Performance and Aging Diagnostic on Lithium Iron Phosphate Batteries for Electric Vehicles and Vehicle-to-Grid Strategies

- From the cell to the system level -

Von der Fakultät für Elektrotechnik und Informationstechnik der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades eines Doktors der Ingenieurwissenschaften genehmigte Dissertation

vorgelegt von

Master of Science
Andrea Marongiu
aus Tortolí, Italien

Berichter:
Universitätsprofessor Dr. rer. nat. Dirk Uwe Sauer
Professor Alfonso Damiano

Tag der mündlichen Prüfung: 31. Mai 2017

Diese Dissertation ist auf den Internetseiten der Hochschulbibliothek online verfügbar.
Andrea Marongiu

Performance and Aging Diagnostic on Lithium Iron Phosphate Batteries for Electric Vehicles and Vehicle-to-Grid Strategies

- From the cell to the system level -
When I first thought about pursuing a PhD I could not even remotely imagine what does it mean: how much is the personal involvement, how tiring and sometime frustrating might be doing research, how many weekends have to be spent following a goal which is often fade and unclear until the end of the trip. Nevertheless, I am proud to have undertaken eventually this difficult journey. Never choice was more appropriate: I now love my job and I enjoy every day working in this field. Fortunately, in more than five years I was not alone, luckily I found on the way amazing people who have supported me in decisions and helped me in my professional and personal growth.

I must pleasantly start from my Doktorvater, Professor Dirk Uwe Sauer: I will never be enough thankful to him for giving me the possibility of getting a PhD title. His technical and personal supports have been fundamental for my research. His critical sensibility and his approach to deal with problems have inspired me throughout all my period in ISEA and have given me a new way how to tackle situations and observe every day circumstances. An Italian “Grazie di cuore” can only marginally describe what I really think and feel. A second special thank goes to Prof. Alfonso Damiano, who has taken the role of thesis co-referent. Moreover, his passion towards academic research and his engagement to the academic field has for the first time inspired and push me to follow the same direction. Mille grazie.

I would like to thank all the students I have supervised during my time at ISEA. Without their work and support this thesis would have been much harder. The discussions with them have allowed me to improve myself and give me a wider overview of the dealt problematic. In this sense, I would like to thank particularly Thapakorn Pavanarit, Areeb Khalid, Yao Rong, Felix Nußbaum and Alex Salzmann.

Huge thanks go to all my colleagues at ISEA Institute who has accompanied me for more than five years. I must say that it was not easy at the beginning, but with the time I have learnt to appreciate a different culture and a different way to deal with daily work and personal situations. Thanks for all the technical discussions and for all the funny moment which I had in Aachen. They have made me grow up in a surprisingly manner. Vielen Dank Leute! Special thanks go to Meinert Lewerenz, Philipp Schröer, Florian Ringbeck, Nsombo Nlandi, Ilka Schoeneberger, Izaro Laraesgoiti and Grzegorz Pilatowicz, who has in part or completely revised my work and gave me useful feedbacks.

A separate gratitude goes to the foreign colleagues at ISEA, Izaro, Grzegorz, Merve, Gari, Manop, Luiz, Ralf, Zhuang, Yu and Ghada: you guys have been my small family in a new country, who support me in the daily life. Thanks for the technical conversation, thanks for
your personal support, thanks for the many many Pizza dinners after work by Piero at La Stazione, thanks for being there. You were and will be in the future people I will never forget.

My heartfelt thanks go to my friends in my home town, Tortolí. Even so far, the contact with them has given me every day and in every difficult moment the force to go ahead and to continue towards my objectives and goals. Their smiles have made me smile every time. Grazie di esserci sempre.

To my beloved Izaro: to you I can just say now Eskerrik asko. Our daily life has not been always perfect, but has been what each man can expect from his partner. Thanks for the technical discussion, thanks for your support, thanks to have stand me in my difficult times…thanks to exist. Future is waiting for us together.

And finally: thanks to my mother, my father, Michela and Matteo. Thanks to be there always, Thanks to help me in decisions, thanks to have given me thousands of possibilities, thanks to suffer and be happy with me…grazie, grazie, grazie. All the thanks of this world will never be enough. Grazie di cuore.
## Content

1 **Motivation** ................................................................................................................................. 1

2 **Introduction** ................................................................................................................................. 3

3 **Lithium-Ion Batteries** .................................................................................................................... 7
   3.1 Working principle ......................................................................................................................... 8
      3.1.1 Materials and components of LiBs .................................................................................. 10
      3.1.2 Voltage behavior of lithium-ion batteries ....................................................................... 12
   3.2 Construction and design of lithium-ion cells ............................................................................. 14
   3.3 Aging mechanisms ..................................................................................................................... 16
   3.4 LiFePO$_4$ as a cathode cell material ......................................................................................... 18

4 **Battery Systems in Vehicle-to-Grid** .......................................................................................... 25
   4.1 Battery Management System ..................................................................................................... 26
      4.1.1 BMS structure ..................................................................................................................... 27
      4.1.2 BMS state detection algorithms ....................................................................................... 29
   4.2 The vehicle-to-grid concept ....................................................................................................... 35
   4.3 Improvement of BMS in V2G .................................................................................................. 38

5 **Characterization of a LiFePO$_4$ Battery** .................................................................................. 41
   5.1 Characteristics of the tested cells .............................................................................................. 41
   5.2 Electrical characterization .......................................................................................................... 42
      5.2.1 Influence of current and temperature on the total capacity ............................................. 43
      5.2.2 Electrical impedance spectroscopy ..................................................................................... 48
   5.3 Accelerated aging tests .............................................................................................................. 50
      5.3.1 Calendar aging investigation ............................................................................................. 51
      5.3.2 Cycle aging investigation .................................................................................................. 52
      5.3.3 Non-uniform aging and capacity recovery ......................................................................... 54
   5.4 Analysis of the quasi-OCV curves .............................................................................................. 56
   5.5 Investigation and modeling of the hysteresis of the open circuit voltage ............................ 63
      5.5.1 Experimental investigation ................................................................................................. 66
      5.5.2 Experimental results ........................................................................................................... 71
      5.5.3 Discussion .......................................................................................................................... 78
      5.5.4 Modeling of the minor loops .............................................................................................. 82
      5.5.5 Relaxation effects and hysteresis vanish ............................................................................ 85
   5.6 Post-mortem analysis as application tool .................................................................................. 88
      5.6.1 Quasi-OCV curve of single electrodes ............................................................................ 90
6 DIAGNOSTIC OF LiFePO₄ CELLS ................................................................. 99

6.1 A novel approach for on-board capacity estimation in LiFePO₄ cells ............... 99
   6.1.1 Degradation model for LiFePO₄ cells .................................................. 101
   6.1.2 Novel BMS structure for SoC and SoH estimation ............................. 105
   6.1.3 Actual battery capacity estimation .................................................. 110
   6.2 Hysteresis model for SoC estimation ................................................ 121
      6.2.1 Modeling of the hysteresis minor loops for online estimation ............ 121
      6.2.2 Working principle of the algorithm for SoC estimation .................... 123
      6.2.3 OCV modeling and SoC tracking .................................................. 128
      6.2.4 Recalibration of the hysteresis model ............................................ 131
   6.3 Further system development towards microcontroller implementation ........ 132
   6.4 Summary .................................................................................. 134

7 AGING OF LITHIUM-ION BATTERIES IN A V2G SCENARIO ............... 135

7.1 Batteries in the V2G system .................................................................... 135
7.2 Model of aging in a V2G environment .................................................. 136
   7.2.1 Battery models ................................................................................. 139
   7.2.2 Time manager subsystems .............................................................. 143
   7.2.3 Optimization strategy ................................................................. 144
   7.2.4 Simulation data and scenarios ...................................................... 147
7.3 Results and discussion ........................................................................... 150
   7.3.1 Improvement of the car fleet utilization by means of intelligent strategies .... 150
   7.3.2 Effect of inhomogeneous aging ................................................... 156
   7.3.3 Influence of the battery prices ...................................................... 158
7.4 Summary .................................................................................. 159

8 SUMMARY AND OUTLOOK .................................................................. 161

9 BIBLIOGRAPHY ........................................................................... 165

10 APPENDIX ................................................................................ 179

10.1 Constants .................................................................................. 179
10.2 Symbols .................................................................................. 180
10.3 Abbreviations ........................................................................... 182
10.4 Influence of current, temperature and rest period on the total capacity ......... 184
   10.4.1 Temperature variation dependency .............................................. 184
   10.4.2 Presence of rest periods ............................................................ 185
10.5 Investigation and modelling of the hysteresis of the open circuit voltage: additional tests results .......................................................... 187
   10.5.1 Minor loops identification ......................................................... 188
   10.5.2 Current dependency of the minor loops ...................................... 192
10.5.3 Temperature behavior of the OCV and of the minor loops .............................. 193
10.5.4 OCV modeling .................................................................................................. 199
10.5.5 Hysteresis after long relaxation behavior.......................................................... 200
10.6 OCV evaluation for single electrodes ...................................................................... 200
10.7 Estimation of the battery capacity: additional results ........................................... 203
   10.7.1 Simulation of aging through a mix of DMs ................................................ 204
   10.7.2 Capacity estimation results and plateaus scalability ...................................... 209
10.8 SoC estimation: additional results........................................................................ 213
10.9 Additional results of V2G scenarios ..................................................................... 215
   10.9.1 Resistance degradation for the \textit{Cell NMC} ................................................... 215
   10.9.2 Supplementary calendar aging models employed for V2G simulations .... 215
   10.9.3 Additional results by means of the supplementary aging model ............... 217

11 \textbf{LIST OF PUBLICATIONS} ........................................................................ 221

11.1 Journal Articles .................................................................................................... 221
11.2 Conference Proceedings ......................................................................................... 222
1 Motivation

Electrochemical energy storage systems (EESS), commonly known as batteries, play a fundamental role in everyday life. They are present in different forms in many types of applications, from stationary (e.g. the storage system of a photovoltaic installation or uninterruptable power supply), over portable (e.g. mobile phones and tablets), to mobile (e.g. passenger cars and fork-lift trucks) devices. Nowadays, where the need for safe energy supply is one of the main causes of wars and conflicts, EESSs, with their flexibility, limited maintenance requirements, adaptable dynamic response and high efficiency, can represent a key component of the energy systems. Especially in the context of a future sustainable mobility, with the goal of limiting the CO$_2$ emissions, batteries are seen even now as the only feasible solution, which can be considered at the same time economically affordable, practicable in a limited time and with an impressive impact. Due to this, in recent years, an enormous amount of funds have been invested in the field of electro-mobility. The electrification of the existent vehicles, either partially in form of hybrid electric vehicles (HEV) or plug-in hybrid electric vehicles (PHEV) or complete in form of electric vehicles (EV), is the path which is being followed by all OEMs (Original Equipment Manufacturers), and the results can be seen by all. In 2014 almost two millions HEVs were sold worldwide. In the same year approx. 77,000 EVs were sold in China, while in December alone roughly 55,000 EVs reached the final customers [1]. In 2016, the number of EVs registered in whole Europe passed the 22,000 units, and the growth tendency is maintained in the first months of 2017 [2]. In line with this trend, the increasing restrictions in terms of emission which will be set in the near future (e.g. according to European regulations a CO$_2$ emission from 130 g/km in 2015 to 95 g/km in 2020 [3]) will push OEMs to a complete electrification of their car fleets in the coming decades.

Among the EESS technologies, only two are actually considered as candidates for the mobility. In the short-term, lead-acid batteries (PbA) are and will be still present in every kind of vehicles. The increasing hybridization of conventional vehicles makes PbAs the optimal solution for all the micro-hybrid and parts of the mild-hybrid vehicles, mainly due to their low prices and robustness. For higher autonomy and performance requirements, lithium-ion batteries (LiB) are the outstanding technology which today allows the full electrification of vehicles at an affordable cost. On the one hand LiBs guarantee good energy density, outstanding cyclability and considerably higher efficiency than other technologies [4][5]. On the other hand, in respect to PbAs, LiBs must always be operated in a defined range (in terms of current rate, voltage windows and temperature), in order to avoid safety issues. This is the key motivation to equip LiBs whether they are a single cell for a mobile phone or a battery pack for an EV with a battery management system (BMS). Besides guaranteeing the correct use of the batteries, a BMS has the important task to correctly diagnose the actual battery state.
in the long and short term. To achieve this, intelligent systems are required, which are able to re-adapt themselves to the actual battery behavior during its lifetime and to properly react on the basis of the battery’s actual state. Such systems cannot be developed without understanding LiBs deeply, i.e. how the cells work in a normal operation, which physico-chemical processes take place during the discharge and charge operations, and what the main causes of the degradation and performance fade are. Once these processes have been understood, an inexpensive BMS can be developed flexibly and efficiently. Thus, the way how the LIB behavior is investigated plays a fundamental role. This includes the test routines which are employed and the specific methodologies which are used to investigate a defined behavior.

The development of intelligent BMSs, together with low cost LiB, is the base for a future breakthrough of EVs in the car market. Apart from guaranteeing safe operations, the full battery potential can be exploited, without the fear of exceeding safety operation limits. Moreover, the system can be fully utilized, without reducing the battery lifespan due to additional stresses. In this scenario, the double use of PHEV and EV batteries as mobile storage system for grid operation services is significant, namely the vehicle-to-grid (V2G) approach. Here, vehicles are used either for a normal driving operation or, when connected to the net, as a flexible storage system. This is an enormous help for peak shaving, load leveling or for covering the fluctuation and randomness of the renewable energy production systems.

The battery in the vehicle, together with the BMS intelligence, is seen as the center of the system: on the one side (on the bottom) there is the deep understanding of the battery behavior for an optimal battery utilization; on the other side (on the top) there is the system, which takes advantage of the car and of its battery completely without worrying about over-utilizing or over-stressing it. In this scenario, a deep penetration of PHEVs or EVs in the car market appears not to be prohibitive in the very near future.
2 Introduction

In order to properly exploit the full performance of LiBs and to completely integrate them in the actual system, the knowledge and understanding of their working principle plays a key role. Moreover, an in-depth knowledge of the degradation processes and of the aging mechanisms facilitates the optimal use of the batteries throughout their entire lifespan, and thus their operation within the safety margins. This knowledge is the basis for the optimized design of intelligent algorithms for battery state detection, which initially can be easy to parametrize (in terms of time consuming and effort) and are able to adapt their parameters or employed relations based on the actual operating conditions, in the short and long term.

This work explores all possible layers of a LiB and investigates every area of interest related to its working principle and its correct use and integration in the electric system. The adopted bottom-up approach is shown in Figure 2-1.

Figure 2-1: Schematic representation of the different research areas which are treated in this work.
The thesis starts from the cell material and the analysis of the battery working principle and proceeds with the investigation of the battery electric performances and comprehension of the different analyzed phenomena. In particular, special emphasis is put on the degradation effects. The intelligent algorithms for battery state detection, which are designed to be used for the entire battery lifetime, are developed on the grounds of the research data. The newly developed BMS concept is designed to be employed in a system where the car is able to exchange information with the electric grid, in order to allow the double use of the battery in EVs (V2G). In this manner, all the possible layers belonging to the research field of LiBs are treated as inseparable rings of a chain. This approach highlights the fact that in the battery world the different research areas cannot be treated separately, but that at each level an interconnection exists which must be heeded. With regards to the design of battery state detection algorithms, this means that the idea at the base of the main concept must rely on the correct knowledge of the physico-chemical phenomena and battery behavior which is behind it. Only in this way will the developed methodology be able to correctly estimate the battery state even though some cells behave differently compared to the mean population. The same discussion is valid for each level. In order to completely achieve this, the focus of the thesis concentrates on a single LiB chemistry, i.e. lithium iron phosphate cells. Only marginally other LiB types are used and treated in this work.

The achieved results within the frame of this work demonstrate the correctness of the employed approach and the interconnection among the different topics and research areas. A profound analysis is carried out in the observation of the particular behavior of LFP cells regarding the hysteresis of the open circuit voltage (OCV) and its modification during the cell lifetime. Novel approaches are presented for the diagnostic and battery state detection based on the obtained information. The presented methodologies are at the base of a new BMS structure, which fills a void in the state-of-the-art methods employed for diagnostic of LFP cells. The new BMS is the central component of EVs which can be employed for V2G operations. The proposed simulation tool analyzes the impact on battery aging of the double use of energy in an EV fleet, and proposes a successful strategy which aims to age the battery packs in a uniform manner.

The thesis is structured as follows. After the motivation and introduction chapters, the chapter 3 gives a short description and background of the working principle of LiBs, highlighting the particular characteristics of LFP cells. This does not aim to be a complete review of the subject matter, but intends to give a brief insight into the complexity of batteries for readers confronted with the topic for the first time. The chapter 4 introduces the interconnectivity among the different topics related to batteries and more specifically to LiBs. A general description of BMSs in terms of hardware and software is given, with a special emphasis on battery state detection algorithms. Moreover, the chapter demonstrates and discusses the possibilities V2G offers. Chapter 5 presents the experimental analysis executed on a LFP cell. Electrical test are carried out in order to analyze the behavior of the cell in the short term, i.e. the operation under different conditions (current rate, ambient temperature etc.). Special emphasis is put on the analysis of the OCV behavior and of the hysteresis, and how these characteristics change with the battery lifetime. Accelerated aging tests are carried
out in order to understand the behavior of the cell under various conditions. A basic post-mortem analysis concludes the process and investigates the cell behavior on all levels. The chapter 6 deals with the diagnostic of LFP cells. Thanks to the knowledge gained during the observation of cell behavior in the short and long term, a novel BMS structure is presented. The main battery state detection methodologies presented allows an estimation of the actual battery state-of-health (SoH) and state-of-charge (SoC). The information obtained by the SoH estimation is used for the first time in order to adapt the actual hysteresis behavior of the cell, which is a fundamental component for describing the cell’s electric behavior. Chapter 7 introduces a simulation tool which allows investigating the effect of the additional V2G operation on an EV fleet. The simulation results explore the effectiveness of an optimization strategy which allocates vehicles for V2G services aimed at optimizing their lifespan. The developed simulation environment can examine the mentioned effect for vehicles with different history and equipped with different LiBs, which thus are characterized by different degradation behavior and aging rate. Chapter 8 concludes the work and provides a short outlook.

The proposed work can be used as an instrument for understanding the interconnection among the different battery research areas, and gives an indication of the approach which may be used to understand LiBs and to operate them properly. This work reveals the complexity of battery working principles and emphasizes the necessity of a proper BMS design in order to allow the correct integration of LiBs in electrical systems.
Introduction
3 Lithium-Ion Batteries

In recent years LiBs have gained an increasing attention among all the EESSs, due to the possibility of employing them in an enormous number of applications. Figure 3-1 shows a qualitative comparison among four different storage system technologies, in terms of gravimetric energy, specific power, efficiency, lifetime, safety and current market price. Figure 3-1a) introduces the features for PbA and nickel-based batteries, while Figure 3-1b) shows the features for LiBs and supercapacitors. The criteria are weighted in a scale from zero (worst) to five (best).

![Diagram showing comparison between storage systems](image)

**Figure 3-1:** Qualitative comparison between the different electrical storage systems in a scale from zero (worst) to five (best), a) lead-acid and nickel-based batteries, b) lithium-ion batteries and supercapacitors.

As it can be observed, LiBs excel in the majority of the specified criteria: long cycle life and very high efficiency make them suitable for mobile and portable applications compared to PbAs and nickel-based cells, while the high specific energy endorses them compared to supercapacitors in applications where the weight together with the high energy content play a fundamental role. PbAs are still superior in comparison to LiBs in terms of price, but the current trend shows that in the near future they will become competitive with PbAs, reaching price values of around 200 €/kWh (at system level) in 2020 [6]. Regarding the safety issue, LiBs still present various drawbacks, with regards to the danger they exhibit in operations carried out under extreme conditions (overcharge, overheating, mechanical stresses etc.). However, if the system is equipped with an intelligent BMS and sufficient safety precautions and redundancies (e.g. temperature sensors or electrical breakers), LiBs can be operated in
safely manner and particularly critical situation can be detected in time and thus neutralized. The outstanding merits of LiBs with respects to other EESS technologies can be understood when observing the so-called Ragone’s plot [7][8][9][10]. It is evident how the wide range of gravimetric energy and specific power which LiBs can make available give them ulterior advantages compared with others EESSs.

This chapter provides a short introduction of the main characteristics of LiBs and explains the working principle and the main physico-chemical phenomena which are involved in the short and long term. A brief overview of the material used and the construction characteristics is given. Special emphasis is put at the end of the chapter on LFP cells, which are the main focus of this work.

3.1 Working principle

The first LiB was planned by M. S. Whittingham in the middle of 1970s [11]. However, the first commercial LiB, which was marketed by Sony [12], was not launched onto the market until 1991. Since then, this technology has evolved and improved its performances, but its working principle has never changed. A LiB consists of two electrodes, the positive and negative electrodes, an electrolyte solution and a separator. A schematic representation is shown in Figure 3-2 for the case of an LFP cell.

