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A NOVEL ELECTROCHEMICAL BATTERY MODEL FOR STATE OF CHARGE AND STATE OF HEALTH ESTIMATION

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To my family

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Contents

Abstract **ix**

Zusammenfassung **xi**

Nomenclature **xiii**

1 Introduction **1**
1.1 Grading of Li-ion cells for large-scale and automotive applications 1
1.2 Relevance of electrochemical modeling 3
1.3 Objectives of the thesis 3
1.4 Contributions of the thesis 4
1.5 Publications associated with this thesis 6
1.6 Organization of the thesis 6

2 Derivation of novel single-particle battery model **9**
2.1 State-of-the-art electrochemical battery modeling 9
2.1.1 Physical background and first principle modeling . 9
2.1.2 Single-particle (SP) model 11
2.1.3 Challenges in electrochemical modeling for battery management systems 11
2.2 Novel single-particle (NSP) model 12
2.2.1 Approximate solution for electrolyte potential and electrolyte lithium-ion concentration 13
2.2.2 Diffusion in solid material appearing state of charge dependent 15
2.2.3 Balance equation for temperature considering radiation 17
2.2.4 Nonlinear model structure 18

3 Structured model parameterization **21**

3.1 Nonlinear optimization problem of parameter estimation . 21
3.2 Method of combined analysis and identification 22
3.2.1 Parameter analysis based on Fisher-information matrix and parameter sensitivities 22
3.2.2 Parameter group assignment 23
3.3 Model parameterization by means of selected load cases . . 25
3.3.1 Application of the combined parameter analysis and identification 26
3.3.2 Simultaneous solution of model and sensitivity differential equations 26
3.3.3 Model parameterization with five experimental data sets 27
3.4 Comparison of model simulations with real cell experiments 29
3.4.1 Operating cell in very low current regime 30
3.4.2 Operating cell at varying ambient temperature levels 30
3.4.3 Operating cell under potentiostatic conditions . . . 32
3.4.4 Conducting standard test profile of manufacturer . 33
3.4.5 Operating cell with maximum discharge current . . 34

4 Electrode-individual state of charge (SOC) estimation 37
4.1 Discrete-time model reformulation 38
4.2 Observability analysis for NSP model 38
4.3 Design of unscented Kalman filter (UKF) 39
4.3.1 Unscented transform 40
4.3.2 UKF algorithm 41
4.4 Verification of UKF for various load cases 43
4.4.1 Constant current charge/discharge 44
4.4.2 Pulsed current profile 47

5 State of health (SOH) monitoring for cells 51
5.1 Classification of cell degradation mechanisms 51
5.2 Determination of key parameters for cell degradation . . . 53
5.2.1 Battery cell model and aging effects 53
5.2.2 Online estimation of degradation 56
5.3 Experimental validation 57
5.3.1 Cycling behavior of the cell 57
5.3.2 Quantification and separation of power and capacity fade 60

6 Summary and conclusion **63**

A Nomenclature of batteries **65**
A.1 Load current expressed by means of cell capacity 65
A.2 Open circuit potential and terminal voltage 66
A.3 State of charge and power capability 67

B Reference model equations **69**

C Approximate solutions of electrolyte potential **71**
C.1 General considerations 71
C.2 5S-model: Ohmic drop in electrolyte 72
C.3 6S-model: Ohmic drop and local concentration dynamics . 75
C.3.1 Modal transform and modal solution 75
C.3.2 Calculation of modal differential equations 77
C.3.3 Calculation of modal initial conditions 78
C.3.4 Solution for electrolyte potential by means of modal coordinates 79
C.3.5 Analysis of modal solution 79
C.3.6 Self-adjoint eigenvalue problem of modal transform 80

D Systematic parameterization of open circuit potential **83**

E Observability analysis for nonlinear systems **87**
E.1 Global observability 87
E.2 Local observability 89

F Model scaling **91**

List of Tables **93**

List of Figures **95**

Bibliography **99**

Curriculum Vitae **109**

Abstract

This thesis presents a novel electrochemical lithium-ion cell model, which can be used in battery control units.

