Which model complexity is required to enable model-based process and design optimization, and which further requirements exist for such electrochemical models. To address this scientific question, applications and limitations of modeling in the context of production are investigated in this dissertation.

1.3 Outline

The outline is as follows: First, fundamentals of lithium-based batteries with liquid and solid electrolytes are reviewed. Then, modeling related to battery production is discussed. In Section 2.4, fundamentals of parameter estimation and identifiability are given. In Chapters 3 to 6, applications of models in production are addressed. In Chapter 3, parameters of the classical Doyle-Newman model are estimated and uniqueness of the derived parameter set is analyzed. In Chapter 4, uncertainty quantification of cell parameters related to electrode production is carried out to identify the relevant parameters and processes in cell production. In Chapters 5 and 6, two productions steps, mixing and calendering, are investigated simulation-based to highlight the potential of the application of models in the context of production. Therefor, a micro structure model is introduced which is used to enhance the structure-model parameter relations of the electrochemical model. The results of this work support the introduction of models to the production of LIBs and help to reduce cost, waste and rejection rates of production, while further increasing cell performance.

Chapter 2

Fundamentals

In this chapter, fundamentals of lithium-based batteries are introduced. This includes liquid electrolyte and solid-state electrolyte cells. In addition, cell production and modeling approaches are briefly reviewed.

2.1 Lithium-based Batteries

2.1.1 Cell Chemistry and Active Materials

Generally, a battery cell consists of anode, separator, electrolyte, and cathode. This structure is illustrated in Figure 2.1. The separator avoids an electrical short circuit between anode and cathode, while the electrolyte enables ion transport between the electrodes. A conducting additive-binder domain ensures high electrical conductivity and mechanical stability of the electrodes. The current collectors connect active material and external electric circuit. Further, it provides mechanical stability to the electrode. Commonly, current collectors are made of copper at the anode side and aluminum at the cathode side. Different materials are used due to the different potentials at both electrodes and the electrochemical stability of aluminum and copper at the respective potentials.

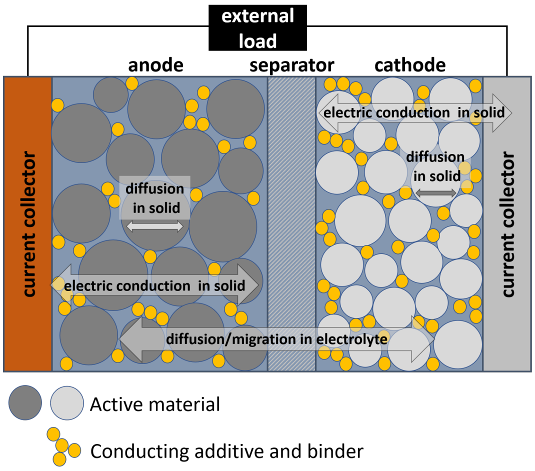

Figure 2.1: Schematic structure of a battery containing anode, separator and cathode. Large grey circles are active material, yellow circles represent the conducting additive-binder-domain and the pore space between the different particles is filled with electrolyte.

The governing processes (see arrows in Figure 2.1) are solid state diffusion of lithium in the active material, diffusion and migration of ions in the electrolyte and electric conduction in the solid between the point of intercalation reaction and current collector.

For cells containing two intercalation electrodes, the main reactions at the particle surface can be summarized as

$$\mathrm{LiC_6} \leftrightharpoons \mathrm{Li}_{1-x}\mathrm{C_6} + x\mathrm{e}^- + x\mathrm{Li}^+ \tag{2.1}$$

for the anode,

$$\mathrm{LiM} \leftrightharpoons \mathrm{Li}_{1-x}\mathrm{M} + x\mathrm{e}^- + x\mathrm{Li}^+ \tag{2.2}$$

for the cathode, and

$$\mathrm{LiM} + \mathrm{C_6} \leftrightharpoons \mathrm{Li}_{1-x}\mathrm{M} + \mathrm{Li}_x\mathrm{C_6} \tag{2.3}$$

for the full cell. In Reaction 2.2, LiM denotes a lithium metal oxide or phosphate like lithium cobalt oxide ($LiCoO_2$, or LCO), mixed nickel-manganese-cobalt dioxide ($LiNi_{1\text{-}y\text{-}z}Mn_yCo_zO_2$, or NMC) or lithium iron phosphate ($LiFePO_4$, or LFP).

The most important properties of a battery are capacity, i.e. charge, and cell voltage, i.e. potential difference between anode and cathode. The capacity is limited by the utilizable concentration difference in the intercalation materials, and cell voltage by the potential difference between anode and cathode materials. Thus, an anode with a low potential and a cathode with a high potential are aimed for. Further important properties of batteries are a high discharge capacity at high current densities, low aging rates, thermal stability, and safety. Due to different weighting of those requirements, different active materials are used today [2].

A comprehensive review on cathode materials was published by Whittingham [7]. Therein, cell voltage, capacity, lattice structure, and volume changes due to intercalation are addressed. More recent reviews focussed on current trends in optimization of electrode materials [8], e.g. coating of LCO with magnesium and phosporus to enhance battery cycle life [8] and coating of NMC with SiO_2 or $Ti(OH)_4$ [9].

Today's development on cell chemistry and active material shows some general trends. At the anode, the silicon content in hybrid graphite-silicon electrodes is increased steadily to increase electrode capacity [10, 11, 12]. At the cathode, the cobalt content in mixed oxides like NMC is reduced due to increasing raw material cost of cobalt. Further coating, doping and compositing of active materials is applied to improve electric conductivity, diffusivity, and capacity [8]. And eventually, as safety is gaining more and more interest, liquid electrolytes are tried to be replaced by solid-state electrolytes.

2.1.2 Liquid and Solid Electrolytes

The objective of the electrolyte is to enable ion exchange between anode and cathode. Therefor, liquid electrolyte of LIBs consists of lithium salt, e.g. $LiPF_6$, and organic solvents like ethylene carbonate or dimethyl carbonate. Solid-state electrolytes are mainly of these types: polymers [13], oxides and sulfides [14]. Polymers are used in combination with lithium salt, while oxides and sulfides are ion conductors enabling lithium transport through their structure. A review about different ion transport mechanisms has been published by Aziz et al. [15].