![Figure 3-2: Schematic representation of the working principle of a lithium-ion cell for the case of an LFP cell.](image)
As for each battery, the two electrodes are the sources of ions, which travel through the electrolyte, an ion conductive solution. The separator is a membrane which allows the passage of ions but blocks electrons. The main reaction of the battery during a normal operation is reported for the general case in equation (3.1):

$$\text{LiM} \text{etallO}_y + C_6 \xrightarrow{\text{Discharge/Charge}} \text{Li}_{1-x} \text{M} \text{etallO}_y + Li_x C_6$$

(3.1)

Equation (3.2), equation (3.3) and equation (3.4) show the main reaction in the negative and positive electrode and the overall reaction for the case of a LFP cell respectively.

Negative electrode:

$$C_6 + xe^- + xLi^+ \xrightarrow{\text{Discharge/Charge}} Li_x C_6$$

(3.2)

Positive electrode:

$$\text{LiFePO}_4 \xrightarrow{\text{Discharge/Charge}} xLi^+ + xe^- + Li_{1-x} \text{FePO}_4$$

(3.3)

Overall reaction:

$$\text{LiFePO}_4 + C_6 \xleftrightarrow{\text{Discharge/Charge}} \text{FePO}_4 + Li C_6$$

(3.4)

The overall reaction is a so-called redox process, as depicted in Figure 3-2. During the discharge process the negative electrode is oxidized: lithium ions are de-intercalated from the electrode and travel through the electrolyte towards the positive electrode. At the same time the released electrons travel in the external circuit and supply a load. In turn, the positive electrode is reduced: the lithium ions present in the electrolyte are intercalated and react together in the electrode material with the electrons from the external circuit. The opposite reactions take place during the charge process. In contrast to a PbA, the electrolyte theoretically does not take part in the main reaction. In practice, as will be described later, side reactions can cause the slow consumption of the electrolyte solution. The above explained mechanism takes the name of “rocking chair”. This refers to the fact that the lithium ions are inserted (intercalated) and disinserted (deintercalated) in the respective electrode during the charge/discharge, “rocking” from one side of the battery to the other [13][14]. For this reason the electrode materials are called insertion materials. When considering the battery construction again, during the discharge positive ions leave the negative electrode and travel to the electrolyte. In this case the negative electrode is oxidized and the current is defined as an anodic current. Therefore the negative electrode is defined as anode. In the same way, during the discharge process positive ions are intercalated into the positive electrode from the electrolyte. In this case the positive electrode is reduced and the current is defined as a cathodic current, so the electrode is named cathode. As a rule the
negative and positive electrode are defined also during the charging process as anode and cathode respectively in every battery. This happens although the term anode indicates an electrode where an oxidation process takes place, and the term cathode indicates an electrode where a reduction process takes place. For the sake of simplicity, the same convention is used in the following of this work.

3.1.1 Materials and components of LiBs

There are several types of LiBs currently available on the market. The different types are determined by the different materials used for each of the components.

Concerning the anode, carbon materials are normally employed as insertion elements, usually coated on a copper current collector\(^1\), in order to assure good electron conductivity and avoid oxidation. Carbon materials assure high specific capacity and more negative redox potential than metal oxides and high dimensional stability which guarantee high cyclability [15]. The two different kinds of carbon materials which can be used as intercalation elements can be classified as non-graphitic and graphitic. The former group is also known as “hard carbon” materials. Graphite belongs to the latter group: this is characterized by a lattice layered structure with graphene layers stacked in order. Graphite is the most used anode material for LiBs. Nowadays the research lines are pointing to the use of pure lithium as anode electrode [7]. Lithium electrodes are not considered as insertion materials and were the first materials used as anode in LiBs. They are characterized by higher specific capacity with a resulting potential for considerably increasing the gravimetric energy and energy density. The problems are related to the reaction of the lithium surface with the electrolyte, resulting in the formation of dendrites (i.e. possible internal short circuit) and fast capacity fade.

Materials for cathodes are mostly metal oxide substances, which are normally coated on an aluminum current collector. The choice of aluminum instead of copper is determined mainly by the cheaper price of the first. For the active material, different metals are nowadays used. However, each one brings some merits and drawbacks, in terms of cost, safety, stability during lifetime and potential level. Examples of such materials are cobalt, nickel, manganese and iron-phosphate [15][16]. In order to combine the advantages and disadvantages, a blend of different materials, such as mix of nickel, manganese and cobalt (NMC) or nickel cobalt and aluminum (NCA) in different stoichiometry [17], is also used. A more detailed discussion of the use of these cathode materials in LiBs and their effect on the battery performances is carried out in section 3.4. As for anodes, also for cathodes the intercalation takes place as placement of lithium ions in the free space of the crystal structure. Therefore, cathode materials can be classified based on the dimension of the structures which are used to model the crystals’ configuration. This configuration is specified based on the intercalation direction of the lithium ions [15]. A schematic representation is shown in Figure 3-3. Therefore, the 1D structure representing the crystal configuration of LFP cathodes allows the intercalation of

\(^1\) In case of lithium titanate cells, aluminum is employed as anode current collector.
cations only in one direction. Lithium cobalt oxide (LiCoO$_2$) cathodes can be represented through a 2D structure (intercalation possible in x and y directions), while lithium manganese oxide (LMO) cathodes can be represented through a 3D structure (intercalation possible all directions). Current research concentrates on the development of the so-called 5 V cathode materials, which allow an increase in the specific energy and therefore a decrease in price in future EVs [18]. These materials exist already, but cannot be easily employed in present LiB due to the problems related to electrolyte stability [8][19].

**Dimensionality of the Li$^+$-ions transport**

![Diagram showing 1D, 2D, and 3D structures of cathode materials](image)

**Figure 3-3:** Different structures of cathode materials used in LiB.

The electrolyte used in a LiB is generally a liquid organic solution together with lithium salts and other different components, used often to improve the ions conductivity. Aqueous electrolytes cannot be employed, due to the activation of the electrolysis process at potential over 1.23 V, which takes place practically in all the battery operating range. The commonly used salt is the known lithium hexafluorophosphate (LiPF$_6$), while a mix of ethyl carbonate (EC) and dimethyl carbonate (DMC) is employed [15][20] as solvent. As already mentioned, the electrolyte can be considered as the most sensitive component in a LiB: generally it is not stable in the entire cell operating voltage window, but reacts with the electrodes in some conditions in order to form passivation layers. In particular, as will be discussed in section 3.3, the electrolyte reacts with the anode active material to form the so-called solid electrolyte interphase (SEI). This is mainly due to the low potential of the anode close to the potential of the pure lithium in a wide SoC range during the cell operation. This passivation layer is at the base of the working principle of a LiB: in fact, its presence protects the anode active material from an additional interaction with the electrolyte, allowing at the same time the normal ion intercalation. Therefore, without the SEI LiBs would not be able to deliver the outstanding performances in terms of long lifetime and high cyclability. Other types of electrolytes are the solid and polymer electrolytes, which have been introduced for special application but are nowadays rarely used in commercial LiB [15][19].
The separator used in LiB has the task of assuring mechanical stability, electrically isolating the two electrodes and avoiding the passage of the electrons between them. Moreover, the distance between the electrodes is reduced, thus increasing the ion conductivity. It is normally a foil of polypropylene or polyethylene, possibly mixed with ceramic materials in order to increase the temperature stability under extreme operating conditions. In case of polymeric electrolyte, the role of the separator is accomplished by the electrolyte itself [15].

In a LiB, the active material particles in both electrodes are kept together by using binder materials. These are also needed to mechanically connect the active material to the current collectors. As a binder, a polymer binder such as polyvinylidene fluoride is often employed [21].

### 3.1.2 Voltage behavior of lithium-ion batteries

The variation of the LiB voltage during operation due to a current flow can be denoted in the following standardized way [22][23][24][25]:

\[
U_{\text{batt}} - U_{\text{EMF}} = \eta_{\text{ohmic}} + \eta_{f,\text{pos}} + \eta_{f,\text{neg}} + \eta_{\text{act, pos}} + \eta_{\text{act, neg}} + \eta_{\text{con}}
\]  

(3.5)

According to equation (3.5), the voltage which can be measured across the battery terminals of a LiB \( U_{\text{batt}} \) can be expressed as the sum of different overvoltage contributions.

The term \( U_{\text{EMF}} \) indicates the so-called electromotive force (EMF), i.e. the voltage that the battery reaches in the steady state without any load. The value of \( U_{\text{EMF}} \) can be calculated by means of the Nernst’s equation [26][27]:

\[
U_{\text{EMF}} = E_0 - \frac{RT}{nF} \cdot \ln(Q_{\text{activity}})
\]

(3.6)

where \( E_0 \) represents the standard cell potential, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( F \) is the Faraday’s constant, \( n \) is the number of moles of electrons transferred in the cell reaction and \( Q_{\text{activity}} \) is the reaction quotient (related to the activity of the species).

In the second member of equation (3.5) different overvoltage effects are considered. \( \eta_{\text{ohmic}} \) is the pure ohmic voltage drop, due to the ohmic contributes of connectors, current collectors, active materials and electrolyte. \( \eta_{f,\text{pos}} \) and \( \eta_{f,\text{neg}} \) are the polarization voltages due to the presence of passivation films/layers in the cathode and anode respectively. \( \eta_{\text{act, pos}} \) and \( \eta_{\text{act, neg}} \) are the polarization contributions resulting from the interfacial charge-transfer reactions between cathode/anode and electrolyte. This phenomenon is described by the well-known Butler-Volmer equation, which is reported in [27]:

where $i$ is the overall current imposed by the activation overvoltage $\eta_{\text{act}}$; $i_0$ is the exchange current density, which can be expressed as the product between the specific exchange current density $i_0'$ and the available surface $A$; $\alpha$ is a symmetric factor between the charge and discharge process. The equation describes only one electrode, and can therefore be employed to express both the $\eta_{\text{act,pos}}$ and $\eta_{\text{act,neg}}$. Moreover, it describes the velocity of the electrochemical process in terms of current rate on the interface between active material and electrolyte. $\eta_{\text{con}}$ is the remaining polarization due to the concentration-related effects such as diffusion, migration and convection (the analysis of the separation and contribution of the different terms is beyond the scope of this work).

All the described terms are related to particular physical phenomena, i.e. they are characterized by a specific dynamic behavior. Therefore, some of them can be neglected depending on the application. In the case of high power applications, $\eta_{\text{con}}$ can often be neglected if the requested power has to be delivered in a time range of 10-100 ms. In contrast, in EV applications, in which situations with a requested constant power for duration of 10-20 s are not rare, this assumption is no longer valid. Furthermore, the effects of some of the overvoltage effects presented in equation (3.5) are clearly visible and important in some specific cases. For example, the authors in [24] have shown that $\eta_{\text{act,neg}}$ can appear only in the low-temperature range, and in the described case it is limited with respect to $\eta_{\text{act,pos}}$, and thus negligible. Nevertheless, this kind of statement cannot be assumed as a general rule. Similar analyses can be carried out for the terms $\eta_{\text{f,neg}}$ and $\eta_{\text{f,pos}}$. The former term refers to the well-known phenomena of the SEI layer on the anode. As already mentioned, this effect is at the base of the working principle of LiB. However, it can sometimes be neglected for some battery chemistries as described in [8][19], where it does not appear. $\eta_{\text{f,pos}}$ refers to a solid permeable interphase layer on the cathode. With the exception of single cases [28], the existence of a passivation layer on the positive electrode has not been completely demonstrated and accepted yet. Therefore, this term is rarely considered in the description of the LiB voltage.

The battery voltage behavior can be described by means of an equivalent electric circuit model (EECM). The EECM normally consists of a voltage source, which describes the $U_{\text{EMF}}$, in series with a resistance which describes the $\eta_{\text{ohmic}}$, an inductance to describe the battery inductive behavior and a series of R\|$C$ branches [24][29][30]. The latter describes the different polarization phenomena during the normal operation ($\eta_{\text{f,pos}}, \eta_{\text{f,neg}}, \eta_{\text{act,pos}}$ etc.). The described EECM is depicted in Figure 3–4. The number of described phenomena (number $n$ of R\|$C$ elements) in terms of polarization depends on the requested precision in the representation of the battery behavior and on the available computational power. All are related to the employed application, which defines the compromise between accuracy and circuit complexity.
**Figure 3-4:** Generic equivalent electric circuit used for battery modelling with a generic number of R||C elements.

### 3.2 Construction and design of lithium-ion cells

Due to the variety of applications, LiBs can be found in the market in different shapes and designs [10][31][32]. LiBs are nowadays designed in four different forms, namely cylindrical, prismatic, coin and pouch-bag cells, as depicted in Figure 3-5.

**Figure 3-5:** Different design of LiB batteries (based on [31][32]).
Cylindrical or round cells are the most common LiBs. They are mainly used in portable devices such as laptops, but nowadays they are starting to be employed for battery electric vehicles (BEV), as is the case in TESLA [33]. One of the most used is the so-called 18650 type (18 mm of diameter, 65 mm of height), which is mainly produced in Asian countries such as China, Korea and Japan, with a volume production of billions of units per year [34]. Known suppliers are Sony, Samsung, Panasonic (Sanyo), BYD and LG. As these types of cells were the first type of LiBs introduced to the market, a lot of experience has been gathered on their design. They generally guarantee a long life time, but present some complexity regarding the design of the cooling system. The pouch-bag cell design (also called “Coffee Bag”) is characterized by a flat shape: the electrode and separator materials are not rolled as in the case of the cylindrical cells, but placed in layers on top of each other in a flat position. The light packaging guarantees a higher specific energy and energy density, while the flat shape allows easy cooling. However, the cells usually lack safety mechanisms, such as pressure release valves, which are typical for cylindrical cells. This makes pouch-bag cells more dangerous in comparison to other designs. Known suppliers are LG, KOKAM and LiTec among others. Prismatic cells combine the general characteristics of cylindrical and pouch-bag cells. Car-makers currently believe these cells to be the best solution in the construction of battery packs for BEVs, due to their volumetric energy density and easiness in the design of cooling systems. Suppliers are for example Panasonic and Hitachi. Nowadays the coin cell design is not as common as the other three mentioned. They are mainly used in small portable devices or in applications where the space is limited. Another typical field of use is the research environment, as coin cells provide a fast solution to test the performance and working conditions of new materials.

Another typical distinction among LiBs is the classification between high power (HP) and high energy (HE) cells. As the name suggests, the difference lies in the application for which the cells are designed. Thus, HP cells are designed for applications in which the requested power rate for short time periods may be significant, e.g. HEVs or PHEVs. HE cells on the other hand are employed in applications in which the amount of energy plays a fundamental role, while the requested power rate is generally limited, such as BEVs. Such a behavior is obtained by means of special cell designs. As depicted in Figure 3-6, HP cells are characterized by a higher amount of passive materials (current collectors) compared to HE cells, where the amount active materials is considerably higher. In the first case this allows a reduction in the overvoltage drop during high current pulses, and therefore an increase in power capability. In contrast a higher amount of active material in HE cells produces a considerable increase in the gravimetric energy (capacity). Moreover, the particle size in the active materials may be also different in the two cases: while in HP cells the particle diameter is in the range of 0.5-1 μm, in HE cells the diameter might be in the range of 2-4 μm [35]. This produces for example coating thickness in anodes of 70-80 μm for HE cells and 40-50 μm for HP cells [36]. These values can change depending on cell manufacturers [37]. The use of reduced particle sizes limits the lithium ion concentration polarization due to the diffusion in the active materials, and therefore the overvoltage effect if high current rates are requested [38].
3.3 Aging mechanisms

The investigation of the aging mechanisms which cause performance degradation of LiBs during lifetime is a fundamental topic which has been the main focus of several studies over the last 10-20 years. Several phenomena are already known and have been extensively documented [39][40][41][42][43][44]. On the one hand, it can be stated that most of the aging mechanisms are mainly known and understood during the so-called calendar aging. This concerns the conditions under which the cell is operated without any external load, and no external current is theoretically flowing inside the cell. As will be described later, factors such as ambient temperature and actual cell voltage can accelerate or slow down the degradation. On the other hand, there are still many doubts and unknown answers behind degradation due to cycling operation, i.e. the operation where the cell is charged or discharged under defined conditions. Additionally to the factor listed for the calendar aging, other parameters such as current rate, depth-of-discharge (DoD), average SoC, charge and discharge current rates have to be considered.

An exemplary overview of the aging mechanisms in LiBs is given by Vetter et al. in [40]: the authors separate the aging in two categories, namely the aging on the anode and on the cathode. Of fundamental importance for this work are not the causes of each degradation phenomenon, but the effects or consequences on the operation of the batteries. In this work these effects are named degradation modes (DM), and are fundamental for understanding the working principle of the proposed battery state detection algorithms. Therefore, they will be
introduced here in terms of physical effects, and again considered and discussed in depth in chapter 6.

The most documented DM in LiBs is the loss of lithium inventory (LLI). This involves the loss of lithium ions in particular side reactions, which can no longer participate in the main energy conversion process. The most common cause of LLI is the formation of the SEI on the anode surface [45][46], due to the reaction with anode active material particles. The other known cause of LLI is the metallic deposition of lithium on the anode surface, also known as lithium plating [47][48][49]. This process is accelerated by charging under low ambient temperatures or under high current rates. In extreme cases, lithium plating can lead to the formation of dendrites which may short circuit internally the two electrodes.

Another DM is the so called loss of active material (LAM). This can take place on both electrodes. The cause of LAM might be the isolation of the grains of the active material from the electronic network due to the degradation of binders. Another reason for LAM is the change in the electrode composition or in the crystal structure of the active material [44]. This can lead to the formation of layers which are not permeable to lithium ions and therefore completely isolate the interested portion of active material. An example is shown in Figure 3-7.

![Figure 3-7](image)

**Figure 3-7:** Differences between the anode of two 8 Ah HP LiFePO$_4$ cells after disassemble, a) anode of a pristine cell, b) anode in the case of an aged cells, with the evidence of different layers on the active material surface.

Regarding the positive electrode, the LAM mechanism is generally related to the type of cathode employed in the LiB. Some of the causes of LAM are common to all electrode type, such as micro cracking of particle, binder decomposition or gas evolution [40]. Some other mechanisms are related to the crystal structure of the employed cathode. An overview of some of the effects is reported in [19][39][40][43].

In reality it is often difficult to distinguish and separate the LLI from the LAM, as during the battery lifetime these two DMs can be correlated. For example, as will be introduced later in this work, the LAM can take place in the lithiated and delithiated phase (referring to the cases
in which this mechanism take places in a lithiated or in a delithiated state). In the first case, the loss of ionic contact of active material particle with intercalated lithium ions can be directly related to LLI, as these ions can no longer take part in the main intercalation reaction.

The last DM which can be considered is the increase of impedance. This may be caused by an increase in the ohmic contribution of the electrolyte, of the connectors or current collectors, for example due to oxidation or corrosion. Other causes are related to the exfoliation of electrodes, formation of passivation layers on the surface electrodes, a decrease in the ionic conductivity of active materials and retardation in the charge transfer kinetic process on the surface between electrode and electrolyte. In some cases it might be difficult to demonstrate (e.g. in a laboratory environment after cell disassembly) the separation between the increase in the internal battery impedance and the LLI or LAM, as the loss of performance might be attributed to different DMs.

### 3.4 LiFePO₄ as a cathode cell material

Cathode materials in LiBs play a fundamental role. The combinations of materials allowing a stable and long life operation under specific conditions are numerous. However, the combinations which finally made a breakthrough on the market can be counted on two hands. These materials allow reaching a good compromise among different factors, such as high gravimetric energy and energy density, long cycle life, low price, high rate capability and safety. It has to be said that some of these characteristics are interdependent, so that, for example, a rise in the battery energy density coincides with a limitation of safety and battery cost.

In 1997 John B. Goodenough et al. [50][51] presented a new intercalation cathode material, which is renowned today and is employed in the field of LiBs, the LFP cathode material. In 2014, LFP was the third most demanded material for LiBs with circa 20 kt (17% of the market), only preceded by NMC and LiCoO₂ cathode materials [1]. Mainly due to the explosion of the Chinese EV and PHEV market, LFP reached a share of 27%. LiBs based on LFP cathode materials present some merits and drawbacks in respects to their direct competitors. Figure 3-8 compares qualitatively some of the characteristics of four different LiB types. The first fact that is revealed is that LFP based cells offer a good compromise in terms of performance among the considered LiBs, delivering outstanding features in fields, such as safety and cell’s price, nowadays critical and deciding factors when choosing the right technology. LFP based systems present a wide temperature operating range and good lifespan, both in terms of calendar and cycle aging. The LFP active material is non-toxic and less expensive in comparison to others, such as Cobalt or Nickel oxides. This reduces the battery price directly, but at the same time makes a profitable recycling process difficult, in contrast of what happens for PbAs [52]. LFP presents a so-called olivine structure, which is depicted in Figure 3-9, in contrast to other type of cathodes (spinel). This structure presents a high stability and high intercalation/deintercalation reversibility [8]. This produces a significantly stable system both in a normal and in extreme operations. In fact, while some of the presently used cathodes become unstable when a defined amount of lithium ion is deintercalated or
intercalated, the high stability of LFP material allows the complete deintercalation of the ions from the crystal structure without any consequence.

**Figure 3-8:** Qualitative comparison between different LiB chemistries in a scale from zero (worst) to five (best) [31]. For the price, a higher value of the coefficient means a lower cost.

