Martin J. Brand

Lithium-ion battery cells and systems under dynamic electric loads

Herbert Utz Verlag · München

Ingenieurswissenschaften

Zugl.: Diss., München, Techn. Univ., 2018

Bibliografische Information der Deutschen Nationalbibliothek: Die Deutsche Nationalbibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über http://dnb.d-nb.de abrufbar.

ISBN 978-3-8316-4752-1

Printed in Germany
Herbert Utz Verlag GmbH, München
089-277791-00 · www.utzverlag.de

Abstract

There is a certain gap between fields of research and the knowledge needed to develop a commercial product that contains a battery system. Scientific publications mostly deal with single battery cells and with load profiles showing slow dynamic changes. On the other hand, multi-cell battery systems are of increasing importance for commercial trends, such as the electrification of mobility. What is more, battery systems in real-world applications are stressed by electric loads with dynamics ranging from a few microseconds to several days.

The present thesis is a contribution to narrow this gap. It focuses on the effects of dynamic electric load profiles applied to batteries and on peculiarities when connecting single battery cells to form a multi-cell battery system. Therefore, equivalent electric circuit models are deployed to characterize and simulate the dynamic electric behavior of battery cells and systems.
The first part of the thesis aims to better understand the electrophysical and electrochemical processes inside a battery that is stressed with dynamic electric loads. To keep an application-oriented point of view, only the current and voltage changes at the terminals of a battery are investigated. Above all, a new method is developed to analyze the ohmic and inductive behavior of a battery in the time-domain. This method is also used to proof that the inductive behavior of a battery cell mainly depends on the geometry of the current path.
Furthermore, the influence of the dynamics of current profiles on the aging behavior of battery cells, in particular on lithium-ion battery cells, is investigated. After more than 2000 cycles and 290 days of testing, slightly less degradation was observed for battery cells cycled with alternating current with high frequencies.

To practically get on the multi-cell level, single battery cells have to be connected together. Within this thesis, the most common joining techniques - press contacts, resistance spot welding, ultrasonic welding, and laser beam welding - are investigated with focus on the arising electrical connection resistances.
While the current flow in serial-connected battery cells does not need many pages to be explained, the distribution of a dynamically changing current within parallel-connected battery cells is quite a complex topic that is investigated in the last chapter. These investigations on parallel-connected battery cells mark the end of this thesis, narrow the gap between science and application, and serve as starting-point for future research.

Zusammenfassung

Zwischen den Themen, die von der Wissenschaft untersucht werden, und dem Wissen, das notwendig ist um einen Batteriespeicher für eine wirtschaftliche Anwendung zu entwickeln, besteht eine gewisse Diskrepanz. In wissenschaftliche Publikationen werden meist nur Einzelzellen und meist nur Lastprofile mit langsamen Stromänderungen untersucht. In realen Anwendungen, wie zum Beispiel Elektrofahrzeugen, kommen aber mehrzellige Batteriesysteme, welche aus einer Verschaltung vieler Einzelzellen bestehen, zum Einsatz. Zudem ändern sich elektrische Lastprofile je nach Anwendung im Bereich von einigen Mikrosekunden bis einigen Tagen.

Die vorliegende Arbeit trägt dazu bei, diese Diskrepanz abzubauen. Sie fokussiert sich auf die Auswirkungen von dynamischen elektrischen Laständerungen auf Batterien und auf Besonderheiten, die nur bei mehrzelligen Batteriesystemen in Erscheinung treten. Um die Batteriezellen und -systeme zu beschreiben und Simulationen durchzuführen werden in dieser Arbeit elektrische Ersatzschaltbilder benutzt.
Zu Beginn der Arbeit wird das Verständnis der elektrophysikalischen und elektrochemischen Prozesse in einer Batteriezelle, welche mit dynamischen Lastprofilen belastet wird, geschaffen. Um die Nähe zur Anwendung zu wahren, werden für die Untersuchungen nur die Klemmenspannung und der Klemmenstrom hinzugezogen. In diesem Zuge wurde ein neues Verfahren entwickelt um auch das ohmsche und induktive Klemmenverhalten einer Batterie präzise im Zeitbereich vermessen zu können. Mit diesem Verfahren wird unter anderem gezeigt, dass das induktive Verhalten einer Batterie im Wesentlichen von der Geometrie ihres Strompfades abhängt.
Darauf aufbauend wird die Auswirkung der Dynamik des Stromprofils auf das Alterungsverhalten von Batteriezellen, insbesondere von Lithium-Ionen-Batteriezellen, untersucht. Nach über 2000 Zyklen und 290 Testtagen weisen die Batteriezellen, welche mit Wechselstrom von niedrigerer Frequenz belastet wurden, eine leicht erhöhte Alterung auf.