Based on classical single-particle approaches, a lumped-parameter nonlinear model is developed. It is able to predict accurately the terminal voltages for arbitrary loads, and even for potentiostatic operation. The key points are: (1) an incorporation of the electrolyte potential, (2) a modal decomposition of the partial differential equation of the liquid phase lithium-ion concentration, (3) a correct handling of the SOC-dependent diffusivity in the insertion materials of both electrodes, and (4) a consideration of temperature-dependent kinetic processes. A combined parameter analysis and identification is successfully applied for the parameterization of the model. Using a Fisher-information matrix approach in combination with a sensitivity analysis, the identifiability of each parameter is estimated in dependence on the measurement information. Using this information, it is possible to choose a small number of relevant experiments, which are sufficient to fully parameterize the model.

In order to determine the internal model states that account for the actual stored amount of charge an unscented Kalman Filter is employed. It allows for the distinction of electrode individual state of charges. This inherently discrete-time state estimation approach provides a decoupling of model and filter correction update and is therefore well suited for stiff differential equations. Besides, no Jacobians of the highly nonlinear state space battery model have to be computed. The UKF shows an extraordinary tolerance against parameter errors. This property makes it a promising candidate for the monitoring of cell aging effects.

In a last step, the estimated states of the UKF are used to track cell degradation effects. By means of the cell model parameters that account for

the capacity of the cathode and the overall conductivity of the electrolyte, the currently available maximum charge and power can be predicted. For this reason, the estimated states are compared for congeneric load profiles but different stages of age. Deviations are then addressed to shifts in the respective model parameters. This approach provides the distinction of capacity fade due to active material losses and due to rate capability fade as well.

Zusammenfassung

In dieser Arbeit wird ein neues elektrochemisches Modell einer Lithium-Ionen-Zelle, welches sich für die Verwendung in Batterie-Steuergeräten eignet, vorgestellt.

Basierend auf dem bekannten Ein-Partikel-Ansatz wird ein nichtlineares Modell mit konzentrierten Parametern entwickelt. Es erlaubt die genaue Vorhersage der Klemmenspannung und der Zelltemperatur für beliebige Lastströme und sogar für den potentiostatischen Betrieb. Dabei sind folgende Kernfunktionalitäten identifiziert worden: (1) Die Miteinbeziehung des Elektrolyt-Potentials, (2) die modale Zerlegung der partiellen Differenzialgleichung der Lithium-Ionen-Konzentration im Elektrolyten,
(3) der korrekte Umgang mit der ladezustandsabhängigen Diffusivität im Interkalationsmaterial beider Elektroden und (4) die Berücksichtigung temperaturabhängiger, kinetischer Prozesse. Eine kombinierte Parameteranalyse und -identifikation ist erfolgreich zur Parametrierung des Modells umgesetzt worden. Mittels eines Fisher-Informations-Matrix-Ansatzes wird zusammen mit einer Sensitivitätsanalyse die Identifizierbarkeit jedes einzelnen Parameters auf Basis der Messinformation geschätzt. Unter Verwendung dieser Information ist es möglich, eine kleine Anzahl relevanter Experimente, die hinreichend für die vollständige Parametrierung sind, auszuwählen.

Um die internen Modellzustände, welche beispielsweise für die gespeicherte Ladung stehen, zu bestimmen, wird ein unscented[1] Kalman Filter (UKF) verwendet. Der UKF ermöglicht die Unterscheidung elektrodenspezifischer Ladezustände. Dieser grundsätzlich zeitdiskrete Zustandsschätzer erlaubt die Entkoppelung des Modell- und des Filterkorrekturterm-Updates und ist daher für steife Differentialgleichungssysteme sehr gut

[1] wörtl.: unparfümiert. Der Begriff bezieht sich vermutlich auf die exakte Abbildung von Erwartungswert und Varianz einer Variabeln bis auf Terme 3. und höherer Ordnung.

geeignet. Darüber hinaus entfällt die Berechnung der Jacobi-Matrizen des hochgradig nichtlinearen Zustandsraum-Batteriemodells. Der UKF zeichnet sich im vorliegenden Fall durch eine ausserordentlich hohe Toleranz gegenüber Parameterfehlern aus. Diese Eigenschaft macht ihn zu einem vielversprechenden Kandidaten für das Monitoring von Alterungseffekten in der Zelle.