Thereby a higher stability is accomplished under extreme operating conditions, such as overcharge or overdischarge as well. LFP active material has a density of 3.6 g/cm³ and a specific capacity which has grown in the last years, from 100 Ah/kg to 170 Ah/kg [15][53].

**Figure 3-9:** Schematic structure of a LiFePO₄ cathode material in a LiB in the charged and discharged state (based on [54]).
The performance of the first LFP cathodes was very limited, due to the poor electrical conductivity. Recently, improvements have been achieved by reducing the particle size (nanoparticle), which is in the range of less than 100 nm [55], or by the addition of carbon black to the active material. A normal value of lithium diffusivity can be found between $10^{-16}$ cm$^2$/s and $10^{-8}$ cm$^2$/s, while the electronic conductivity amount is between $10^{-7}$ S/cm and $10^{-11}$ S/cm [55]. Besides the low conductivity, which today is no longer an issue, LFP cathodes present an electrochemical potential compared to Li/Li$^{+}$ of circa 3.5 V, which is lower than the potential of other chemical substances (4 V of manganese oxides and 3.9 V of LiCoO$_2$) [15][53]. This leads to a reduced specific energy compared with other LiB cells and is one of the most critical drawbacks, particularly if also calculated in terms of energy density.

Another important difference compared with other cathode materials is the voltage characteristic curve. Figure 3-10 shows the potential trend with respect to Li/Li$^{+}$ of three different cathodes materials, namely LFP, LMO and NMC cathodes. As can be observed, LFP cathodes present a voltage profile which is fairly constant during the entire intercalation process. This process is a first order transition process called two-phase transition and involves the contemporary existence of phases with two different states. Regarding LFP cathodes the process involves the formation of a lithium rich shell and a lithium poor core region for each particle during the intercalation and of a lithium poor shell and a lithium rich core region during the deintercalation. Between the two regions a phase barrier exists, which moves towards the core of the particles or in the opposite direction, in a way that the concentration of lithium inside the region remains constant. As the potential of a particle is directly correlated to the composition and ion concentration on the shell surface [53][56], a characteristic voltage plateau, i.e. zone at two-phase transitions, is visible in the electrode potential curve [54][57]. This concept is of fundamental importance for understanding the working principle of LFP cells; therefore it will be discussed in detail in chapter 5 too.

![Figure 3-10: Voltage profile of different cathode materials during constant current charge at 0.1C. The voltage is measured in a coin cell setup with electrodes of 16 mm diameter against a reference electrode of metallic lithium at ambient temperature.](image-url)
A flat voltage profile on the cathode produces a particular full voltage curve in the full cell. LiBs based on LFP cathodes materials are often coupled with graphite negative electrodes. The characteristic potential vs. Li/Li$^+$ of a graphite electrode is depicted in Figure 3-11. As shown in the graphic, the lithium intercalation process takes place again through different two-phase regions (coexistence of two phases). These are characterized by a rather flat voltage behavior, and three of them (I$\text{L}$+IV$L$, III$\text{L}$+II and II+I) are particularly visible [58][59]. Among each of these phases, the so-called stage formation takes place, i.e. the formation of a number of unoccupied layers of graphite in series (which defines the stage number) among two guest layers [15].

![Figure 3-11: Stage formation during the intercalation/deintercalation process of lithium into a graphite electrode. The voltage is measured in a coin cell setup with a graphite electrode of 16 mm of diameter against a reference electrode of metallic lithium at ambient temperature (based on [15][58][59]).](image)

The combination of the graphite voltage profile and the flat voltage curve of an LFP cathode produces a typical full cell voltage curve, depicted in Figure 3-12. Figure 3-12a) shows the full voltage curve during the charge process of an HP 8 Ah LFP cell. As can be observed, the full cell also presents a rather constant voltage value around 3.3 V, which drops and rises dramatically in correspondence to the empty and fully charged states respectively. At a closer look, it becomes apparent that the curve is not constant but presents some interesting characteristics related to the graphite features.
**Figure 3-12:** Characteristic voltage of an HP 8 Ah LiFePO₄ cell, a) cell voltage during a charging process with constant current of 0.1C at ambient temperature of 23 °C, b) stage process visible in the full cell voltage curve during the charging process.

In Figure 3-12b) the full voltage profile is obtained by subtracting the cathode and the anode voltage curves, considering the cell stoichiometry, as it will be discussed in detail in chapter 6. The combination of the flat voltage curve of the LFP cathode characterized by a single plateau (indicated with A), and the staged voltage curve of the graphite anode characterized by three flat regions (indicated with I, II and V according to [60]) produces a full voltage curve with three flat regions of different width, namely plateau IA, IIA and VA. The peculiarities of these plateaus and how their widths and positions change with the battery lifetime is at the base of the developed battery state detection methodology which will be introduced later in this work.

The last important feature of LFP-based LiBs is the characteristic hysteresis behavior of the OCV, i.e. the voltage between the poles of the battery in absence of load current (normally considered after a defined relaxation period). This voltage should not be confused with the EMF, which corresponds to the voltage between the battery poles in a perfect steady state condition (all the processes are in equilibrium and all the kinetics and diffusion processes can be considered concluded). Considering the same value of SoC, the OCV of a LFP cell assumes different values based on the short-term history. This means that if the cell is in a fully charged state and is then discharged until 50% SoC, the value of the OCV between the poles of the battery is higher than the one obtained charging a cell to a 50% SoC starting from an empty state. The repetition of this process in all the SoC scale produces the characteristic hysteresis curve depicted in Figure 3-13. The width of this hysteresis is not constant but changes in the SoC range. Moreover, as it will be described in chapter 5, the characteristics of the hysteresis change with the battery lifetime. All the introduced physical and electrical features give additional value to LFP based cells compared to other similar chemistries, so much so that in some countries of the world they are nowadays favored in application such as PHEVs and EVs. Nevertheless, the peculiarities regarding the flatness of the voltage profile and the evident hysteresis behavior in the entire SoC range make the on-board state diagnostic of these cells particularly challenging.
In order to give an impression of what the challenges in the understanding process of this technology are, in this section only fundamentals are described. In the following of this thesis some of these characteristics are investigated and discussed in greater detail.
24 3 Lithium-Ion Batteries
Automobiles have been a feature of life for more than 100 years. Even after this long time, fossil fuels still dominate our mobility behavior. Only in recent years sustainable mobility has been identified as one of the possible solution to the problem of world pollution. In order to make mobility sustainable, two factors are of fundamental importance:

1. People must accept responsibility for their actions. This means that every person must be made aware of the fact that his or her lifestyle has a fundamental impact on the environment and that resources must not be wasted but should be saved and shared in order to provide a good quality of life for everyone, now and in the future.

2. The design concept of automobiles and the way they are used must be changed. On the one hand this entails a radical change in technology away from the combustion engine to greener and more sustainable engineering. On the other hand automotive vehicles can be integrated into systems in which they can be productive even if they are immobile.

Regarding the second point, it is clear that batteries are one of the best candidates to fulfill this role. Their integration into vehicles can assure a gradual reduction of the dependency on fossil fuels, thus leading the way to complete electric mobility (e-mobility). However, this is under the assumption that batteries, cars and additional components are produced with renewable energy. In other directions, batteries of electric vehicle can be also used as a kind of stationary systems in two ways. As vehicles spend the majority of their time parked somewhere, when connected to the net their batteries can be employed as an energy reserve, which can support the power grid in terms of frequency regulation and meeting the load demand. This assumes interesting connotes if the number of electric cars connected to the net are thousands or even millions. This idea is the aforementioned V2G concept. The second task for which battery in BEVs/PHEVs can be employed is (after meeting the power demands of automobiles) in a so-called “second life” as stationary systems, again in the role of grid power regulation or to compensate the differences between the predicted and real production of renewable energy. In both cases batteries are completely integrated in the energy system, both for mobility and grid services (Figure 4-1). In this scenario the energy management system (EMS), together with the BMS, plays a fundamental role. They are not only in charge of ensuring the correct operation of batteries during normal operations, the maximization of their performances and the prolongation of the battery lifetime, but also of assuring the correct communication among all the actors participating in the system. This is a very complex and sensitive role. Therefore the design of such components requires not only technical competences, but also economical skills and intelligent thinking.
This chapter tries to give an overview of the main actors of the system, trying to close the circle and making a connection among them. The fundamentals and the requirements of a BMS are given, the general structure is introduced and a state-of-the-art of the methodologies for battery state detection is presented. Moreover the concepts related to the V2G ideas are introduced, with an indication of the market segments where the EV as a system can participate. These concepts are crucial for understanding the idea of this thesis and the central concern of this work.

4.1 Battery Management System

The BMS is one of the main components of a battery system. It consists of all the hardware components and software intelligences in charge of the continuous and safe operation of the batteries. In particular among the tasks of a BMS are [61]:

- The safe operation of a battery, avoiding extreme conditions, such as overcharging, overheating, short circuiting etc. and protecting it from damages. In this sense, the respect of the limit suggested from the manufacturers in terms of voltage window, temperature range and current rate represents a key factor in the management of the batteries.

- The maximization of battery performance, i.e. the exploitation of the main battery features in order to satisfy the load requests and the demand in terms of energy and power at every moment.

- The prolongation of battery lifetime and the limitation of the degradation mechanisms. This can be accomplished either by the aforementioned respect for the safety limits defined by the battery manufacturer, or by the employment of intelligent operating strategies. These should curtail factors which might accelerate battery degradation considerably. One example for this is the definition of a charging strategy for periods with very low ambient temperature, in order to avoid or limit the lithium plating phenomenon. This can be accomplished by deciding at which minimum temperature the battery has to be charged and at with which maximum current rate.
- The accurate and precise detection of the battery state in terms of SoC, SoH and state-of-function (SoF). This allows the complete exploitation of the battery features so that the cells can be operated near the safety window without fear of exceeding the limits due to an inaccurate estimation of the battery state.
- The correct and efficient communication of information with external sources, either inside the vehicles (e.g. communication with the car EMS of the actual SoC in order to estimate the driving range and the permissible load) or with external systems (e.g. in a V2G scenario the communication of the actual SoH of the battery pack for the consequent calculation of the benefit of using the additional battery energy for grid services).

As can be clearly perceived, meeting at the same time all these requirements represents a challenging task which has been the main focus of research and development in recent years. In fact, the key role of an efficient and operative BMS is not only to accomplish those tasks, but also to synchronize them.

### 4.1.1 BMS structure

Figure 4-2 shows a schematic representation of a BMS structure which is normally used for battery packs in BEVs. The main configuration can be separated in BMS master board and slave boards (or cell board controllers).

![BMS Master Board](image)

**Figure 4-2:** Schematic representation of the hardware configuration of a BMS (based on [62]).

The BMS master board is the central intelligence of the system. Its task is the bidirectional communication both with the general vehicle intelligence (extern) and with each one of the slave boards. Furthermore it is in charge of the complete verification and processing of the information originating from each slave, which is, for example, employed by the algorithms for the estimation of the actual battery state. The BMS board is also responsible for the safety of the whole battery system. The computational power performance of the microcontroller (μC) installed on the BMS master boards has grown rapidly in recent years [63]: it is expected
that the limited amount of ROM and RAM memories available in standard cars μC will be easily exceeded in the coming years with the massive penetration of EVs onto the market. This is due to lower costs of the components and to higher demands on computational power.

The different cell controller boards have the main task of supervising the single battery modules into which the battery pack is divided. Each slave acquires the data relative to the single cells such as voltage and current, and the temperature measurement for a group of cells. In fact, the temperature is generally not acquired for each single cell, but only measured at some critical points, due to the reduced criticism of this parameter compared to the single cell voltage and in order to limit the number of sensors (cost limitation). The measurement data is converted into digital signals, filtered from noises and measurement errors and sent to the BMS master intelligence for processing. Each board is also in charge of balancing of battery modules, i.e. the equalization of the battery charge in each series connected cells, and of detecting possible failure, such as the one which can occur due to the defection of cell wires.

In some cases, the BMS architecture contains an additional board, the HVI-board (high voltage and current board): the main task of this board is to measure the total battery pack voltage and current and to monitor some of the contactors present for battery safety.

The software architecture of a BMS master unit is schematically represented in Figure 4-3. As shown the structure contains three main layers. The bottom layer bears the hardware, where the entire software system runs. The second layer is the system level, or so called “low level” software. To this group belongs the operating system which is in charge of managing the entire software and hardware resources and which is needed for operating the individual applications. In automotive applications, the operating system and the software architecture are developed according to the standard AUTOSAR (Automotive Open System Architecture). To the system level belong also all the drivers and the bootloader system, which is in charge of loading the operating system into the memory where it is executed. The third layer is called the application level or “high level” software. On this level the various applications can be grouped into three categories:

- Applications which are in charge of the battery management, such as the battery state detection, the preprocessing of the data which comes from the slave boards, the management of the balancing procedure and the thermal management.
- Applications which are in charge of battery safety, such as the control of the breakers, of the maximum current interruption systems etc.
- Applications for general control, such as authentication and identification control, the control of switches, the application of the management of the CAN receiver and transmitters etc.

The BMS master unit communicates with the car main control unit, sending the detected information on the battery state and receiving the desired BMS state modus. Within the BMS, the master unit communicates with the slave units (it receives the information related to the measured data and sends the control or management information) and with the HVI-board if present.
4.1.2 BMS state detection algorithms

Battery state detection algorithms are the main intelligence of the BMS. Their task is to estimate the main figures of merit which can completely characterize the performances of the battery and the actual aging state. Plentiful of methodologies have been introduced in the literature by date and patented in the recent years. However, it is common and accepted that each method has to meet different requirements, as discussed in [64]:

- The estimation of the variable and parameters has to be accurate and precise within a defined tolerance. This allows the exploitation of the complete battery operating range without the danger of overpassing the battery operation limits.
- The methodologies have to have a simple design and user-friendly working principles so that the implementation in cheap μC is possible.
- The algorithms have to work as an intelligent system which is able to adapt its parameters during the battery lifetime. This guarantees that the acquired data is valid for the entire battery lifespan. This can be achieved only when the algorithms are partly based on fundamental physico-chemical battery phenomena, together with the
typical physical laws which describe to some extent the battery degradation. It is clear that fully empirical methods do not satisfy this requirement.

- Except for some cases, the methods normally need an initial parametrization. This should be as limited as possible in terms of number of parameters. Moreover, these parameters should be easy to obtain with parametrization tests of a limited duration and effort.

- The algorithms should also deliver accurate information on the quality of the obtained results and an error margin between a maximum and minimum value. With this data the goodness of the delivered information can correctly interpreted.

Besides these fundamental requirements, there are other secondary features which are additionally requested, such as the scalability of the initial parametrization, or the ability to use the same method for different battery chemistries. Especially the last requirement is particularly challenging or rather not practicable for LiBs. An extensive review of several methods for estimating battery state is given in [61][63][65][66]. In the following the three main figures of merits, namely SoC, SoF and SoH are introduced and a brief resume of the methodologies and algorithms used for LiBs for their estimation is shortly given. The aim is to provide a summary of the existing options and to identify the areas where improvements are needed.

4.1.2.1 Algorithms for SoC estimation in LiBs

The SoC of a battery gives an indication of the amount of energy which is still available inside the battery compared to the total actually available. It can be expressed in % according to equation (4.1):

\[
\text{SoC} = \frac{\text{Remaining capacity [Ah]}}{\text{Total actual capacity [Ah]}} \cdot 100
\] (4.1)

The definition of the SoC may be ambiguous, depending on which value of total actual capacity is considered (i.e. for which current rate, at which ambient temperature etc.), as discussed in detail by Sauer et al. in [67]. Therefore the definition can change based, for example, on the application. The most common way of calculating the battery SoC is based on a pure Ampere-hour counting, i.e. the integration of the charge/discharge current over time [68][69]. This method is a very simple approach and works very accurately for LiBs, because in the short-term the battery side reactions are nearly negligible. However, the method needs knowledge of the initial SoC, information which may not be always available, or might be difficult to obtain. Furthermore, knowledge of the actual capacity is needed in order to recalibrate the actual SoC scale. The use of the Ampere-hour counting in the long-term may be affected by a significant inaccuracy, due to the accumulation of measurement errors. Therefore this method is often coupled with other approaches, which correct possible error sources. The relation OCV-SoC is often used as a support algorithm. It is based on the fact that knowing the value of the OCV, through the known relation, the SoC can be directly obtained [70][71]. The value of the OCV can be either measured (after extensive rest period),
or estimated during the relaxation [72] or by means of EECMs [73][74]. Nevertheless, most of the presented methods take into account that the initially parametrized OCV-SoC relation does not change during battery lifetime. This assumption is not verified in every case, as will be discussed in detail in chapter 5 and chapter 6 for LFP based cells. Moreover, as already mentioned earlier in this work, the OCV of an LFP cell is rather flat for a wide SoC range. Therefore this method should not be used for this kind of cell without certain precautions.

SoC can be further estimated by using EECMs, as the one shown in Figure 3-4. This approach consists in describing the model in form of equations which connects the SoC variable with other electric parameters. However, in this case too, the SoC value is inferred by the relation OCV-SoC. The estimation can occur in an open loop or in a closed loop. In the second case, various filters techniques can be used to estimate and correct the SoC value, such as Kalman filters or its variants [75][76] or least-squares based filters [77]. The advantage of this approach is the high accuracy as soon as the model maintains its validity. If the parameters of the model are not adapted during the lifetime, the loss in accuracy may be dramatic.

Other model types, which can be used, are the electrochemical models [78][79]. These models are based on physico-chemical phenomena, therefore their estimation may be more accurate but with additional higher complexity. Thus, they are generally not used for this scope. Additional methods regard the use of the relation among the battery impedance and the SoC [80], or other sophisticated techniques, such as artificial neural network approaches [81].

Summarizing, the development of SoC methodologies seems to have reached a state-of-the-art conditions. The different approaches offer a range of possibilities, from the simple, less accurate, to the more complex and also more accurate methods. Nevertheless, as will be introduced in chapter 6, some improvements can still be achieved for some LiB chemistries, such as LFP cells, where the flat curve and the evident hysteresis still create evident problems in Ampere-hour counting based methods.

4.1.2.2 Algorithms for SoF estimation in LiBs
The SoF gives an indication about the power capability of a battery. The definition may differ slightly depending on the considered application. Concerning PbA (SLI – starting, lightning and ignition application), as indication of SoF the capability of cranking a car during the start process is considered. For LiBs, SoF indicates generally more the capacity of a battery to deliver the requested constant power for a defined time period, without exceeding the operation limits suggested by the manufacturer in terms of maximum and minimum both current and voltage. Therefore, this figure of merit is strictly related to the actual battery impedance. The method for the on-board prediction of power can be divided in two categories [63][65]. To the first group belong all the methods which are based on characteristic maps. This means that the characteristics of the battery in terms of impedance and power capability are firstly obtained for a new cell in a laboratory environment and then stored in maps or a lookup table and extracted during the operation. The main advantage is that the algorithm for SoF estimation is in this case very simple. The drawback is that if these maps are not adapted based on the actual battery state, the delivered information loses its accuracy during battery
lifetime, due to the change of the battery resistance. Examples of these methods can be found in [71][82][83][84]. To the second group belong the methods which are based on the online estimation of the battery impedance [66][75][76][77]. The advantage is that intelligent algorithms are able to adapt themselves during the lifetime. However these techniques may be often characterized by a higher complexity, which makes the implementation on cheap μC difficult. Therefore the estimation of the battery resistance plays a fundamental role in the estimation of SoF. According to Waag [65][66], the methods for estimating battery resistance can be divided into three categories. The first group denotes the method based on the electrochemical impedance spectroscopy (EIS) approach. This is a very common method for investigating battery behavior in the frequency domain, and for characterizing a defined cell through a complex EECM [22]. The methods based on EIS can be further divided into ones which use active EIS [85] and ones which use passive EIS [82]. In the first case the battery is excited with an external source of defined frequency and the answer in terms of voltage (in case of galvanostatic approach) or current (in case of potentiostatic approach) is used to identify the complex battery impedance. In the second case the battery impedance is obtained by analyzing the frequency domain of the battery answer based on the voltage or current signal during normal operation, without the need of any external excitation. The second group of methods is based on the online parametrization of a chosen EECM. A typical model is already presented in Figure 3-4. The parametrization of each of the model elements is carried out with different techniques, such as extended Kalman filter [86], sigma-point Kalman filter [87], recursive least-squares [88], varied-parameters approach (VPA) [89], or a mix of some of them [90]. To the last group of methods belong those which are based on electrochemical models [79][91]. This kind of approach does not directly calculate a value which can express the battery internal resistance, but tries to reproduces all sources of overvoltage or polarization by means of electrochemical laws which regulate these phenomena. As already mentioned, the high accuracy of these approaches goes hand in hand with a significant complexity and the difficulty of adapting the initial parametrization online during the battery lifetime.