Für mehrzellige Batteriesysteme müssen einzelne Batteriezellen elektrisch und mechanisch miteinander verbunden werden. Im Rahmen dieser Arbeit werden die gängigsten Verbindungstechniken - Presskontakte, Widerstands-Punktschweißen, Ultraschallschweißen, Laserschweißen und Löten - insbesondere im Hinblick auf den resultierenden elektrischen Kontaktwiderstand untersucht.
Der Stromfluss durch seriell verschaltete Batteriezellen bedarf kaum Erklärungen. Die Aufteilung dynamischer Stromprofile zwischen parallel verschalteten Batteriezellen ist dagegen komplex und wird im letzten inhaltlichen Kapitel dieser Arbeit genau betrachtet. Mit diesen Betrachtungen bei parallel verschalteten Batteriezellen schließt die Arbeit und schließt damit auch ein wenig die Lücke zwischen Wissenschaft und Anwendung.

Contents

0. Framework conditions of present thesis **vii**
0.1. Journal contributions as lead author . . . viii
0.2. Journal contributions as co-author . . . viii
0.3. Selection of conference presentations . . . ix

1. Introduction **1**

2. Dynamic electric behavior of battery cells **5**
2.1. Real-world applications and their dynamic electric characteristics . . . 6
2.2. Overview on processes causing the electric dynamic behavior of a battery cell . . . 8
2.3. Requirements for the chosen battery cell model . . . 9
2.4. Inductive and ohmic behavior: Impedances with time constants below 10 ms . . . 10
2.4.1. Fundamentals of the ohmic resistance . . . 11
2.4.2. Fundamentals of the inductive behavior . . . 12
2.4.3. Fundamentals of the skin effect . . . 12
2.4.4. Modeling of the inductive and ohmic behavior . . . 14
2.4.5. Pulse-method for to analyze the inductive and ohmic behavior . 15
2.4.6. Measurement set-up to test battery cells with the pulse-method 18
2.4.7. Chosen lithium-ion battery cells for practical investigations . . . 19
2.4.8. Wiring and connection of battery cells for an accurate measurement of the dynamic electric behavior . . . 21
2.4.9. Operational capability and robustness of the pulse-method . . . 24
2.4.10. Comparison of the pulse-method with the electrochemical impedance spectroscopy . . . 26
2.4.11. Dependencies of the ohmic resistance and the external inductance 30
2.5. Electrode-electrolyte interface: Impedances with time constants of 0.1 ms to 30 s . . . 34
2.5.1. Fundamentals of the solid electrolyte interface . . . 35
2.5.2. Fundamentals of the electric double-layer capacitance . . . 35
2.5.3. Fundamentals of the charge transfer . . . 37
2.5.4. Modeling of the processes at the electrode-electrolyte interface . 39
2.5.5. Parametrization of equivalent electric circuit elements representing the electrode-electrolyte interface . . . 41

2.6. Mass transport: Impedances with time constants above 0.1 s 44
2.6.1. Fundamentals of the diffusion processes 44
2.6.2. Modeling of the diffusion processes with Warburg impedances . 45
2.6.3. Parametrization of the diffusion model's elements 46
2.7. Equilibrium voltage 50
2.7.1. Explanation of the electrochemical origin of the equilibrium voltage 50
2.7.2. Modeling and parametrization of the equilibrium voltage 53
2.8. Overview on and validation of the chosen battery cell model 55