In einem letzen Schritt werden die mit dem UKF geschätzten Zustände verwandt, um die Degradation der Batterie im Betrieb zu verfolgen. Mit Hilfe der Modell-Parameter, welche die Kathoden-Kapazität und die Leitfähigkeit des Elektrolyten repräsentieren, können die verfügbare Ladung und Leistung vorher gesagt werden. Hierzu werden die geschätzten Zustände für verschiedene Alterungsgrade aber bei identischen Lastprofilen verglichen. Abweichungen können somit Änderungen der zugehörigen (Alterungs-) Parameter zugeordnet werden. Dieser Ansatz ermöglicht die Unterscheidung des Kapazitätsverlusts in den Anteil verursacht durch Verlust an aktivem Material und in jenen, der auf den Rückgang der Stromtragfähigkeit (Leistungsverlust) zurückzuführen ist.

Nomenclature

Acronyms

$MCMB$	Mesocarbon mircobead
$MOPS$	Multi-objective parameter synthesis
NSP	Novel single particle
ODE	Ordinary differential equation
$PD(A)E$	Partial differential (algebraic) equation
SDE	Sensitivity differential equation
SEI	Solid-electrolyte interface
SOC	State of charge
SP	Single particle

Indices

$\overline{(.)}$	Volume averaged magnitude
1	Related to the solid active material
2	Related to the electrolyte phase
a	Active material of the anode
c	Active material of the cathode
cc	At the current collector of the anode
i	Index of a certain parameter
j	General index for spatial cell segment
k	Temporal mode number
l	Electrolyte phase
m	General index for a phase segment
n	Index of a uncorrelated parameter
s	Related to the separator
w	Index of a certain data point

ξ	Index of a certain measurement
υ	Index of a certain output

Symbols

a_j, b_j, d_j	Time-varying coefficents, $(mol\, m^{-3})$
$a_{s,j}$	Active surface area, (m^2)
$c_{1/2,j}$	Bulk lithium-ion concentration, $(mol\, m^{-3})$
$c_{1,s,j}$	Surface lithium-ion concentration, $(mol\, m^{-3})$
$c^*_{2,k}$	Temporal mode of c_2, $(-)$
D_F	Diagonalized Fisher-information matrix, $(-)$
$\mathbb{E}$	Expectation value, $(-)$
$\mathbf{f}$	State function vector, $(-)$
$f_\pm$	Mean molar salt activity, $(m^2\, s^{-1})$
F_{info}	Fisher-information matrix, $(-)$
$\mathbf{h}$	Output function vector, $(-)$
$i_{0,j}$	Exchange current density, $(A\, m^{-2})$
$i_{1/2}$	Cell internal current, $(A\, m^{-2})$
I	External load current, $(A\, m^{-2})$
j_j	Reaction rate, $(mol\, m^{-2}\, s^{-1})$
N	Total number of data points, $(-)$
N_θ	Total number estimated parameters, $(-)$
p	Probability density function, $(-)$
$q_{1/2,j}$	Lithium-ion flux, $(mol\, m^{-3})$
r	Independent variable, radial direction, $(-)$
R_j	Radius of active particle, (m)
$R_{SEI,j}$	SEI film resistance, $(\Omega\, m)$
$S_{x/y}$	Sensitivity w.r.t. parameters, $(-)$
t	Time, (s)
t^0_+	Transference number, $(-)$
T	Cell temperature, (K)
T_{corr}	Temperature correction for kinetics, $(-)$
T_∞	Ambient temperature, (K)
u	Input magnitude, $(-)$
U	Terminal voltage of the cell, (V)
U_{ocp}	Open circuit potential, (V)

V	Total number of experiments, $(-)$
$\mathbf{x}$	State variable vector, $(-)$
$\boldsymbol{\mathcal{X}}$	Sigma point state matrix, $(-)$
$\mathbf{y}$	Output vector, $(-)$
$\boldsymbol{\mathcal{Y}}$	Sigma point output matrix, $(-)$
z	Independent variable, across cell sandwich, $(-)$
Z	Transformation matrix, $(-)$
γ	Variance boundary for identification, $(-)$
Γ_j	Spatial domain in z, $(-)$
η_j	Surface overpotential, (V)
$\boldsymbol{\theta}$	Parameter vector, $(-)$
λ_{min}	Minimum eigenvalue of F_{info}, $(-)$
σ	Variance, $(-)$
$\widehat{\theta}$, θ^*	Estimated parameter, true parameter, $(-)$
τ_j	Diffusion time constant, (s)
$\Phi_{1/2,j}$	Electrochemical potential, (V)