4.1.2.3 Algorithms for SoH estimation in LiBs

The SoH is the third important figure of merit which is considered as fundamental for defining the actual battery state. It is related to the battery degradation and the loss of performances during battery lifetime. The degradation of a battery produces a limitation of the power capability (increase in the resistance) and of the energy capability (fade of capacity). Even if a standard definition does not exist, in the field of EVs as end-of-life (EOL) criteria for batteries, a reduction of the battery capacity of 20% in respect to the initial or nominal value or an increase in the internal resistance with a factor two or three [92][93] are commonly employed. These are reported in equation (4.2) and equation (4.3):

\[
SoH_c = \left( \frac{Q_{\text{actual}} - Q_{\text{EOL}}}{Q_{\text{BOL}} - Q_{\text{EOL}}} \right) \cdot 100
\]
\[ \text{SoH}_R = \left( \frac{R_{EOL} - R_{\text{actual}}}{R_{EOL} - R_{BOL}} \right) \cdot 100 \]  

(4.3)

where \( Q_{\text{actual}} \) is the value of the actual battery capacity, \( Q_{BOL} \) is the battery capacity at the beginning-of-life (BOL), \( Q_{EOL} \) is the capacity value for which the battery is considered at EOL, \( R_{\text{actual}} \) is the value of the actual battery internal resistance, \( R_{BOL} \) is the battery resistance at the BOL, and \( R_{EOL} \) is the resistance value for which the battery is considered at the EOL. With this notation, a SoH of 100% indicates a battery at BOL, while a SoH of 0% indicates a battery at EOL. Errors in the estimation of the SoH are more critical compared to SoC or SoF. In fact, considering SoHC, an error in estimation of the capacity of 3% in respect to the real actual value can be considered as an error of 15% compared to the real usable capacity value, which defines the EOL criteria. Moreover with EOL it is intended that the battery is still able to work, but it should be exchanged for the specified application, as it can no longer deliver the requested performance.

With regard to the SoHR, the defined value of the battery resistance may differ depending on the specified application [22]. Standard conditions are then applied to the chosen resistance definition, to normalize it and to compare values acquired in different operating conditions (i.e. ambient temperature, current rate etc.). Techniques and methods for estimating the internal resistance of a battery are summarized in section 4.1.2.2.

Concerning the SoHC, the definition of the battery capacity may be ambiguous, as introduced in [94]. The methodology for its estimation can be grouped into four categories, as shown in Figure 4-4.

![Onboard Capacity Estimation](image)

**Figure 4-4:** Different methods for on-board capacity estimation in LiBs [94].

The first group contains all the concepts based on the estimation or measurement of the EMF and consequently on the OCV-SoC relation. Through this relation the actual battery capacity
is estimated by counting the Ampere-hour throughput between two SoC values [95][96]. The EMF can be measured after a long relaxation period, or estimated through the use of EECMs, as mentioned in section 4.1.2.1. The use of this method for the estimation of the capacity is the most commonly accepted in literature, but as it will be discussed in chapter 6, it cannot be used for LFP-based cells, due to the not-monotony of the OCV-SoC relationship and to the evident change of this during battery lifetime. For other LiB chemistries this method is commonly and successfully employed [72][73][97][98]. The second group of methods is based on electrochemical models. In this case the physico-chemical modeling of the normal battery behavior is coupled with the laws which regulate the main battery degradation mechanisms, in order to predict and simulate the fade of capacity during the lifetime. The estimation of the parameters is then carried out by filtering techniques [99]. As already mentioned, high accuracy coincides with high complexity. Therefore the reduction of the model order causes a reduction of precision, which is why these types of methods are rarely used for on-board SoH estimation. The third group of methods consists of the aging prediction based approaches. In this case a batch of new cells is subjected to accelerated calendar and cycling aging tests. Cell degradation is monitored periodically through parametrization tests, where actual capacity and resistance trends are analyzed. The data is then used to develop models which are able to predict the degradation based on operation conditions. These models are then implemented on-board and used to predict the actual battery’s SoH [100][101]. This approach is not very common due to the expensive of resources needed for the initial parametrization. Finally, a fourth group of methods collects all the approaches based on differential analysis of the Ah-throughput or of the voltage [102][103]. The differential analysis has been known for years, but only recently it has been applied for the on-board estimation of the battery’s SoH. It allows the qualitative and quantitative analysis of the degradation mechanisms of a battery during the lifetime by observing the voltage curve obtained while charging or discharging a battery with a limited current rate. The differential methods have a big impact especially in batteries with flat OCV curves, which is the case in LFP cells. A detailed description and discussion of these methodologies is given in chapter 5 and chapter 6, as they are one of the main motivations which have given impulse to this work. Differential methods provide a good understanding of the battery degradation offline. However, for the on-board diagnosis they may present some difficulties when analyzing the voltage signal characterized by a high amount of noise. In this case, differentiation can increase the possibility of misinterpreting the signal and therefore the information related to the degradation.

The SoH estimation includes all methods which are related not only to the estimation itself but also to the prediction of the remaining useful life (RUL). Like the above mentioned aging prediction based methods, the RUL is often obtained by offline parametrized aging prediction models [100]. These models are then recalibrated during the lifetime based on the information collected during the operation. This allows the correction of models which may differ during the lifespan to the real battery behavior and thereby extend their validity.
4.2 The vehicle-to-grid concept

Passenger vehicles, which render individual mobility, are a fundamental part of modern life. A projection estimates that in 2030 in countries such as Italy or Germany 781 or respectively 705 vehicles will be registered per 1000 people [104], which is nearly one vehicle per person. According to [105], 80% of trips undertaken in Europe are shorter than 25 km and 50% are even under 10 km long. In the USA, 60% of the daily journeys are not longer than 50 km, while 85% stay below 100 km. This data proves that, most of the time, vehicles are not in movement, but they stay parked in an idle state. If all cars currently on the road were PHEVs or EVs, and the grid was equipped with a charging infrastructure, all these vehicles could be plugged into the grid for the entire parking period. Hartmann et al. in [106] state that the daily availability of passengers cars that can be connected to the grid is higher than 89%. In this scenario it is easy to imagine that in the near future BEVs and PHEVs could be plugged to the grid for an average time of 20 to 22 hours per day provided a good grid infrastructure is accessible. An example of a typical daily journey of an average worker in Europe is shown in Figure 4-5.

![Figure 4-5: Example of daily trip with EV with the possibility of charge in public places](http://www.clipartbest.com)

The assumptions is that an EV with a 20 kWh battery pack and a consumption of 0.20 kWh/km (100 km driving range) is available. The vehicle could be charged in all public infrastructures with a slow charging mode. Driving for a range of 95 km, the SoC of the car never falls below 45%, and most of the time the vehicle is plugged to the grid, either in a public place or in a private charge infrastructure (home). According to the data introduced
above, it can be assumed that in the majority of the cases a vehicle will travel a daily distance which is significantly below 100 km. Therefore, the idea of employing the EVs’ battery packs as a moving and flexible storage system seems to be feasible. This recalls the aforementioned concept of V2G.

The V2G [108][109] concept was initially used in the early 1990’s by the company AC Propulsion Inc. in order to demonstrate the dual usability of all the EVs and PHEVs connected to the grid every day: the vehicles can communicate with the grid and sell the remaining energy in the battery pack during the high peak power demand (high energy price) and buy energy from the grid for the charging process when the energy price is low. This concept is briefly resumed in Figure 4-6, where in part a) the process of recharging the EVs during a period of energy overproduction and low electricity price is shown, and in part b) where the process of selling the EV’s energy during a period of energy underproduction and high electricity prices is depicted.

**Figure 4-6:** Schematic explanation of the V2G concept, a) recharge of the car battery during period of low electricity price and b) discharge of car battery energy to the grid during periods of high electricity price (base on [110]).

The efficiency of the entire system can improve significantly as soon as the number of PHEVs or EVs taking part in this game becomes significantly larger. The best case scenario is that each vehicle is equipped with a battery pack of sufficient capacity. However, at this point the complexity of the system will grow exponentially. In fact, on the one hand, the grid is constantly regulated by the balance between the produced power and the instantaneous power
requested from each loads. This balance must always be guaranteed within defined safety margins, in order to avoid high oscillation of the fundamental grid parameters (such as the grid frequency and voltage) and to avoid critical situations (such as blackouts). On the other hand, the central intelligence of each vehicle has to be able to communicate with the grid and exchange information, in order to decide if the car has an active part to play in the V2G system (selling or buying energy from the battery). This decision is determined by several factors. Firstly, the vehicles should be put in the center of the system; this means that regardless of the use in V2G, the vehicles must be ready (battery with the full SoC) at the moment of departure. Secondly, the vehicle has to belong to an aggregate of car (fleet) which can apply to the electricity market selling or buying a certain amount of energy. In fact, for a specific amount of energy, this can happen only with a defined predicted quantity which has to be communicated in advance. To do so, it is vital to obtain information in terms of prevision of the energy price and prediction of the loads. An intelligent system may have the task of processing all this information, in order to decide when the car should sell energy (discharge) and when it should buy energy (recharge) from the market.

Another important point is related to the additional use of the car batteries. As introduced in section 3.3 and elaborated in the following of this work, the use of a battery for additional V2G services involves additional degradation related to the subsequent cycling operation. This effect must be limited in order to not reduce the battery lifetime and limit its duration compared to the lifetime of the entire vehicle (predicted time of substitution). To achieve this, the BMS of the vehicle has to be able to predict the additional battery degradation, and decide how best to use the battery for V2G services. This limits the aging process while also attaining economic advantages. The complexity of the entire system, when the number of participants becomes innumerable, can only be supposed: the grid has to be equipped with algorithms able to manage the information derived from the single vehicles, while each car has to deliver all the information that the grid needs in real time. The steps to follows before the V2G system is in place are still numerous, but the path seems to be paved, as soon as the EV technologies will breakthrough. Some of the concepts introduced in this section will be resumed and discussed again in chapter 7, where a V2G simulation scenario is introduced, with particular emphasis on battery aging.

Another important aspect concerns the market segment which the V2G services can be located. Of particular attention is the frequency regulation process on the electricity grid. A complete explanation of this mechanisms would be beyond the scope of this work but can be found in [111][112]. The frequency regulation takes place by means of three types of reserve. The primary reserve is automatically activated in order to stabilize the grid frequency within 30 s from the perturbation (available for 15 minutes) by modifying the speed of the turbines in the production power plants. The secondary reserve is also automatically activated after approx. 5 minutes in order to completely compensate the frequency deviation or to correct unexpected oscillations not corrected by the primary reserve action. The power must be delivered for 1 hour. The tertiary reserve (or minutes-reserve) is activated per request as soon as the primary and secondary regulations are not sufficient for the correction of the frequency deviation. It must be activated within 15 minutes and be available for 1 hour. The amount of
power which must be supplied to the different regulation reserve can change depending on the regions and areas. The segment of the V2G can be easily located in the secondary or tertiary reserve markets when a fleet of EVs is enough large to make a competitive offer on the market. A further option links the fast development of the EVs market with the necessity of integrating into the electricity grid of renewable energy sources. Since the production of renewable energy is marked by significant uncertainty and randomness, the difference between the predicted and real production can be covered by stationary energy storage systems. To this scope the V2G seems to meet all the requirements perfectly.

4.3 Improvement of BMS in V2G

As already mentioned, the possibility of using the EVs in a V2G system has to rely on an intelligent system which is able to process a large amount of information in real time. Moreover, it must satisfy the requirements of the electric grid and manage the available energy storage system optimally, in terms of performance and lifetime. In order to achieve this task, the BMS needs to assume another form and structure compared to those traditionally used [66][75]. An example of a new BMS structure, which can satisfy these requirements, is shown in Figure 4-7.

![Figure 4-7: Example of BMS core software and battery state detection/prediction algorithms.](image)

The subsystems for the prediction of the battery aging and for the participation to the V2G services (blocks in green) are added to the normal subsystem which are involved in the SoC estimation (blocks in blues), to the impedance estimation (blocks in red), to the capacity detection (block in yellow) and to the remaining energy (block in brown) and power
prediction (block in violet). As mentioned above in section 4.1.2, an aging prediction model can be used firstly as an indication of the actual battery’s SoH, and as a RUL estimator as soon as its initial parametrization is adapted to the actual battery characteristics. These types of models may be additionally used to decide how the battery pack for V2G services must be operated, in order to limit the additional battery aging. This means that each of the EVs of a fleet connected to the grid can receive a request with different power profiles for V2G services: the BMS can process them in the “Aging load profile calculation” and calculate the degradation each battery will be involved in for each of the suggested profiles. A central intelligence, which collects the information of all the cars, can choose the best car combinations which can satisfy the energy requested from the grid and at the same time can control battery degradation. The model developed in this work is based on this concept and its application and results will be shown in chapter 7.

Furthermore, some of the LiB chemistries such as LFP cells present particular characteristics, which make their behaviors differ from others. As a consequence, for the monitoring of these battery chemistries, BMSs require additional intelligent methods for battery state detection. One of the aforementioned features is the hysteresis behavior of the OCV, which may require (but not always need) an additional hysteresis model for the estimation of the SoC and for the general reproduction of the battery behavior. Moreover, as will be presented extensively in chapter 6, the estimation of the actual battery capacity is already a challenging task for batteries, and is even a bigger challenge in case of LFP cells, where the voltage curve presents flat characteristics for a wide SoC range.

In the next chapters the development of new BMS concepts for LFP cells, based on new evidences from cell testing and analysis will be presented. Furthermore, a study of the impact of the V2G on the battery aging behavior will outlined. This process achieves a system analysis which starts from the bottom with the post mortem analysis and the cell testing, goes through BMS development, and terminates with the integration of the battery with the power grid through the V2G idea.
Battery Systems in Vehicle-to-Grid
5 Characterization of a LiFePO$_4$ battery

In this chapter the experimental results obtained through the characterization of a LFP-based LiB are shown and discussed. The tests carried out concern the electrical characterization of the battery, while the thermal aspects are beyond the range of this work. Besides the tests normally carried out for LiBs (e.g. rate capability, energy capability and impedance behavior), the results shown in this chapter concentrate mainly on the investigation of particular features of LFP cells. Among these, the behavior of the cell capacity based on the operating conditions, the flatness of the OCV curve and the investigation of the OCV hysteresis are discussed in detail. Routines for the investigation of the observed behaviors are developed. These aspects are treated mainly with respect to the battery degradation, in order to understand how the investigated phenomena influence battery performances and how these are affected by aging. Modeling of some of the observed phenomena is shown and validated.

As a background for this work, on the one hand, the focus of the conducted experimental investigations lies on the necessity to understand the battery behavior with all its merits and drawbacks, to thus maximize battery performance during operations and to prolong the cell lifetime. On the other hand, this understanding facilitates the modeling, and therefore the design of intelligent diagnostic algorithms for a proper battery state detection. The content of this chapter are partially based on [113].

5.1 Characteristics of the tested cells

The cell tested in the frame of this work is a cylindrical HP LFP cathode-based LiB, as shown in Figure 5-1. The cell is designed for automotive applications.

![Figure 5-1: Cylindrical LFP-based LiB tested.](image)
The main characteristics of the LFP cell are shown in Table 5-1. According to the datasheet, the sample shows a high power capability during discharge, while the charge process is also allowed with a high current rate. The valid temperature operating range is also in accordance with other LiBs, particularly regarding the limitation of the charge process for ambient temperature below 0 °C (avoid or limit lithium plating).

**Table 5-1: General characteristics of the tested LFP cell.**

<table>
<thead>
<tr>
<th>Type</th>
<th>OMLIFE8AHC-HP (High Power)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Capacity / Ah</td>
<td>8</td>
</tr>
<tr>
<td>Operation voltage / V</td>
<td>Nominal - 3.2</td>
</tr>
<tr>
<td></td>
<td>Maximum - 3.65</td>
</tr>
<tr>
<td></td>
<td>Minimum - 2</td>
</tr>
<tr>
<td>Internal resistance / mΩ</td>
<td>&lt; 4</td>
</tr>
<tr>
<td>Maximum continuous charge current / A</td>
<td>80 (10C)</td>
</tr>
<tr>
<td>Pulse peak discharge current / A</td>
<td>240 A (30C)</td>
</tr>
<tr>
<td>Standard charge/discharge current / A</td>
<td>8 (1C)</td>
</tr>
<tr>
<td>Operating temperature / °C</td>
<td>Charge - 0...+45</td>
</tr>
<tr>
<td></td>
<td>Discharge - -20...+60</td>
</tr>
<tr>
<td>Dimension / mm</td>
<td>Ø38.5 x 122</td>
</tr>
<tr>
<td>Weight / g</td>
<td>310</td>
</tr>
</tbody>
</table>

All the results presented in this work refer to this type of cell, but several findings and new evidence can be at least associated qualitatively with cells of the same chemistries (LFP) or of the same type (LiBs).

### 5.2 Electrical characterization

In this section results obtained through basic electrical characterization of the cells are shown. Particular focus is put on the behavior of the total cell capacity, which is one of the parameters investigated in depth in this chapter and discussed in chapter 6.

As introduced in section 3.4, the charge and discharge voltage curve of a LFP cell is characterized by a particularly flat behavior in a wide SoC range. The influence of the current rate and temperature on the cell’s discharge behavior is depicted in Figure 5-2. Figure 5-2a) and b) show the voltage of the cell during a constant current (CC) discharge process with different current rates (from 0.25C to 10C) and the related temperature trend on the cell surface respectively. Each test starts with the cell in a fully charged state and terminates when the cell reaches the end-of-discharge voltage (EODV). The initial temperature is 23 °C. As can be expected from a HP cell, the change of the current rate does not significantly affect the capacity. A maximum difference of 0.361 Ah (4.05% of the highest capacity) is observed. Moreover, after a certain C-rate value, the effect of the increased temperature due to the high current enhances the cell energy capability. A similar conclusion can be drawn from Figure 5-2c) and d), where the cell voltage during a CC discharge process with 0.1C under different
ambient temperatures and the relative temperature trend on the cell surface are shown respectively.

![Figure 5-2](image-url)

**Figure 5-2:** Discharge curves for a new LFP cell for different conditions, a) voltage profile during the CC discharge with different current rates for ambient temperature of 23 °C, b) cell temperature during the CC discharge with different current rates, c) voltage profile during the CC discharge with current rate of 0.1C for different ambient temperatures, d) cell temperature during the CC discharge for different ambient temperatures.

In this case too, the ambient temperature seems to not significantly influence the cell’s performance, although the current rate is limited (this allows limiting the consequent increase of the temperature during discharge for low temperature values). A difference of 0.083 Ah (0.95% of the highest capacity) is obtained between the capacities at 40 °C and 10 °C. Similar results can be won during the charging process. In the next section the effect of different parameters on the cell total capacity is investigated in more detail.

### 5.2.1 Influence of current and temperature on the total capacity

The question which arises after observing Figure 5-2 is whether the variations of the operating conditions may influence the total battery capacity or not, and if this behavior can be influenced by the battery aging state. The aim is to investigate the behavior of the battery capacity during dynamic conditions, and to use the obtained information for the development of battery state detection algorithm for available capacity estimation. As will be shown, only in extreme conditions does the total battery capacity change substantially, while remaining unchanged in most of the test setup.

Tests on two cells in different aging states investigate this issue. The tests are performed with a battery test bench manufactured by Digatron Industrie-Elektronik GmbH, while the cells are always inside a temperature chamber manufactured by BINDER GmbH. The characteristics of the two samples are reported in Table 5-2. The chosen aged sample is taken from a batch of
Characterization of a LiFePO4 battery aged cells which were subjected to calendar and cycle aging. The tests carried out can be grouped in three categories: tests to investigate the current and the temperature variation dependency and tests to investigate the presence of rest periods during the discharge process. Some of the important findings are shown in the following of this section. More detailed information can be found in [114] and in appendix 10.4.1 and 10.4.2. For a general understanding, the value of the considered SoC is referred to the actual battery capacity, while the value of the current rate is referred to the battery nominal capacity. Before diving into a discussion of the results, it is important to highlight a fundamental aspect: during the tests, the value of the total battery capacity taken as reference (i.e. discharge the battery from 100% SoC until the EODV with 1C current rate for an ambient temperature of 23 °C) changed continuously, both for the new and aged cell.

Table 5-2: Overview of the cells’ characteristics used during the measurements.

<table>
<thead>
<tr>
<th>Cell name</th>
<th>Actual/Initial capacity</th>
<th>Aging history</th>
</tr>
</thead>
<tbody>
<tr>
<td>New</td>
<td>8.8 Ah/8.2 Ah</td>
<td>New cell.</td>
</tr>
<tr>
<td>Aged</td>
<td>7.21 Ah/8.16 Ah</td>
<td>Significantly aged cell after 1312 equivalent full cycles (EFC) at 30 °C with 10% DoD, SoC average of 50% and current rate of 3C.</td>
</tr>
</tbody>
</table>

In particular, the value of the reference capacity decreased for the aged battery, starting at an initial value of 7.21 Ah (90% of the nominal value) and terminating with a final value of 5.88 Ah (73.45% of the nominal value). As is shown in section 5.3, these cells show lifetime in the range of thousands equivalent full cycles (EFC). Therefore, the reason of the fast aging shown cannot be found in normal lifetime degradation processes, but may be related to some accelerated lithium plating phenomenon which could have taken place during the charge and consequent discharge process at 0 °C with current bigger than 1C. The value of the reference capacity has changed from an initial value of 8.2 Ah (102.4% of the nominal value) to 8.8 Ah (110.02% of the nominal capacity) for the new battery. An increase in capacity at the beginning of the lifetime has often been documented in literature [35][115][116], but it is not yet fully explained and clarified. Nevertheless, in order to take into account this phenomenon for both cells, a measurement of the reference capacity is periodically carried out, in order to compare results obtained under different conditions.