3. Lifetime of lithium-ion battery cells depending on the dynamics of electric loads 61
3.1. Hypothesis on the degradation phenomena derived from published research 62
3.2. Investigation of the corner frequency 63
3.3. Measurement matrix 66
3.4. Set-up for the experimental series 69
3.5. Experimental results and evaluation of the aging behavior 71
3.5.1. Increase of impedances 74
3.5.2. Capacity fade 77
3.6. Comparison of the results to other series of experiments 79

4. Cell joining techniques for battery cells and their electrical connection resistances 83
4.1. Measuring and calculation method for the electrical contact resistance . 84
4.2. Reversible electrical connection of battery cells by press contacts 86
4.2.1. Fundamentals on the electrical connection of press contacts . . . 88
4.2.2. Test bench to measure the electrical contact resistances of press connections 90
4.2.3. Measurement matrix to investigate dependencies of press contacts 91
4.2.4. Influence of contact pressure on electrical contact resistance . . 94
4.2.5. Influence of surface roughness on electrical contact resistance . . 96
4.2.6. Suitability of press contacts for battery assemblies 98
4.3. Resistance spot welding for connecting battery cells 98
4.3.1. Functional principle of resistance spot welding 99
4.3.2. Influence of the welding energy on the connection quality 100
4.3.3. Suitability of resistance spot welding for connecting battery cells 101
4.4. Ultrasonic welding for connecting battery cells 102
4.4.1. Influence of sonotrode pressure on weld quality 104
4.4.2. Suitability of ultrasonic welding for connecting battery cells . . 105
4.5. Laser welding for connecting battery cells 106
4.5.1. Advantages of superimposed beam oscillation 106
4.5.2. Suitability of laser beam welding for connecting battery cells . . 107
4.6. Electrical resistances of soldered battery cell connections 108

4.6.1. Fundamentals and functional principle of soldering 108
4.6.2. Considerations on and modeling of the current paths in soldered connections 110
4.6.3. Influence of electrical conductivity of joint metals on the electrical connection resistance 115
4.6.4. Solders with different liquidus temperatures and their influence on the connection quality 116
4.7. Comparison of the five connection techniques 117
4.7.1. Comparison of the heat input caused by joining processes 117
4.7.2. Comparison of joining techniques in terms of the electrical connection resistance 121
4.7.3. Comparison of joining techniques in terms of tensile strength . . 124

5. Current distribution within parallel-connected battery cells 127
5.1. Parallel-connected battery cells in commercial products 128
5.2. Publications on the current distribution of battery cells in parallel . . . 129
5.3. Goal and scope of this chapter 131
5.4. Precise measurement set-up with low additional impedances 133
5.4.1. Design of the test bench in principle 133
5.4.2. Sensors chosen for the test bench 134
5.4.3. Wiring and terminals of battery cells for insertion in test bench 136
5.4.4. Acquisition and processing of sensor data 137
5.5. Evaluation of the influence of the measurement set-up 138
5.6. Theoretical considerations about the fundamentals of current distributions 141
5.6.1. Considerations about parallel battery cells with differing impedances 143
5.6.2. Considerations about parallel battery cells with differing capacities 145
5.7. Measured and simulated current distributions of different pairs of battery cells 147
5.7.1. Selection of battery cells for practical experiments 147
5.7.2. Current distribution of parallel battery cells with differing impedances 150
5.7.3. Current distribution of parallel battery cells with differing capacities 154
5.8. Lessons learned and advice for connecting battery cells in parallel . . . 158

6. Summary and outlook 159

A. Appendix 163
A.1. Wiring and connection of ICR18650HB2 battery cell by the LG Chem. Ltd. 163
A.2. Robustness of pulse-method checked with further battery cells 164
A.2.1. Aged IHR18650A lithium-ion battery cells by E-One Moli Energy Corp. 164
A.2.2. ICR18650HB2 lithium-ion battery cells by LG Chem. Ltd. . . . 164

A.2.3. SPB463048 lithium-ion battery cell by Enertech International Inc. 167
A.3. The confidence interval 168
A.4. The Gaussian filter for discrete signals 169
A.5. First and second derivatives of the real part of the impedance spectrum 171
A.6. Pairing check for chosen resistance parameters 172
A.7. Increase of charge transfer and direct current (DC) resistances for different dynamic loads 174
A.8. Relative capacity of pairs of ICR18650HB2 battery cells 176

References **177**