The presented results show the influence of the current rate variation during the discharge process on the total capacity and observe if this variation influences only the last part or the entire discharge process. Moreover, the impact of the aging is also analyzed. Table 5-3 and Table 5-4 show a summary of some of the performed tests. Firstly, through reference tests the battery is discharged from a fully charged state (cell charged with CC-constant voltage (CV) process) to an empty state (cut-off voltage) with three different current rates (0.2C – 1C – 5C): the aim is to have a reference with respect to the discharge process with an inconstant discharge current. Afterwards (Table 5-3), starting in a fully charged state the battery is
discharged to 50% SoC with a current $I_1$, and from 50% SoC to the empty state (reach of the cut-off voltage, EODV) with a current $I_2$ different than $I_1$.

**Table 5-3:** Test matrix for current variation investigation with two steps (1\textsuperscript{st} step: 100\%\(\rightarrow\)50\% SOC. 2\textsuperscript{nd} step: 50\%\(\rightarrow\)0\% SOC) at three different ambient temperatures.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Current / C-rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 °C</td>
<td>23 °C</td>
</tr>
<tr>
<td>1</td>
<td>0.2C</td>
</tr>
<tr>
<td>2</td>
<td>1C</td>
</tr>
<tr>
<td>3</td>
<td>0.2C</td>
</tr>
<tr>
<td>4</td>
<td>5C</td>
</tr>
<tr>
<td>5</td>
<td>1C</td>
</tr>
<tr>
<td>6</td>
<td>5C</td>
</tr>
</tbody>
</table>

The test is repeated with inverted current values. Tests are carried out for the three mentioned current rates and for three different temperatures. The second part of the test routine is shown in Table 5-4, and it repeats the routine of Table 5-3 but with three steps of current change and only for an ambient temperature of 23 °C.

**Table 5-4:** Test matrix for current variation investigation with three steps (1\textsuperscript{st} step: 100\%\(\rightarrow\)66\% SOC – 2\textsuperscript{nd} step: 66\%\(\rightarrow\)33\% SOC – 3\textsuperscript{rd} step: 33\%\(\rightarrow\)0\% SOC) at ambient temperature of 23 °C.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Current / C-rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>00%(\rightarrow)66% SoC</td>
<td>66%(\rightarrow)33% SoC</td>
</tr>
<tr>
<td>19</td>
<td>0.2C</td>
</tr>
<tr>
<td>20</td>
<td>0.2C</td>
</tr>
<tr>
<td>21</td>
<td>1C</td>
</tr>
<tr>
<td>22</td>
<td>1C</td>
</tr>
<tr>
<td>23</td>
<td>5C</td>
</tr>
<tr>
<td>24</td>
<td>5C</td>
</tr>
</tbody>
</table>

An example of the obtained voltage trend during one of the shown test routines is depicted in Figure 5-3, where the effect of 0.2C and 1C current rates is shown. Figure 5-4a) and b) show the result in terms of relative capacity for a new and aged cells respectively for the test carried out according to Table 5-3 (23 °C). As can be observed, the first evident difference in terms of capacity is basically related to the value of the current rate in the last part of the discharge process. As the discharge process is stopped when the cell reaches the cut-off voltage, it is clear that the bigger the current rate is, the bigger the contribution of the diffusion overvoltage at the end of the process is, and this brings the cell to reach the voltage limit faster. This behavior seems to be valid for both cells in qualitative terms, although for the new cell the difference between the test couples no. 8&10 (end with 0.2C) and no. 7&12 (end with 1C) is bigger (6\%) than the one for the aged sample (2\%).
Figure 5-3: Performance comparison among different discharge operating conditions at ambient temperature of 23 °C.

If the tests with the same current rate at the end of the process are compared, one can see that the small difference in capacity is related to the value of the battery temperature when the current rate is changed (50% SoC) and at the end of the process.

Figure 5-4: Trend of the normalized available capacity for two steps current tests at ambient temperature of 23 °C for a) new cell and b) aged cell.

Considering for example the tests no. 7 (0.2C – 1C) and no. 12 (5C – 1C), the phase at 5C current rate generates a temperature increase of 4 °C for the new cell (from 24.8 °C to 28.8 °C) leading to an increase in the final capacity of 0.5%. The same behavior can be found for the aged cell, although more limited quantitatively. Only the tests no. 9 (0.2C – 5C) and no. 11 (1C – 5C) do not respect this trend for the aged cell, despite the fact that the temperature in the middle and at the end of the discharge process is higher for test no. 11 than for test no. 9. Nevertheless, as could already be expected, the temperature plays a fundamental role, in the way the current rate influences not only the last part, but indirectly through the
temperature, the early discharge process. This behavior is not found in Figure 5-5, where the results of the same tests are shown for an ambient temperature of 0 °C. In this case the low ambient temperature effect joined with the high current rate could lead to difficulties during the diffusion process, making the effect of the increased battery temperature in the middle of the discharge process negligible. The same qualitative behavior is found for both cells, but once again with a clear difference in test no. 3 (0.2C - 5C) and test no. 5 (1C - 5C) between the two cells, showing that the actual aging state completely changes the battery behavior in terms of final battery capacity. As shown in Figure 5-6, an accurate study of the same data for the ambient temperature of 40 °C shows a similar trend to the one shown from the tests carried out for an ambient temperature of 23 °C: this indicates that the battery aging state influences the behavior of the cell only in some conditions (test no. 9&11, no. 3&5 and no. 15&17), while temperature becomes a crucial parameter when its value starts to decrease below a certain limit (no. 1&6 compared with no. 7&12 and no. 15&17).

**Figure 5-5:** Trend of the normalized available capacity for two steps current tests at ambient temperature of 0 °C for a) new cell and b) aged cell.

**Figure 5-6:** Trend of the normalized available capacity for two steps current tests at ambient temperature of 40 °C for a) new cell and b) aged cell.

Figure 5-7 shows the results of the test discharging the battery in three steps for an ambient temperature of 23 °C. In this case too, the current rate in the last part of the process plays an important role for both cells: the difference in quantitative terms between the test couples seems to be respected (e.g. difference no. 20&23 and no. 19&21 is between 5 and 7.5%).
Figure 5-7: Trend of the normalized available capacity for three steps current tests at ambient temperature of 23 °C for a) new cell and b) aged cell.

Considering the tests in couple, based on the current rate in the final part of the process for both cells, the differences between the values of the total capacity are negligible, which is a sign that the variation of the current in the early part of the process now plays a smaller role. What is more, a different behavior between new and aged sample becomes apparent in the tests terminating with a 5C current rate. For the new cell, test no. 19 (0.2C – 1C – 5C) has shown more capacity than test no. 21 (1C – 0.2C – 5C), while for the aged cell the opposite occurs: once more the influence of aging on the cell when discharged with a high current rate in the final part of the process, is observed when comparing the two cells, although the difference between test no. 19 and no. 21 is for the new cell negligible.

In conclusion, the results suggest that the current rate has a relevant influence on the total battery capacity only in the last part of the discharge process. During the most part of the discharge this effect can be considered as negligible. This dependency is maintained also during the lifetime. This information plays a key role in the design of battery capacity estimation algorithms to be employed during the driving operation of EVs and PHEVs, as will be presented in chapter 6.

5.2.2 Electrical impedance spectroscopy

Among the characterization tests carried out on a LiB, the investigation of the impedance behavior is of a fundamental importance. However, a detailed analysis of the impedance behavior of the tested LFP cell is beyond the scope of this work. Only a brief overview for the sake of completion is given in this thesis. As already mentioned in section 4.1.2.2 and reported by Pilatowicz et al. in [22], defining the internal battery impedance is a difficult task, and it is based on several factors, such as frequency range, application, SoC, temperature and aging. Generally two methods are employed to evaluate the impedance behavior of a LiB. Existing standards [117][118][119] are mainly focused on the use of “current pulses/voltage response” relations. Different pulse durations with different current rates are employed to determine battery impedance behavior which characterizes a LiB completely. Once the current and voltage trend are obtained the battery impedance can be obtained by the use of Ohm’s law [120]. As mentioned earlier, another common non-intrusive method to ascertain
battery impedance is the EIS technique. This is a reliable technique where the dynamic effects that characterize the cell’s or system’s behavior can be separated, with respect to different operating conditions or different cell characteristics (shape, size and chemistry). Information regarding this technique and how to interpret the acquired information can be found in [23][24][25][121]. Figure 5-8 shows exemplarily the EIS for a new LFP cell. Figure 5-8a) shows the impedance dependency compared with the ambient temperature at SoC of 50%, while Figure 5-8b) shows the SoC dependency for ambient temperature of 23 °C. All the measurements are carried out without a superimposed DC current: this simplification is allowed in LiBs due to the limited current dependency of the battery impedance in contrast to other technologies (e.g. PbAs).

![Figure 5-8: EIS measurements for a new LFP cell without superimposed DC current in a frequency range of 2 mHz to 5 kHz, a) for different ambient temperature at SoC of 50%, b) for different SoC at ambient temperature of 23 °C.](image)

As expected, as for each LiB, the decrease of the ambient temperature corresponds to the increase of the battery impedance, due to the slower kinetic of the intercalation/deintercalation and diffusion processes and to the increase of the ohmic resistance (electrolyte contribution). Instead, a limited dependency on the SoC is observed. In particular, the ohmic contribution and the charge transfer resistance are SoC-independent for the specified temperature, while the impedance part related to the diffusion process results mainly affected as soon as the cell is near to the fully charged state. Figure 5-9 shows the impact of aging on the EIS measurement of the tested LFP cell. As documented in literature [121], cell degradation directly influences the battery impedance. The ohmic and the diffusion contribution are clearly higher for the aged cells, while the charge transfer impedance seems qualitative to not change significantly. A better and quantifiable understanding of the cell behavior can be gathered through extensive experiments, in which the effect of different impact factors can be examined in-depth in a batch of for example 50-100 cells. However, in order to completely understand the impedance behavior, analysis not only on the cell level but also on the single electrode (e.g. using half-cell setup with lithium as reference electrode) must be executed.
5.3 Accelerated aging tests

In recent years, the LiB degradation has been one of the main topics in several research activities [39][40][41][42][43][44]. This is mainly due to the still relevant market price of this technology, which has generated the need of understanding battery degradation in order to optimize the operation of the batteries and therefore to prolong their lifetime. As happens also in other fields, in order to gather information about the cell degradation mechanisms in a reasonable time period, accelerated aging tests are performed. These involve bringing some of the parameters which impact aging to extreme conditions, such as cell temperature or current rate. In this way, the degradation is accelerated and once the information is gathered, the extrapolation of the cell’s behavior under normal operating conditions is possible. In order to achieve a correct modeling and extrapolation of the battery lifetime, the main impact factors must be investigated extensively and their combination and interaction considered. This translates into the necessity of testing a considerable amount of samples (i.e. big test matrix), and therefore employing a large amount of test equipment. Moreover, for each of the investigated points, more than one sample has to be considered and tested, in order to take into account the cell variability, which may play a critical role in the evaluation of the information, as demonstrated in [122]. In the literature to date, several authors have already focused on the investigation of the aging behavior on metal oxide-based LiBs with extensive degradation matrices [123][124][125][126]. Instead LFP cells have been investigated only partially and therefore the information in this sense is limited [115][127][128][129]. In the following sections the results of an accelerated calendar and cycle degradation study of the tested LFP cells is presented. The presented data integrates the results relative to the

**Figure 5-9:** EIS measurements for different aged LFP cell without superimposed DC current in a frequency range of 2 mHz to 5 kHz at ambient temperature of 23 °C and at SoC of 50%.

As shown later, this approach is used in this work to understand the hysteresis behavior of the OCV, and is of a great importance in LiBs for a profound understanding of the phenomena related to battery degradation.
characterization of the examined LFP cell. Moreover, an aging prediction model based on the obtained experimental results is presented in chapter 7.

5.3.1 Calendar aging investigation

Calendar aging tests aim to investigate the degradation behavior of the cells without any load, i.e. theoretically no current is drawn from or flows into the cell. In other words, during the calendar aging investigation the effect due to the storage conditions is dominant in respect to the cycling (which is represented only by the periodical parametrization tests). In this case the investigated impact factors are the cell temperature, the SoC (or cell voltage) and the overall time. To perform the tests, the cells are located inside a temperature chamber for a defined period at the selected temperature and SoC level. Periodically a parametrization test (checkup) is carried out to measure the actual capacity and the resistance of the battery, as shown by Ecker et al. in [120]. The checkups are carried out at the beginning of the entire test procedure and every month. In this case, during the storage period the voltage between the battery’s poles is not kept constant, i.e. in case of self-discharge the desired battery state may change during the storage period. Table 5-5 shows the test matrix for the calendar aging investigation.

<table>
<thead>
<tr>
<th>SoC / %</th>
<th>Temperature / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
</tr>
<tr>
<td>20</td>
<td>✓</td>
</tr>
<tr>
<td>50</td>
<td>✓</td>
</tr>
<tr>
<td>80</td>
<td>✓</td>
</tr>
</tbody>
</table>

For each of the indicated points, three cells are tested under the same conditions in order to run a statistical analysis and to include the cell variability. The value of the SoC for each point is adjusted through an Ampere-hour counting calculation. The results in terms of capacity fade and resistance increase (normalized in respect to the initial value) are depicted in Figure 5-10 for all six tests. Each of the considered curves is obtained as an average among the three tested samples. Considering the trend of the total capacity (Figure 5-10a), as expected and according to Arrhenius’s law [130], the data shows a clear dependency on the temperature. As soon as the temperature increases, the degradation takes place with a faster rate. At 50 °C the cells reach the EOL criteria after around 400 days, while at 40°C after more than 1200 days (more than three years). The trend obtained for the temperature of 70 °C should not be included in this analysis, as such a temperature value is outside the range defined by the manufacturer, and in this case different degradation mechanisms may take place. The SoC

2 After six months, due to the impossibility of age the cells in reasonable time, the temperature of the temperature chamber was set to 50°C.
dependency is also apparent: as soon as the cell voltage increases the degradation takes place in a more accentuated manner.

![Graphs showing capacity fade and resistance increase](image)

**Figure 5-10:** Evolution of the capacity fade (a) and resistance increase (b) during the calendar aging tests for the overall cell batch.

Nevertheless this effect is very limited compared to other LiB chemistries [116], due to the flat behavior of the voltage curve of LFP cells (20% SoC corresponds to 3.258 V, while 80% SoC corresponds to 3.325 V). This may be related to different side effects which take place on the cathode side when the cell is in an empty state. Figure 5-10b) shows the evolution of the battery resistance. As reference, the value of the resistance measured through pulse duration of 2 s with a 1C current rate for SoC of 50% is used\(^3\). Taking into account that the tested battery is an HP cell, the resistance increase is not as clear as the capacity fade. In particular, while the temperature dependency of the resistance seems to be evident, there is no difference in the degradation obtained storing the cell at 50% or 80% SoC. Instead, at 20% SoC, the rate of the degradation is limited.

### 5.3.2 Cycle aging investigation

Cycle aging tests investigate the degradation behavior of the cells under load, i.e. when current is drawn from or flows into the cell. In other words, opposite to the calendar aging, during the cycle aging investigation the effect due to the cycle conditions is dominant in respect to the storage. In this case there are several impact factors which can be investigated, such as current rate during charge and discharge, DoD, SoC average and cell temperature. In the case that all the named parameters must be included, the resulting test matrix may be enormous, with a large number of tested cells and equipment. Therefore, in this work only the effect of DoD and current rate (symmetric for charge and discharge) are considered. The DoD is always considered for an average SoC of 50%. The temperature chambers are set in order to have a cell temperature of 30 °C. Also in this case, a checkup test is carried out to measure the actual capacity and the resistance of the battery, as described in the previous section. The

---

\(^3\) The resistances measured with pulses of duration of 10 s and 18 s have shown the same trend.
checkups are carried out at the beginning of the entire test procedure and after a defined value of Ah-throughput. Table 5-6 shows the test matrix for the cycle aging investigation. Again, for each of the indicated points, three cells are tested under the same conditions for a statistical analysis and in order to study cell variability.

**Table 5-6: Test matrix for the cycle aging test.**

<table>
<thead>
<tr>
<th>DoD / %</th>
<th>Cycle aging</th>
<th>SoC range</th>
<th>1</th>
<th>3</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>45%-55%</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>25%-75%</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>10%-90%</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
</tr>
</tbody>
</table>

The results in terms of capacity fade and resistance increase (normalized in respect to the initial value) are depicted in Figure 5-11 for the entire test matrix. Each of the specified curves is obtained as an average among the three tested samples. Looking at the evolution of the capacity fade shown in Figure 5-11a), it can be noticed that no clear trend can be identified. In fact, grouping the tests with the same DoD, in one case (DoD of 10%), the degradation is higher with a current rate of 1C, while for a DoD of 80% the capacity fade for a current rate of 1C is the lowest. The same trend is observed if the cells are grouped according to the same current rate. For a current rate of 1C, the highest degradation is registered for a DoD of 10%, while for a current rate of 6C, the capacity fade has the highest rate for a DoD of 80%. Figure 5-11b) shows the trend of the internal resistance. The resistance value considered is calculated through discharge pulses of 1C of 2 s duration. Again, the resistance increase evolution seems to do not follow a clear trend and it is difficult to identify the dependencies on the impact factors. In particular, for most of the tests characterized by limited DoD and current rate, the resistance remains unchanged after more than 2000 EFCs. Only for the extreme conditions (6C current rate or 80% DoD) the increase of the internal resistance is evident, even if the trend is not always monotonous.

![Figure 5-11: Evolution of the capacity fade (a) and resistance increase (b) during the cycle aging tests for the overall cell batch.](image)

Figure 5-11: Evolution of the capacity fade (a) and resistance increase (b) during the cycle aging tests for the overall cell batch.
5.3.3 Non-uniform aging and capacity recovery

As can be drawn from the discussion in the previous sections, the accelerated aging tests can deliver important information regarding the lifetime of the investigated cells, although for some phenomena only a qualitative interpretation can be obtained. The calendar aging of LiBs is a phenomenon which has been already studied since long, including the relation cause-effect involved in the degradation. According to the calendar aging results shown in this work, the cells have aged rather uniformly. This means that three cells which aged under the same conditions have produced the same capacity and resistance trend, not only qualitatively but also quantitatively (with a certain tolerance). This demonstrates a clear dependency of the aging on the investigated impact factors. The same conclusion cannot be drawn for the cycle aging test. Firstly, degradation during cycling is a phenomenon which is still being studied and which is currently subject to numerous researches. It involves the iteration among several factors, whose effect cannot be easily separated. The cycle aging tests carried out in this work have confirmed this trend. In fact, no clear dependency on any impact factors can be observed. Thus, no statement can be made relative to the influence of a parameter on the battery capacity or resistance. One of the main causes of this is the non-uniform aging which cells under the same test conditions have shown. Figure 5-12 shows the trend of capacity and resistance for two different cycle test conditions. Especially for the case of the battery impedance, several samples have shown similarly ambiguous behavior, which does not allow the drawing of clear conclusions. Moreover, for some aging test conditions, the typical sudden and abrupt deterioration of the performances has been observed, which appears with the increase of the battery capacity drop rate. Such behavior has already been reported in the literature and generally associated with lithium plating [131].

\[ \frac{Q_{\text{end}}}{Q_{\text{initial}}} \]
\[ \frac{R_{\text{end}}}{R_{\text{initial}}} \]

**Figure 5-12:** Example of different aging under same test conditions, a) capacity fade during cycle aging with 1C current rate, 50% DoD at 30 °C cell temperature, b) resistance increase during cycle aging with 6C current rate, 50% DoD at 30 °C cell temperature.

Another interesting effect is the increase in the battery capacity for some calendar test conditions, in particular for the cells which are stored at 30 °C ambient temperature. As mentioned in section 5.2.1 this phenomenon has been already reported in the literature but has not yet been fully explained and understood. In [35] Dubarry et al. relates the increase of
capacity measured with a rate of 1C and 0.5C with the improved kinetic of the positive electrode and the consequent release of the “lithium reservoir”. This suggests that this kind of effect should be visible only at BOL, when the cell is put in operation for the first time. Figure 5-13 shows another interesting point.

![Graph showing capacity over time and temperature](image)

**Figure 5-13:** Comparison between the capacity increase during the calendar aging tests of three cells (20% SoC, 30 °C temperature) and the capacity increase of an aged cell after long rest period.

The results in terms of capacity fade obtained for cells aged under calendar conditions at 20% SoC and 30 °C of temperature are compared with the capacity measured from an aged cell, which is put into operation after a long rest period (orange curve with triangle signs). This cell belongs to the cell batch described in section 5.3.2: after the cycle aging test, the sample was stored in a refrigerator for more than one year at around 50% SoC, then brought into operation again and employed to characterize its OCV behavior. This means that the cycle effect on the cell during the tests was significantly limited (ulterior aging mainly due to calendar effects). Its total capacity was measured periodically. As can be observed in the graphic, the rate of capacity increase detected is similar and comparable. This may indicate that this effect may not only be related to a change in the electrode kinetic, but generally to some aging related phenomena. As explained by Laregoiti e coauthors in [132], during the cycling operation of a cell the SEI on the anode is continuously subjected to continuous fracture and subsequent reparation and re-stabilization of the layer. The new available surface can react actively with the electrolyte, generating a restructure of the crystal structure. In this process, lithium ions might be released and once again could take part in the main reaction. Such an effect may also be present in cells that remain under a rest condition for a long period of time, and brought back into operation. At this point one might imagine the structure of the cell receiving a “shake” after the idle time followed by a re-adjustment period, with a possible minor amount of the lithium entrapped in the electrode layers (either anode or cathode) being released. This only partly explains the phenomenon, which may well be due to the interaction of different effects. It is certainly clear that in order to gain a better
understanding of the phenomenon, a larger amount of cells in different conditions and with different histories is needed, so that the effect can be proven and its real causes identified in reproducible manner.

5.4 Analysis of the quasi-OCV curves

As already mentioned in section 3.4, one of the main features of LFP cells is the flat voltage curve in a wide SoC range. In reality the OCV curve is characterized by different voltage plateaus. Their observation gives meaningful information on processes which take place during the normal cell operation. Moreover, observing the changes of these plateaus during the battery lifetime provides a better understanding of the degradation processes which have taken place. Among the drawbacks, this represents a fundamental skill of LFP cells, which may be used not only for laboratory analysis, but also for on-board state estimation, as will be introduced in chapter 6. First of all, the analysis of the voltage curve can be carried out by evaluating the so called quasi-OCV curve, i.e. voltage curves measured by completely charging or discharging the cell with a rather low current rate⁴. Thus, the overvoltage and polarization effects can be limited, making a clear distinction between the different flat regions possible. For the tested cell, the plateaus can be clearly distinguished starting from a current of 0.3C downwards. The methods most commonly used for studying the characteristics of the plateaus are the differentiation analyses. Two types of analysis are used. The first one is known as incremental capacity analysis (ICA) [92][103][133][134][135]. The analysis is achieved by the differentiation of the charged or discharged battery capacity in respect to the terminal voltage. The obtained curves V vs dQ/dV transform the plateaus present in the cell voltage in peaks. The underlying area and the amplitude of these peaks depend on the amount of capacity which is involved in the two-phase transitions. An example of the quasi-OCV charge curve at 0.1C for the LFP tested cells and the correspondent ICA curve is shown in Figure 5-14a) and b) respectively. The curve is characterized by three peaks, namely the peaks 1, 2 and 3, which correspond to the plateaus VA, IIA and IA shown in Figure 3-12b) respectively. In reality more peaks can be identified [44], but only the three shown give precise and quantitative information about the cell operation and degradation. The second method is known as differential voltage analysis (DVA). It is equivalent to the ICA analysis and it is obtained by the differentiation of the charge or discharge voltage curve in respect to the battery capacity or equivalent SoC [102][60][136][137]. The obtained curves SoC (or capacity) vs dV/dQ transform the stages present in the voltage curve (transition between two plateaus) in peaks. The underlying area of each peak is related to the amount of capacity which is involved in the stage transitions, while the distance between each peak represents the amount of charge which can be associated to each two-phase transition.

⁴ In case of LFP cells, a limited current rate is the value of the charge/discharge current which allows clearly distinguishing the different plateaus in the voltage curve. For other kind of LiBs, a quasi-OCV is normally obtained with current rates smaller than 0.5C.
Figure 5-14: Differential analysis of the quasi-OCV curve of a new LFP cell, a) and c) quasi-OCV curve during charge with 0.1C at 23 °C, b) ICA plot and d) DVA plot.

An example of the quasi-OCV charge curve at 0.1C for the LFP tested cells and the correspondent DVA curve is shown in Figure 5-14c) and d) respectively. The curve is characterized by three peaks, respectively 1, 2 and 3. The presence of two peaks 1 and 2, which correspond to the first stage, is related to the presence of more two-phase transitions in the anode curve for low intercalated lithium content, as shown in Figure 3-11 and mentioned in section 3.4. The DVA can also be carried out only by the voltage differentiation (difference between the voltage measurements of two near samples) without normalizing the value in respect to the capacity difference: the curve would assume the same shape of a standard DVA, and supplies the same information. Hence, this work will treat the two analyses as equivalent.

The DVA and ICA methods deliver the same type of information; therefore they can be used interchangeably for the same scope. However, some authors prefer the use of the ICA [44], especially when the curves must be analyzed in terms of battery degradation. In fact, while the ICA is referred to the cell voltage (x-axis), which directly gives a sign of the battery state, the DVA is referred to the capacity, a value which changes with the degradation. Therefore, this value could lose its meaning as a reference and the comparison of cells with different aging states may become more difficult. The type of information obtained by using differentiation analysis is the same as when considering a charge or discharge curve. As is shown later, this is valid also throughout the entire battery lifetime.

Figure 5-15a) and b) show respectively the ICA and DVA curve for quasi-OCV charge and discharge curve at 0.1C rate for different ambient temperatures. A look at the ICA plot shows that for both the charge and discharge process the peaks are placed in correspondence to different voltage levels. This demonstrates that the overpotential due to the temperature
difference shifts the voltage level on which the plateaus are placed, or precisely the potential on which the two-phase transitions take place.

**Figure 5-15:** Differential analysis of the quasi-OCV curve of a new LFP cell for different ambient temperatures for the charge and discharge process with 0.1C, a) ICA plots and b) DVA plots (the SoC is calculated compared with the capacity at 40 °C).

If the DVA curves are observed, the distance between each peak seems to not change significantly. This means that the amount of charge which is involved in the change of phase remains rather unchanged varying the ambient temperature from 10 °C to 40 °C. This is in agreement with the data shown in Figure 5-2, where it can be noticed that the energy capability of the tested cell is slightly dependent on the ambient temperature. A similar analysis can be carried out if the differentiation is executed on quasi-OCV curves which were obtained with different current rates, as shown in Figure 5-16. Figure 5-16a)-e) shows the ICA plots for the charge process, while Figure 5-16f)-l) shows the DVA curves for the discharge process. The tested current rates are in a range between 0.025C (40 h discharge/charge) and 0.5C. Higher currents would not show the plateaus distinctly and therefore the differential analysis would not deliver clear information. The ICA plots again show the shifting of the peaks’ position, due to the different polarization effects related to the variable current rates: the higher the current rate is, the higher (or the lower during discharge) the characteristic voltage of the peak will be. In contrast to the case analyzed before, the DVA now also delivers similar information. The amount of charge involved in the two-phase transitions is related to the current rates as well. It is imaginable that the two-phase transformation would always involve the same amount of charge, independent of the current rate which is needed. This would produce a DVA plot where the peaks are placed in the same position on the SoC scale. This is valid only if the battery is represented with a single particle. As will be discussed later in this chapter, a composite electrode can be represented as a multi particle system. In such a system with non-ideal characteristics, the intercalation occurs differently depending on the current rate used in the cell, the single particle size and position in the electrode material mass, and the local characteristics of the electronic network.
Characterization of a LiFePO4 battery

Figure 5-16: Differential analysis of the quasi-OCV curve at 0.1C of a new LFP cell for different current rates at 23 °C, a)-e) ICA plots for the charge process and f)-l) DVA plots for the discharge process (the SoC is calculated compared with the maximum measured discharge capacity).

This means that if the intercalation/deintercalation process can proceed uniformly in all the particles with low current rate, the increasing current rate increases also the inhomogeneity of lithium content among the particles [55]. Therefore some particles in the cathode can show a standard two-phase transition process, while others can show a single phase process. In extreme cases all the particles may simply follow a single phase process. The resulting full voltage curve is a mix of the potential of the single particles, where the plateaus now have different characteristics based on the current rate used for the discharge/charge process. If the current is very high, the mix of potential may lead to the disappearance of a clear separation between two plateaus, due to the different particle SoC (or intercalation/deintercalation mechanisms).

As already mentioned, the differential analysis is a powerful tool especially as a non-invasive method for analyzing the battery degradation. Both ICA and DVA have already been used for a long time for this scope [35][44][92][134][60][138]. The manner how the ICA and DVA can be interpreted in terms of aging is presented by Dubarry et al. in [44][103]. Figure 5-17 shows an example of this for the tested cell: the ICA and DVA are conducted for three differently aged cells from the cell batch described in section 5.3 and compared with the curves obtained for a new sample. The information related to the aging conditions of the three samples is recorded in the legend of Figure 5-17.
Characterization of a LiFePO4 battery

Figure 5-17: Differential analysis of the quasi-OCV curve of a differently aged LFP cells, a) and c) quasi-OCV curve during charge with 0.1C at 23 °C, b) ICA plot and d) DVA plot (the SoC is calculated compared with the discharge capacity of the new cell).

The quasi-OCV curves are measured with a current rate of 0.1C. The ICA plots document that some of the peaks have changed their positions and size. Keeping the notation used in Figure 5-14, peak \( \text{ثار} \) changes its position in the voltage scale and size. For the cells cycled at 1C and 10% DoD, and 6C and 50% DoD peak \( \text{ثار} \) is significantly small, a sign that the plateau IA is not visible anymore in the full voltage curve, as shown in Figure 5-14a) and c). This is surely related to the LLI [44]. Change in the peak position is related to the increase in the cell impedance: due to this the two-phase transitions take place on a higher voltage level due to the higher polarization effects. The peak \( \text{ لدينا} \) does not show a visible difference in position, while the shape and the height seem to change for some cells. In order to evaluate it properly, not only the height must be assessed but also the underlying area. This may be a difficult operation, since it is not possible to define clearly where a peak starts and where it ends. Evidently, for the cell cycled at 6C and 50% DoD, the peak \( \text{ لدينا} \) is narrower and smaller in height, as shown clearly in Figure 5-17c) with the smaller length of plateau IIA. This effect may be related to LLI and partly to LAM on the negative electrode, since the effect of the positive electrode would not be visible in this case. Peak \( \text{ لدينا} \) also changes in position and height for some cells, which may be caused by a mix of LLI, LAM on the negative electrode and an increase of internal impedance. Besides delivering the information already obtained with the ICA, the analysis of the DVA plots provides directly a visible idea of the length of the single plateaus. Firstly it is not always possible to distinguish clearly peak \( \text{ لدينا} \) and \( \text{ لدينا} \).
5 Characterization of a LiFePO4 battery

Figure 5-18: Correlation between the length of the plateau regions between the charge and discharge process for cells aged in different conditions, a) meaning of the considered plateau regions (0 Ah→cell empty), b) correlation for the first plateau, c) correlation for the second plateau and d) correlation for the third plateau. Each point represents a cell in different aging state.

Secondly, the distance between peak ⊙ and ⊗ changes with the aging, a sign that the plateau IIA reduces its size based on the degradation. The same happens for the distance between peak ⊗ and the fully charge state, which indicates the reduction of plateau IA. Analyzing the DVA in terms of underlying area and peak height is in this case even more difficult than for the ICA, due to the unclear distinction between the peaks. Nevertheless, as shown in this section, the combined use of the two analyses helps gather a full comprehension of the curves and understand the type of degradation which is involved in battery aging.

As already mentioned, the information, which can be drawn when examining the discharge curves, is also available when examining the charge curves. This characteristic has to be evidently maintained during the entire battery lifetime. An example of this is given in Figure 5-18, where the length of the different plateaus during the charge process is compared with the one during discharge for cells with different aging states. In Figure 5-18a) the meaning of plateau 1, 2 and 3 is given through the use of the DVA analysis (length in Ah). Figure 5-18b), c) and d) shows the aforementioned correlation of the three plateaus respectively. As can be
observed, the charge and discharge plateau are in all three cases related through a linear correlation. An identical correlation is obtained if the plateau’s length is normalized compared with the correspondence length measured on a new cell, or if the plateau’s length is evaluated in percentage compared to the total battery capacity (the results are not reported in this work). This concept is of fundamental importance as soon as the plateau’s information is used online for battery state determination, even though these relationships are only of a mathematical meaning and are not known a priori.
5.5 Investigation and modeling of the hysteresis of the open circuit voltage

The hysteresis phenomena have been well known for a long time and have been studied in several areas, such as mechanical [139] and magnetic fields [140]. A first comprehension of the hysteresis as a phenomenon can be gained through the work of Everett et al. [141][142][143]. Given a defined physical characteristic \( y \) that depends on a certain number of independent variables \( x_n \), \( y \) is characterized by a hysteresis behavior if its value depends both on the actual and on the past values assumed from \( x_n \). In particular, if the changes of the variable \( y \) are tracked, these have to be represented by a series of stable and reproducible points. Moreover these values have to be stationary. If these conditions are not satisfied, then the phenomenon is called supersaturation or metastability.

Concerning electrochemical storage systems, the hysteresis is a phenomenon observed in different battery chemistries. For some of them, the nature and the origin of the hysteresis is well established, while for other chemistries, such as LFP cells, further and deeper analysis of the mentioned phenomenon seems necessary. The hysteresis of the OCV of nickel metal hydride (NiMH) cells is treated in several publications [144][145][146]. In [145] the authors report that the open circuit potential is a mix between the effect due to the intercalation reaction in the nickel hydroxide electrode and the effect due to the oxygen evolution side reaction. These two effects are not separable, and they contribute concurrently to the hysteretic behavior of the OCV. In this case the hysteresis is observed as permanent, and is described by the use of domains [146]. It is mentioned that the hysteresis can appear either due to the change of the minimum energy between the intercalation and extraction process, or due to a first-order phase transition. Additionally, the paths followed within the external boundaries, the so-called scanning curves, are also investigated: these paths obey seven theorems, describing the laws which regulate this phenomenon.

If in NiMH battery the hysteresis has been extensively studied and mainly understood, in LiBs the issue is still open. In [147] Gerschler et al. give an overview of the hysteretic behavior that can be found in the world of LiBs. They associate the hysteresis behavior of the OCV to the existence of a two-phase transition process. In this case, the hysteresis is mainly due to the dissipation of energy in the crystal structure of the electrode during these phases. Examples of this can be found for both cathode and anode. In 1991, Sleigh et al. [148] reported the existence of a hysteresis behavior in LiBs, after studying the insertion processes in LMO based electrode. Hysteresis was also studied in the intercalation/deintercalation process of a LiCoO\(_2\) based electrode in [149] by Carlier et al. Small hysteretic phenomena are visible for each two-phase transition present in the OCV of the cell. In [150] and [151] traces of hysteretic behaviors in the potential of carbon and graphite electrodes are also reported. However, among all lithium-based batteries, the LFP cells are renowned for their remarkable hysteresis behavior of the OCV, and strong dependency on the short-term history. Several authors have described how the intercalation and deintercalation processes take place in the cathode’s active material FePO\(_4\) [50][152], and under which processes the interaction among lithium ions and active material particles happens. Srinivasan et al. [153][154] debate this topic in detail by means of the introduction of the shrinking core theory. According to this
theory, the two-phase transition in the cathode takes place through a first-order phase transition, i.e. the formation of a lithium-rich shell and a lithium-poor core region during intercalation, and of a lithium-poor shell and a lithium-rich core region during deintercalation. Between the two regions a phase barrier exists which moves towards the core of the particles or in the opposite direction, in a way that the concentration of lithium inside the region remains constant. As the value of the potential of a particle is directly correlated to the composition and ion concentration on the shell surface [53][56], a characteristic voltage plateau, i.e. a zone at two-phase transitions, is visible in the electrode potential curve. Based on the shrinking core theory, two main schools of thought can be identified:

- The first denies the hysteresis of the OCV of LFP cells a thermodynamic meaning. In one case the term hysteresis is mainly associated with a rate-dependent phenomenon after testing the battery with different charge/discharge sequences, which disappears with low current rates [153]. The same authors in [154] state that bringing an LFP electrode to 50% SoC from a discharged state or from a charged state results in the same voltage potential, which means the total absence of hysteresis. Moreover, Gerschler et al. [147] observe that the hysteresis phenomena vanish for all the tested batteries after a period of time related to the different LiB chemistry.

- The second school of thought grants the observed hysteresis phenomenon a thermodynamic origin, due to the fact that the active material cannot be treated as a single particle but has to be considered as a bulk, seeing that all the experiments are carried out in a multi particle system [55]. In fact, the existence of a voltage plateau in an LFP cathode is often explained with the simultaneous coexistence of two phases in each particle, while in reality the analysis of a multi-system equilibrium shows the coexistence of fully delithiated or fully lithiated particles. These are rather charged one after the other and not simultaneously [57]. According to Dreyer [155][156], the interaction among the single elements in a bulk electrode (in form of exchange of lithium ions) cannot be neglected. Thus, for a defined battery SoC, depending on the short-term history, the value of the steady state voltage (equilibrium state) is strictly related to the equilibrium states that single particles in the electrode’s active material reach through the interaction with each other. The same approach is employed by Sasaki et al. [157] to clarify a possible memory effect in lithium-ion batteries. In this context, each particle is characterized by a non-monotonous potential [55], which on the one hand generates a plateau between two defined lithium concentrations, on the other hand is responsible for an evident hysteresis, which is visible in the different voltage potential of the plateaus during charge and discharge. These ideas are demonstrated by the fact that a behavior of each particle that follows the shrinking core theory would not explain the high rate capability of LFP electrodes, which resembles more a solid solution behavior. Nevertheless, as stated by Malik et al. [55], a real LFP composite electrode behaves probably in a mixed manner, where some particles go through a solid solution process while others are involved in two-phase transition transformations.
Summarizing, although the phenomena have been known for a long time and various authors have contributed with their studies and theories, there is not yet a clear explanation of the hysteresis of the OCV in lithium-ion batteries. Further and deeper investigations at cell and electrode levels could provide fundamental contributions. Generally, it is hard to find a complete investigation into the hysteresis phenomenon of the OCV in literature in which a possible dependency on short-term history, temperature, current rate and aging are dealt with. Table 5-7 shows a resume of a literature survey related to the hysteresis phenomena of the OCV in batteries at cell level. As can be observed the mentioned factors are often only marginally discussed, while some of them (such as the aging state) have never been considered.

**Table 5-7:** Resume of the literature review related to the investigation of the hysteresis behavior of the OCV in batteries. The symbols have the following meanings: * - Phenomenon not investigated; [*] - Phenomenon only marginally discussed; [**] - Phenomenon partially investigated; [***] - Phenomenon fully investigated. The meaning of the different phenomenon considered is reported in section 5.5.1.

<table>
<thead>
<tr>
<th>Refer. No.</th>
<th>Description</th>
<th>Major loop</th>
<th>Minor loop</th>
<th>Minor loop path</th>
<th>Temperature</th>
<th>Current rate</th>
<th>Aging state</th>
</tr>
</thead>
<tbody>
<tr>
<td>[158][159] [160]</td>
<td>Modeling of the voltage behavior of NiMH cells</td>
<td>[*]</td>
<td>[**]</td>
<td>[*]</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>[147]</td>
<td>Investigation of the OCV of different LiBs</td>
<td>[**]</td>
<td>[**]</td>
<td>[*]</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>[53][56] [161][162]</td>
<td>Investigation of the physical and electrical behavior of the LiFePO4 OCV characteristics</td>
<td>[**]</td>
<td>[**]</td>
<td>[**]</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>[163][164] [165]</td>
<td>Electrical modeling of the LiFePO4 OCV behavior</td>
<td>[**]</td>
<td>[**]</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>[166][167]</td>
<td>Electro-thermal model and aging behavior of LiFePO4 cells</td>
<td>[**]</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>[168][169]</td>
<td>Modeling of OCV through Preisach’s approach</td>
<td>[**]</td>
<td>[**]</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

**Physico-chemical and electrical model**

**SoC estimation**

<table>
<thead>
<tr>
<th>Refer. No.</th>
<th>Description</th>
<th>Major loop</th>
<th>Minor loop</th>
<th>Minor loop path</th>
<th>Temperature</th>
<th>Current rate</th>
<th>Aging state</th>
</tr>
</thead>
<tbody>
<tr>
<td>[170][171][172]</td>
<td>SoC estimation by means of filters</td>
<td>[**]</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>[173][174] [175]</td>
<td>SoC estimation using the OCV and the filtering approaches</td>
<td>[**]</td>
<td>[**]</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>[176]</td>
<td>Balancing of LiFePO4 battery packs</td>
<td>[**]</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>[177]</td>
<td>Electrical model for SoC estimation of LiFePO4 cells</td>
<td>[**]</td>
<td>[**]</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

**System simulation**

<table>
<thead>
<tr>
<th>Refer. No.</th>
<th>Description</th>
<th>Major loop</th>
<th>Minor loop</th>
<th>Minor loop path</th>
<th>Temperature</th>
<th>Current rate</th>
<th>Aging state</th>
</tr>
</thead>
<tbody>
<tr>
<td>[178]</td>
<td>Batteries for full EVs</td>
<td>[**]</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>[179][180]</td>
<td>Batteries for V2G</td>
<td>[**]</td>
<td>[**]</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>
In the next sections, some of the experimental results of a detailed investigation of the OCV hysteresis behavior of the LFP cell are presented, followed by a discussion and interpretation of the observed phenomena.

### 5.5.1 Experimental investigation

The investigation of the hysteresis of the OCV is carried out on cells in different aging states, which belong to the batch of cells described in section 5.3. Their characteristics are reported in Table 5-8.

**Table 5-8: Characteristics of the cells tested in the study.**

<table>
<thead>
<tr>
<th>Cell name</th>
<th>Actual/Initial capacity</th>
<th>Aging history</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell A</td>
<td>8.25 Ah / 8.25 Ah</td>
<td>New cells. Two samples investigated.</td>
</tr>
<tr>
<td>Cell B</td>
<td>7.36 Ah / 8.30 Ah</td>
<td>Aged cell after about 1500 equivalent full cycles carried out at 30 °C, with a current rate of 1C, and a DOD of 50% between 25% and 75% of SoC.</td>
</tr>
<tr>
<td>Cell C</td>
<td>6.83 Ah / 8.33 Ah</td>
<td>Aged cell after about 4900 equivalent full cycles carried out at 30 °C, with a current rate of 6C, and a DOD of 10% between 45% and 55% of SoC.</td>
</tr>
<tr>
<td>Cell D</td>
<td>6.81 Ah / 8.22 Ah</td>
<td>Aged cell after about 1000 days of calendar aging carried out storing the cell at 50 °C and a SoC of 20%.</td>
</tr>
</tbody>
</table>

In order to verify the reproducibility of the results, two new cells are tested in parallel, and subjected only to an initialization process (three charge and discharge cycles with 1C current rate between the end-of-charge-voltage EOCV and the EODV). They are chosen in order to have a similar initial total capacity. The procedure employed to characterize the hysteresis behavior is exemplified in diagram shown in Figure 5-19. The test procedure is composed of eight main test parts. In all test parts, the values of the SoC are determined by Coulomb counting and always refer to the actual total capacity.

1. **Capacity test.** The tests are carried out to identify the actual total cell capacity and consist of a complete CCCV charge process with a current rate of 1C followed by three discharge and charge cycles with a current of 1C between the EOCV and the EODV. The actual cell capacity is calculated as the average between the values of the Ampere-hour throughput during discharge processes.

2. **Quasi-OCV test.** The tests identify the quasi-OCV curves: starting from a fully charged cell a CC discharge process with 0.1C (800 mA) until the EODV is conducted, followed by a pause of 1 h and by a charge process with a current of 0.1C (800 mA) until the EOCV. The tests are conducted at three different temperatures (0 °C, 23 °C and 40 °C). The intention is to investigate the impact of the tests on cell aging within the period of the entire test procedure. Because of this, the tests are repeated at the end of the investigation in the same manner (test part no. 8).
Figure 5-19: Schematic description of the test procedure for the hysteresis investigation. The used abbreviations have the following meanings: qOCV means quasi-OCV, DCH means discharge, CHA means charge, \( t_{\text{relax}} \) means relaxation time. The number in each box indicates the different test parts.
3. **OCV test.** The tests identify the OCV behavior of the cells, or the so-called major hysteresis charge and discharge loops. A schematic representation of the OCV test is depicted in Figure 5-20a) b) and c). Starting from a cell in a fully charged state, discharge processes with a current rate of 0.5C with steps of 5% of the total capacity followed by a relaxation time are carried out, until the voltage reaches the EODV value. The OCV voltage values obtained at the end of each relaxation period define the external OCV discharge boundary (major discharge loop). The entire process is then repeated, charging the cell with a current rate of 0.5C and steps of 5% of the total capacity followed by relaxation times, until the voltage reaches the EOCV value. The OCV voltage values obtained at the end of each relaxation period define the external OCV charge boundary (major charge loop). The whole test is repeated for three different temperatures (0 °C, 23 °C and 40 °C). The value of relaxation time of 3 h is employed in all tests (if not specified in a particular case).

4. **Minor loop identification.** The tests are carried out to identify the so-called minor loops, i.e. the loops that are built inside the major hysteresis boundaries (main loops) each time that a complete cycle (100% \(\rightarrow\) 0% \(\rightarrow\) 100%) is not covered. Therefore, after a defined rest period, the voltage relaxes to an OCV value that lies between the two major OCV boundaries. In this work, a minor loop is defined as a loop which has one extreme that lies on the major charge loop and the other on the major discharge loop (within a defined voltage tolerance, as discussed later), as shown in Figure 5-20d). A loop which has one extreme that lies on the major charge loop for a SoC \(\geq\) 90%, or which has one extreme that lies on the major discharge loop for a SoC \(\leq\) 10% is not considered a minor loop. In fact, in these cases, one of the two branches of the minor loop lies completely on either the major discharge loop or else on the major charge loop respectively. The identification of a minor loop for a defined SoC \(x\) is carried out in two steps. In the first step, starting from a SoC of 100%, the cell is discharged with a current rate of 0.5C with steps of 5% of the total capacity, each one followed by a relaxation time, until the SoC \(x\) is reached. Then the cell is charged with a current rate of 0.5C with steps of 5% of the total capacity, each one followed by a relaxation time, until the EOCV is reached. At the end of each relaxation period the values of the OCV are collected. In this process, the OCV value identified as OCV\(_{x}\) in Figure 5-20d) is the measured value that lies on the major charge loop within a defined voltage tolerance. In the second step, the process of the first step is partially repeated. Starting from a fully charged state with SoC steps of 5% with a current rate of 0.5C and followed by relaxation periods, the stepwise process 100% \(\rightarrow\) SoC\(_x\) is carried out. After that, the procedure continues with the charge process SoC\(_x\) \(\rightarrow\) SoC\(_y\), and closes with the discharge process SoC\(_y\) \(\rightarrow\) SoC\(_x\) (see in Figure 5-20d) the steps a\(\rightarrow\)x with the brown arrows, x\(\rightarrow\)y with the orange arrows, and y\(\rightarrow\)x again with the orange arrows). As defined in Figure 5-19, the two steps described above are repeated for SoC values of 10%, 20%, 30%, 40%, 50% and 60%, and, in all cases, starting from the initial SoC of 100% (point a in Figure 5-20d). The ambient temperature is always kept constant at 23 °C. As will be explained later, due to different behaviors, some variations on the test procedure are introduced for Cell B.
5. **Minor loop path dependency.** The goal of this test section is to investigate the path dependency of the minor loops individuated in the previous test part. With “path dependency” the determination of minor loops starting from a condition in which the cell is in an empty state is intended. In this way, a generic minor loop parameterized in the previous section as 100% \(\xrightarrow{\text{SoC}_x} \text{SoC}_y \xrightarrow{\text{SoC}_x} \) (\(a \rightarrow x \rightarrow y \rightarrow x\) in Figure 5-20d) is once again tested as 0% \(\xrightarrow{\text{SoC}_y} \text{SoC}_x \xrightarrow{\text{SoC}_y} \) (\(b \rightarrow y \rightarrow x \rightarrow y\) in Figure 5-20d). The tests are repeated for all \(y\) values determined in test part no. 4 at an ambient temperature of 23 °C.

6. **Minor loop current dependency.** The tests are carried out to determine the dependency of the minor loops on the current rate employed to reach a defined SoC point. The main goal is to determine if the Ah-throughput necessary to enclose a minor loop within the two major charge and discharge loops is independent of the current rate value employed to reach the SoC level. Three of the minor loops individuated in test part no. 4 are chosen and tested with three different current rate values (0.2C, 1C and 5C). The tests are conducted at an ambient temperature of 23 °C. The curves are measured with SoC steps of 5%. The SoC is always adjusted by using an Ampere-hour counting calculation with the considered current rate. Results relative to this test part can be found in appendix 10.5.2.

7. **Minor loop temperature dependency.** The tests are carried out to determine the dependency of the minor loops on the actual ambient temperature. As for test part no. 6, the main goal is to determine if the Ah-throughput necessary to enclose a minor loop within the major hysteresis loops is independent of the actual ambient temperature. Three of the minor loops individuated in test part no. 4 are chosen and tested. The current rate used to reach each OCV step is 0.5C. The tests are conducted at ambient temperatures of 0 °C, 23 °C and 40 °C. The curves are measured with SoC steps of 5%. Before performing the test at the specified temperature the cells are CCCV charged at 23 °C. Results relative to this test part can be found in appendix 10.5.3.

At this point it is necessary to highlight some important aspects. Firstly, it must be understood that the results shown in this section are valid for the tested cells only; no general statement can be made for cells of the same chemistry but from a different manufacturer: the same type of cells but aged under different conditions might also perform partially differently, even though some of the phenomena can still be observed. Moreover, the obtained OCV-SoC relations always refer to the actual capacity of the battery and not to the nominal one. This allows the meaningful comparison between cells of different aging states, and the proper analogy between the OCV points determined in two comparable tests. To achieve this, at the end of each test part, between number 4 and 8, a capacity test (test according to test part no. 1) and an OCV test (test according to test part no. 3, only for a temperature of 23 °C) are carried out, as shown in Figure 5-19. This way of proceeding takes the fact into account that the entire test procedure could last for a long period time and that within this period the samples might still age significantly. This can lead to a change of both the value of the actual capacity and, therefore, the shape of the major OCV curves. Moreover, the obtained capacity values are used to recalibrate the calculation of the SoC needed to go from one step to another in the definition of the OCV major and minor curves. Furthermore, as discussed in [147] and [153], the current rate employed to proceed from one SoC to the consecutive in each test is limited...
to 0.5C (except in the current dependency test, namely test part no. 6). This reduces the impact of the relaxation time and diffusion processes in reaching the voltage steady state, and therefore isolates the hysteresis effect from other possible causes of deviation of the voltage from the equilibrium.

**Figure 5-20:** Representation of the test procedure for the determination of the OCV curve (a, b, and c) and for the determination of the minor loops (d).

The battery test bench used to perform the tests is manufactured by Digatron Power Electronics GmbH in Germany. For all the tests (except for the quasi-OCV tests), the used test circuits have a maximum current and voltage of respectively 200 A and 18 V. For the tests of test parts no. 2 and 8 the used circuit has a maximum current and voltage range of
respectively ±20 A and 0 V-18 V, in order to have a more precise regulation of the current and a higher measurement accuracy. The accuracy of both circuits is ±0.5% of the desired value in a range of 10-100% \(\frac{I_n}{U_n}\) (nominal current/nominal voltage), and ±0.05% of the full scale in a range < 10% of \(\frac{I_n}{U_n}\). Although the accuracy of the circuits seems to be inappropriate, the recalibration of the circuits has always shown an acceptable accuracy for both current (deviation < 0.1% in respect to the reference value) and voltage measurements (deviation < 0.7% in respect to the reference value). Furthermore, all the tests were conducted inside a temperature chamber manufactured by the company Binder GmbH in Germany.

In the next section the results of the experimental investigation are shown and discussed. In order to keep the workload manageable, only the results of test part no. 2, 4 and 5 are shown. More detailed results related to the remaining test parts can be found in [113] and in appendix 10.5.

### 5.5.2 Experimental results

Figure 5-21 shows the differences between the OCV major hysteresis boundaries measured for the tested cells. As already discussed in section 5.4 and observed in Figure 5-21, the aging mechanisms have a significant impact on the OCV curves of the cell. In fact, comparing the new samples’ curves of Figure 5-21a) with the curves of the three aged samples in Figure 5-21b), c) and d), the disappearance or reduction of the plateau in the high SoC range is evident. Instead, the long plateau characteristic of the middle SoC range, which is attributed to the two-phase transition in the cathode and to the IIL-II phase in the anode (see Figure 3-11), is shifted to the high SoC range. Furthermore, a shift in the small plateau visible in the range of 10% to 20% SoC can be noticed. Comparing the hysteresis of the new samples with those of the aged cells, it can be noted that a maximum value of the hysteresis of 29 mV and 31 mV is measured for the two new cells at SoC of 30% and 25%, while a maximum value of 26 mV, 27 mV and 26 mV is measured at 35% SoC for Cell B, Cell C and Cell D respectively. The hysteresis of the OCV in the middle SoC range is slightly bigger for the new cells (between 18 mV and 20 mV) compared to the aged samples (between 14 mV and 17 mV). Moreover, in Figure 5-21b) and c), for Cell B at SoC of 85%, and for Cell C at SoC of 80%, the hysteresis tends to disappear. There is no trace in literature of a similar behavior in the hysteresis of the OCV of LiFePO\(_4\) cells. A possible explanation can be found in the difficulty to measure in this case the hysteresis for a SoC > 80%, where the hysteresis is generally smaller than 5 mV. Another explanation can be found in the slight shift of the charge SoC scale in respect to the discharge, which can generate a slight displacement of the measured voltage points. In order to better understand the shown phenomenon, an additional representation of the proposed OCV measurements can be found in appendix 10.5.
Figure 5-21: Comparison between the OCV curves obtained for the investigated cells at begin-of-test measured every 5% SoC during charge and discharge at an ambient temperature of 23 °C, a) OCV curves for the two new cells, b) OCV curves for Cell B, c) OCV curves for Cell C, d) OCV curves for Cell D.

5.5.2.1 Analysis of the minor loops

In this section, the results concerning the investigation of partial charge/discharge tests, or the so called minor loops (namely the test part no. 4) are shown. As a general criterion, a minor hysteresis loop is considered as being closed if the extremes of the loops lie on the major OCV boundaries within a defined tolerance: in this work, the difference between each extreme of the minor loops and the major boundaries must not exceed 2 mV. Figure 5-22 and Figure 5-23 show representative results for the minor loops (dotted lines) for each of the investigated samples compared to the respective major hysteresis boundaries (continuous lines), for the low and high SoC range respectively. Additional results can be found in appendix 10.5.1. The loops are measured starting the process with a cell in a fully charged state, e.g. considering Figure 5-22a) the loop is measured with the sequence 100%→10%→30%→10% SoC. Table 5-9 and Table 5-10 resume the results for all the detected loops in a SoC range of 10% to 90%. As can be observed, the investigated samples behave extremely differently in all SoC ranges. Analyzing the behavior of the new cells shows that all the loops enclose between the major OCV boundaries with a SoC interval always greater than 20%. The widest loop is found starting from a SoC of 30% with a SoC interval of 45%. Moreover, the experimental results show that the minor loops can be identified precisely, and no voltage points are measured outside the major OCV boundaries.
Figure 5-22: Comparison between the major hysteresis boundaries and the investigated minor loops which start from 10% SoC, a) New cells, b) Cell B, c) Cell C and d) Cell D. The loops are parameterized starting at a fully charged state. The OCV is measured with a stepwise process of 5% SoC and for an ambient temperature of 23 °C. View the different scale of the axes.

Table 5-9: Resume of the results for the minor loop identification for the new Cells A, Cell C and Cell D (test part no. 4).

<table>
<thead>
<tr>
<th>Cell A</th>
<th>Cell C</th>
<th>Cell D</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Graph" /></td>
<td><img src="image" alt="Graph" /></td>
<td><img src="image" alt="Graph" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test</th>
<th>ΔSoC [%] to enclose the loop</th>
<th>Test</th>
<th>ΔSoC [%] to enclose the loop</th>
<th>Test</th>
<th>ΔSoC [%] to enclose the loop</th>
</tr>
</thead>
<tbody>
<tr>
<td>10→30→10</td>
<td>20</td>
<td>10→25→10</td>
<td>15</td>
<td>10→20→10</td>
<td>10</td>
</tr>
<tr>
<td>20→40→20</td>
<td>20</td>
<td>20→35→20</td>
<td>15</td>
<td>20→30→20</td>
<td>10</td>
</tr>
<tr>
<td>30→75→30</td>
<td>45</td>
<td>30→50→30</td>
<td>20</td>
<td>30→50→30</td>
<td>20</td>
</tr>
<tr>
<td>40→75→40</td>
<td>35</td>
<td>40→70→40</td>
<td>30</td>
<td>40→85→40</td>
<td>45</td>
</tr>
<tr>
<td>50→80→50</td>
<td>30</td>
<td>50→75→50</td>
<td>25</td>
<td>50→85→50</td>
<td>35</td>
</tr>
<tr>
<td>60→80→60</td>
<td>20</td>
<td>60→85→60</td>
<td>25</td>
<td>60→85→60</td>
<td>25</td>
</tr>
</tbody>
</table>
The results of the parameterization tests for the minor loops for the aged cells show a completely different behavior. While in the majority of the cases, for the new cells it is possible to enclose the minor loop within a limited SoC interval, this generally does not happen for the aged cells. Regarding Cell C and Cell D, it is always possible to individuate the single minor loops in all the investigated SoC ranges. No loop is closed for a SoC of 90% (considered as point y in Figure 5-20d). Except for some single values, each loop can be exactly defined within the major hysteresis boundaries. Nevertheless, comparing the results in Table 5-9, it can be noticed that the SoC interval necessary to enclose the minor loops changes for each of the investigated SoC ranges, demonstrating the existence of the impact of aging on the cell’s hysteretic behavior. Regarding Cell B, whose results are resumed in Table 5-10, in the low SoC range, loops starting from 10%, 20% and 30% SoC are parameterized respectively with 15%, 20% and 20% of ΔSoC that are necessary to enclose the loops. Starting from a SoC of 40% (point x in Figure 5-20d) no minor loop can be enclosed in a way that the second extreme lies on the major OCV boundary for a SoC smaller than 90% (point y in Figure 5-20d), which corresponds to the investigated SoC range.
Table 5-10: Resume of the results for the minor loop identification for Cell B starting from 100% SoC and 0% SoC.

<table>
<thead>
<tr>
<th>Test</th>
<th>ΔSoC [%] to enclose the loop</th>
<th>Starting SoC value [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10→25→10</td>
<td>15</td>
<td>100</td>
</tr>
<tr>
<td>20→40→20</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>30→50→30</td>
<td>20</td>
<td>100</td>
</tr>
<tr>
<td>40→90</td>
<td>Not possible to determine a minor loop</td>
<td>100</td>
</tr>
<tr>
<td>50→90</td>
<td>Not possible to determine a minor loop</td>
<td>100</td>
</tr>
<tr>
<td>60→90</td>
<td>Not possible to determine a minor loop</td>
<td>100</td>
</tr>
<tr>
<td>60→40→60</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>70→55→70</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>80→65→80</td>
<td>15</td>
<td>0</td>
</tr>
</tbody>
</table>

Therefore, as shown in Figure 5-23b), the path 50%→90%→50% cannot be considered a minor loop, due to the fact that after the charge process 50%→90%, the subsequent process 90%→50% follows completely the major discharge OCV boundary. The same phenomenon is measured also for the minor loops with the low extreme at 40% and 60% SoC. Another complication that has to be considered is the measurement of the same OCV both after charge or discharge for a SOC of 85%, (Figure 5-23b). In this range, which corresponds mainly to the change of phase of the anode, the OCV points measured during the partial charge/dischage process (minor loops identification) lie outside of the major hysteresis boundaries. Therefore it is not possible to detect whether a minor loop encloses itself in this range or not. At this point it becomes apparent how remarkable the differences between the new and the aged samples are, not only in terms of major OCV boundaries, but especially in terms of minor hysteresis loops. Due to the particularly different behavior of Cell B, tests are carried out to detect if minor loops can be parameterized also in the high SoC range (SoC ≥ 40%), but starting from a cell in an empty state (SoC = 0%). The results of these tests are reported in the bottom part of Table 5-10. The table shows three different loops identified starting a procedure with a cell in an empty state: 60%→40%→60% SoC, 70%→55%→70% SoC and 80%→65%→80% SoC, with respectively 20%, 25% and 15% of ΔSoC necessary to enclose them. The same loops, starting from a cell in fully charged state, and considering as x point in Figure 5-20d) the values 40%, 55% and 65% SoC cannot be identified. The influence and dependency of the starting condition on the single minor loops (whether the cell is full or empty at the beginning of the test, and which major boundary curve is followed to reach the considered SoC value) is treated in the next section.

5.5.2.2 Analysis of the minor loops path dependency

The results reported in this section refer to test part no. 5. Figure 5-24 shows the results of the investigation of the influence of the minor loop direction on the new cells. The figure shows only two of the individuated loops obtained in test part no. 4, namely the loops 10%→30%→10% and 50%→80%→50%. A considerable difference can be observed
between the two minor loops (100%→)10%→30%→10% SoC and (0%→)30%→10%→30% SoC. A maximum difference of 10 mV between the two curves at SoC of 20% in the discharge phase is measured. A slightly smaller difference can be observed when the loops (100%→)50%→80%→50% SoC and (0%→)80%→50%→80% SoC are compared.

Figure 5-24: Path dependency for two of the investigated minor loops for the new cells. The compared loops are parameterized starting from a fully charged (continuous lines) and from an empty state (dashed lines). The OCV is measured with a stepwise process of 5% SoC and for an ambient temperature of 23 °C.

The difference between both minor loops remains approximately 3 mV in all the SoC ranges. Similar results are also evident for the other loops, which are not reported in detail in this work. Generally it can be stated that the path which leads through a loop depends only slightly on the starting point, whereas the shape of the loop is maintained entirely, together with the position of the two loop extremes. Figure 5-25 demonstrates the influence of the minor loop path dependency for Cell B (a) and for Cell D (b). Two of the analyzed loops are shown for both cells. Regarding Cell B, comparing the loops (100%→)10%→25%→10% SoC and (0%→)25%→10%→25% SoC a maximum difference of 7 mV is measured at SoC of 20% in the discharge phase. A maximum difference of 9 mV at SoC of 25% can be measured comparing the loops (100%→)20%→40%→20% SoC and (0%→)40%→20%→40% SoC. Regarding Cell D, comparing the loops (100%→)10%→20%→10% SoC and (0%→)20%→10%→20% SoC a maximum difference

---

5 The values in brackets indicate the short-term history. The term (100%→) means that the test starts with the battery in a fully charged state. The term (0%→) means that the test starts with the battery in an empty state.
of 10 mV is measured at SoC of 10% in the discharge phase. A maximum difference of 2 mV at SoC of 60% in the discharge phase can be measured comparing the loops (100%→50%→85%→50% SoC and (0%→)85%→50%→85% SoC. The path dependency analysis carried out for the other identified minor loops delivers similar results. Moreover, the same path dependency analysis is carried out for Cell B also for a minor loop identified in the high range of SoC, initially parameterized starting from a cell in an empty state, as already discussed earlier. The result is shown in Figure 5-26. In this case, contrary to what is done for the first two loops, the test investigates the path (100%→)40%→60%→40% SoC to compare it with the previously identified loop (0%→)60%→40%→60% SoC, as shown in Table 5-10. As can be seen, it is not possible to overlap the two minor loops, due to the fact that it is not possible to enclose one of them within the major hysteresis boundary.

Figure 5-25: Path dependency for two of the investigated minor loops for the aged cells, a) Cell B and b) Cell D. The compared loops are parameterized starting from a fully charged (continuous lines) and from an empty state (dashed lines). The OCV is measured with a stepwise process of 5% SoC and for an ambient temperature of 23 °C.

While it is possible to identify a minor loop between 40% and 60% SoC charging the battery from an empty cell (green curves), it is not possible to follow the same path discharging the battery from a fully charged state (blue curves). Furthermore, the blue curve shows that not only the OCV measured at 60% does not lie on the major hysteresis charge curve, but for SoC smaller than 50% during the discharge the voltage relaxes to values of OCV that do not lie within the major hysteresis boundaries. The results obtained by repeating the test for a plausibility check show the same behavior, also when the capacity used to calculate the SoC interval is accurately adjusted. What seems to be clear is that for Cell B, unlike the new cells, the path followed in order to rebuild the single minor loops becomes decisive based on the selected SoC range. In fact, considering a SoC range of 10% to 40%, only a slight path dependency is observed. On the other hand, in the range of 40% to 90% SoC minor loops can be identified only following some predefined paths.
Figure 5-26: Investigation of the path dependency for one of the investigated minor loops for Cell B which cannot enclose itself within the major hysteresis boundaries. The compared loop is parameterized starting from a fully charged (continuous lines) and from an empty state (dashed lines). The OCV is measured with a stepwise process of 5% SoC and for an ambient temperature of 23 °C.

5.5.3 Discussion

The most visible effect on the hysteresis of the OCV due to different aging concerns the definition of the minor loops and their characteristics. At first sight, it is not possible to identify a rule, which is followed by the single minor loops for all the investigated samples. Considering the new cells, going from the low to the high SoC range, the SoC interval necessary to enclose the minor loops increases, reaching the maximum for a SoC of 30%. This kind of behavior can be identified also for the aged Cell C and Cell D. In particular, the width of the plateau and therefore the lengths of the transition between the two-phase transformations influence the behavior of the minor hysteresis loops. In fact, for the new cells, where the high SoC plateau (SoC ≥ 85%) can be clearly identified, all the minor loops can be measured in the investigated SoC range. In contrast, in Cell B, where the plateau present in the high SoC range has almost disappeared due to battery aging, the minor loops present an irregular behavior regarding shape and position. Generally, comparing the new cells with the aged samples, the SoC range necessary to enclose the minor loops within the major boundaries changes depending on the loop position. In some cases, e.g. for Cell B, it is not possible to find the point indicated as y in Figure 5-20, as it is the case for the minor loops in the high SoC range.

In order to understand what happens to the OCV when the cell reaches its steady state and which phenomena take place at a particle level, the shrinking core theory can be employed as a first explanation. Figure 5-27 shows schematically what happens qualitatively during one of the test routines of test part no. 4.
Figure 5-27: Schematic representation of the identification of a single minor loop by means of the shrinking core theory. The black frame on the right highlights the status of a FePO₄ particle after a charge process that starts from a cell in an empty state (completely discharged and therefore 100% filled with Lithium).

The representation is valid both for a cell in a new and aged state. During the test, a fully charged cell (point 1) is discharged stepwise until the investigated SoC point 4 is reached. Then, the cell is stepwise charged up to point 6 and again stepwise discharged reaching point 8 (or again point 4). The process is depicted in the upper part of Figure 5-27 on the left side. As mentioned, the shrinking core theory can be employed to explain what happens during this test routine in the cathode based on one particle model. When the cell is in the fully charged state (point 1) the cathode theoretically does not contain active lithium. When the cell is first discharged, the lithium diffuses uniformly in the FePO₄ particle until a lithium-content favorable state is reached, which is defined with subscript y (point 2, blue light color). At this point the material is still in a homogeneous state (solid solution). After this point, two regions with a constant concentration of lithium will appear (point 3) in the particle, which are separated by an energetic barrier. In this way, a shell of lithium (orange color) is formed on the particle surface with a lithium content z (second energetic favorable state, with z > y), which surrounds a lithium-poor core with a lithium content y (two-phase region or first-order transition transformation). Typical values of z and y can be found in [53][161]. As soon as the amount of intercalated lithium increases, i.e. the cell is discharged, the concentration in the regions remains constant, while the separating barrier moves towards the particle core.
(point 4). From this point the stepwise charge process starts. When the cell is charged, the deintercalation process takes place firstly by the extraction of lithium ions from the external shell of the particle (point 5). In this phase, the particle consists of three regions, two characterized by low (external shell and internal core) and one by high lithium concentration (middle region). A new barrier is created (barrier 2). The further deintercalation of lithium ions moves barrier 2 towards the core of the particle (point 6). At this point a further discharge process starts, which is needed to enclose the minor loops. The additional intercalation of lithium ions takes place with the formation of another external shell together with an energetic barrier (barrier 3 at point 7). An additional discharge moves barrier 3 towards the center until point 8 is reached, which corresponds to the same SoC of point 4 (both lying on the major OCV discharge boundary). In this state it is not possible to determine in a qualitative manner whether barrier 3 and barrier 2 have disappeared (point 8a) or still exist (point 8b). This is strictly related to the exact position of point 8 in the SoC range, which influences the positions and dimensions of the minor loops. Taking a look at the described process, the following two aspects can be observed:

- The state represented from point number 6 during the identification process of the minor loop coincides with the one reached through a charge process starting from a cell in a completely empty state (frame in Figure 5-27, from point 9 to point 10). At particle level this means that a particle with a lithium-rich core surrounded by a lithium-poor shell represents the same state as a particle with two energetic barriers, where a lithium-rich ring separates a lithium-poor core and a lithium-poor shell.

- Theoretically, if point 4 and point 8 coincide perfectly in terms of particle state (amount of lithium which constitutes the external shell), point 8a is the one that represents point 8. In reality, it is not possible to define precisely, what the state of point 8 is, because is difficult to place it in a correct SoC value and due to the strong influence of other factors, such as the past history, relaxation time and exact estimation of the actual battery capacity. In this sense, even if extremely limited, the error in the SoC calculation due to the hardware precision can also influence the determination of the correct position of each point.

From the model shown in Figure 5-27, it becomes evident that the impact of aging on the single minor loops on the cell cannot be precisely and completely explained only with the shrinking core theory. The fact that the path and the amount of charges needed to enclose the single loops change between the investigated cells cannot be related exclusively to the different behavior of the cathode particles. In order to consider the aging influence on the single minor loops, the question which could arise is whether the anode could show some kind of evident hysteresis in the steady state voltage profile during its lifetime, or whether the characteristic hysteresis of the cathode changes due to battery degradation. In fact, the appearance of such phenomena could partially explain the impact of the aging state on the partial charge/discharge process characteristics at cell level. However, the results which will be presented in section 5.6.2 do not give any hints in this direction, even though an invasive post mortem analysis on a large amount of samples may show some evidences related to this phenomenon.
Another approach which may be employed for understanding the effect of aging on the hysteresis is based on the analysis voltage curves of each electrode. Figure 5-28 analyzes qualitatively the characteristic shape and potential of one of the measured minor loops at cell level and single electrode level.

![Voltage vs. SoC](image)

**Figure 5-28:** Qualitative representation of the path followed from a minor hysteresis loop at cell level and at single electrode level for a new *Cell A* (Figures a, b and c) and for *Cell D* (Figures d, e and f). a) minor loop $20\% \rightarrow 40\% \rightarrow 20\%$ compared with the major hysteresis boundaries for *Cell A*, b) corresponding potential levels in the cathode compared with the cathode major hysteresis boundaries, c) corresponding potential levels in the anode, d) minor loop $20\% \rightarrow 30\% \rightarrow 20\%$ compared with the major hysteresis boundaries for the *Cell D*, e) corresponding potential levels in the cathode compared with the cathode major hysteresis boundaries, f) corresponding potential levels in the anode.

This is done respectively for a new *Cell A* and for *Cell D*. The specified loop is the one with the extreme x (Figure 5-20d) in 20% SoC, as depicted in Figure 5-28a) and d) compared with the major OCV hysteresis boundaries. Figure 5-28b) and e) show the hysteresis on the cathode and the correspondent voltage potential of the investigated minor loop. Figure 5-28c) and f) show the correspondent voltage potential of the investigated minor loop on the anode.
Characterization of a LiFePO4 battery

voltage curve (note the different voltage scales in which the full hysteresis curves in Figure 5-28a) and d) are reported in respect to the electrode voltage curves). The main difference between the two cells shown in the figures is the different aging. This is indicated by the bigger amount of loss of lithium which takes place, and which generates the shift of the anode curves to the right with respect to the cathode curve. This is visible in Figure 5-28c) and f) respectively in the blue and red rectangles. This is based on the assumption that loss of lithium is the main aging mechanism occurring during battery lifetime and causing the decrease in capacity and change of the OCV characteristics. The aging mechanisms change the potential level in which the anode in particular works for the same SoC range. Especially the SoC corresponding to point number 1 can be placed in one case in correspondence with one of the stages of the anode for the new cell, most likely in correspondence with the transition III+IIL. However, for the aged cell, point 1 seems to fall approximately in correspondence with one of the two-phase transitions of the anode, and precisely between the stages III and IV. This suggests that the main reason for the differences in the minor loops lies in the different correspondence between the battery voltage and the respective SoC due to the aging. This means on the one hand that for a new cell, a defined value of SoC might fall within a two-phase transition. On the other hand, for an aged cell, the same value of SoC calculated with the actual capacity may now be located in correspondence to a change of phase and no longer on a plateau, as schematically shown in Figure 5-28. Therefore the correct comparison of the single loops has to be carried out among loops whose starting point x is placed in correspondence of the same voltage level, or, to be more precise, in correspondence of the same plateau/change of phase. Furthermore, inhomogeneous aging of the active material during its lifetime may also play an important role, changing the length of the single transition in the OCV curves.

5.5.4 Modeling of the minor loops

As discussed in the previous section, the analysis of the minor loops based on the actual characteristics of the voltage curve may explain the observed aging dependency. In particular, the minor loops should not be compared based on the value of the SoC (which in this case is always referred to the actual capacity), but based on two factors:

- The voltage value on the starting point of the minor loop and in which position of the voltage curve this point is placed (in a plateau and in which point of it, or in a transition between two plateaus).
- The actual length (in Ah or in % of the total battery capacity) of a stage or the width of a plateau.

The change of the plateaus’ lengths is related to the different DMs which are involved in the battery aging, while the variation of the stages is mainly due to the inhomogeneous aging on the composite electrode. Moreover, the value of the voltage related to a defined SoC may also change due to the different utilization rate of the single electrodes, which can vary during the lifetime, as reported in [35]. Under these assumptions, the OCV curve measured for each cell in Table 5-8 is divided into six different zones, as shown in Figure 5-29a), each one
associated either to a plateau or to a stage. Two coefficients are associated to each parametrized minor loops reported in Table 5-9 and Table 5-10. The first coefficient $K_1$ describes the zone where the minor loops starts (point x of Figure 5-20d), assuming a value from one to five according to the respective compatibility zone. For each zone the second coefficient $K_2$ represents the position of the loop starting point in the relative zone with regard to its total length, and assumes a value between zero and one. The sum of these two coefficients is $K_{tot}$ which completely characterizes the starting point of a minor loop.

![Diagram](image)

**Figure 5-29:** a) Division of the OCV curve of a new cell in six different zones, b) grouping of the different plateaus based on the calculated $K_{tot}$.

Thus, a loop which starts in the middle of zone 3 is characterized by a $K_{tot}$ equal to 3.5. Now, if all the minor loops are defined by their $K_{tot}$ and related to the $\Delta$SoC necessary to enclose the loops ($\Delta$loop), a precise trend materializes, as is shown in Figure 5-29b). In fact, the trend shows that starting from zone 1 going up to the middle of zone 3 the $\Delta$SoC necessary to enclose the loop remains below 20%, while when the loop starts from the end of zone 3, the $\Delta$SoC increases 45%. Eventually, the $\Delta$SoC decreases passing through zone 4, reaching again 20% at the end of the zone. This trend applies to all the measured loops, except for some which belongs to Cell C. In particular, the fact that each loop is parametrized with a SoC step of 5% does not allow the precise determination of their exact size. Based on the results of this analysis, it is now possible to reconstruct the behavior of an aged sample only knowing:

- The behavior of the loops for a new sample;
- The major hysteresis boundaries of the aged sample.

First of all, each of the trajectories followed by the minor loops of the new cells of Table 5-8 is parametrized according to equation (5.1) [177]:

$$OCV = OCV_{cha} \cdot \Psi + OCV_{dch}(1 - \Psi)$$

(5.1)

The equation describes the value of the OCV after relaxation as dependent on the major hysteresis charge ($OCV_{cha}$) and discharge ($OCV_{dch}$) boundaries. The coefficient $\Psi$ describes in which point between the charge and discharge boundary the measured OCV can be placed,
and it assumes values between 1 (measured OCV lies on the charge boundary) and 0 (measured OCV lies on the discharge boundary). From equation (5.1), the values of $\Psi$ can be obtained for each of the parametrized loops of a new cell for the charge and discharge process. An example is shown in Figure 5-30, where for the loop starting from 20% SoC the obtained $\Psi$ values are plotted with respect to the normalized $\Delta$SoC necessary to enclose the loop. For the discharge process (Figure 5-30b), the term $(1-\Psi)$ is plotted, in order to obtain the same exponential trend.

![Diagram](image)

**Figure 5-30:** Exemplary fitting of the minor loops branch for new cell for a loop starting from 20%, a) during charge and b) during discharge. On the x axis the $\Delta$SoC is normalized in respect to the value necessary to enclose the loop.

The values of $\Psi$ can be fitted with a simple exponential form, as exemplarily shown again in Figure 5-30a) and b). Now, if the minor loop from an aged cell starting from the SoC$_x$ (point x in Figure 5-20b)) has to be reconstructed, the correspondent $\Delta$SoC necessary to enclose the loop can be obtained if the major hysteresis boundaries are known and the correspondent $K_{tot}$ coefficient is calculated. Therefore, the values of the OCV among the major hysteresis boundaries can be modeled by using the acquired exponential relationships and equation (5.1). The reconstruction of two minor loops for Cell B and Cell D with corresponding errors is exemplarily shown in Figure 5-31. Additional results can be found in appendix 10.5.4. As can be seen the model is able to reproduce the behavior of the minor loops not only in a qualitative but also in quantitative manner in terms of values for enclosing the loop and in terms of absolute OCV values. The error remains below 3 mV, except for the OCV points which were identified during the experimental measurements outside the major OCV boundaries. These points cannot be reproduced properly by the model due to its closed formulation, and represent additional effects which are not studied and investigated in detail in this work.
5 Characterization of a LiFePO4 battery

**Figure 5.31**: Validation of the semi-empirical approach for hysteresis modelling, a) comparison between measured and modelled minor loop (starting from 30% SoC) for Cell B, b) corresponding error, c) comparison between measured and modelled minor loop (starting from 40% SoC) for Cell D, d) corresponding error.

### 5.5.5 Relaxation effects and hysteresis vanish

In order to understand whether the hysteresis is a permanent effect (Roscher [56]) or temporary phenomenon, an additional test is carried out. An aged sample from the cell batch described in section 5.3 is firstly discharged with step of 5% of its actual capacity and a current of 0.5C to 50% SoC starting from a fully charged state at ambient temperature of 23 °C. Then, the cell is disconnected from the battery test bench and the voltage between the battery’s poles is measured every three-four days with a precise voltmeter with an accuracy of five digits after the decimal point. The measurements are collected over a period of three months. Thereafter, the same process is repeated charging the battery stepwise up to 50% SoC but starting from a fully discharged state. Again for three months the voltage between the battery’s poles is measured periodically. The results of this test are reported in Figure 5.32a), where the calculated hysteresis is also depicted in green (triangles). As can be noticed, after a discharge process (blue rhomboidal points), the voltage of the cell relaxes at a higher level, due to the disappearance of the overvoltage and polarization effects. After about 15 days the voltage starts to decay, probably due to self-discharge effects. In this case this can be most
likely separated from the normal diffusion processes. Conversely, the voltage after a stepwise charge process starts to decay immediately due to the absence of current and thus to the elimination of the polarization and overvoltage effects. This process continues for the entire measurement, but with a reduced rate, assuming an exponential trend. This may be again a mix between the occurrence of the diffusion processes and self-discharge effects. In reality, if the calculated hysteresis curve is considered, starting from a value of approximately 39 mV six minutes after the disconnection of the battery from the test bench, it reduces to about 6 mV after ten days and to 2.75 mV after 90 days. This can no longer be considered as hysteresis: such a voltage difference may be due to the precision of the voltage measurements or to the imprecision of the SoC calculation for the two directions (charge and discharge). Taking into account the limited ambient temperature of 23 °C, which should exclude or at least limit every effect related to accelerated degradation, the almost complete disappearance of the hysteresis proves the same concept mentioned by Gerschler et al. in [147]. In fact, according to the authors, the observed hysteresis is mainly a matter of “waiting time”, which depends on operating conditions (such as ambient temperature) and on battery chemistries. What can be assumed is that the hysteresis effect may be associated with the slow redistribution of the lithium concentration between the particles which compose the cathode active material, and therefore to the equilibration of the SoC. Thus, this hysteresis can be named a concentration hysteresis, which is not related to a loss of energy but to an equilibration effect. The fact that this effect lasts longer than in other LiB chemistries is mainly due to the particularly different intercalation mechanisms, which take place in LFP cathodes, as described in the introduction of section 5.5. In this context, also shape and slope of the non-monotonous single particle electrochemical potential profile of the LFP cathode play a fundamental role: the smaller the pendency in the central part of the capacity range, the smaller and narrower the hysteresis in the cathode voltage curve and therefore in the full cell voltage. Moreover, from the test description it is possible to give a value of the self-discharge for a period of three months. This is achieved, for example, for the test relative to the relaxation after the stepwise discharge process by comparing the total battery capacity before and after the test and compensating the possible aging by the rest capacity directly after the termination of the three months. The obtained value is approximately 1.7%. There is no detailed data available in literature on LFP cells, while some indicative values can be found in [43][182] for other LiB chemistries.

A rough estimation of the time needed to reach a completely steady state condition can be obtained by the ratio \( r^2/D \), with \( r \) the particle radius and \( D \) the diffusion constant. The relaxation diffusion mechanisms in the LFP cells are limited by the cathode. Therefore, considering the data reported in [181] (\( D = 10^{-15} \) cm\(^2\)/s in the two-phase transition of the cathode, particle radius between 44 \( \cdot 10^{-7} \) cm and 338 \( \cdot 10^{-7} \) cm), the obtained relaxation time is between 5.37 h and 417.34 h (13.22 day). These values falls in the same range of the relaxation times observed during the test. The calculation considers only the ideal diffusion phenomenon of ions into isotropic crystals, according to Fick’s law. Nevertheless, the obtained value gives an indication of the time range of the observed effect.

Points which lie outside of the mentioned trend are mainly due to difficulties which have taken place during the test, such as the interruption of the power supplies of the temperature chamber due to a grid fault.
Figure 5.32: Investigation of the long-term hysteresis behavior at an ambient temperature of 23 °C, a) hysteresis during the relaxation after charge and discharge short-term history, b) relaxation after charging with stepwise process and with CC process.

The same tests repeated with a cell in a different aged state have shown the same behavior, both in terms of hysteresis and self-discharge (2.3%). Another interesting phenomenon, which is worth mentioning, is related to the different relaxation voltage which may appear in relation to the short-term history. Figure 5.32b) compares the relaxation behavior after charging the battery to 50% SoC from an empty state, once with CC process with a 0.5C rate and once with stepwise process (5% ΔSoC) with the same rate. Additional tests results can be found in appendix 10.5.5. As can be noticed, even if the initial relaxation values are completely different, after three months the absolute battery’s pole voltages coincides in the two cases, demonstrating the independence from the short-term history. This effect can be observed in more detail in Figure 5-33, where the relaxation is investigated over a shorter time (ten hours) after different short-term histories. In this case the voltage is measured while the battery remains connected to the test bench during relaxation. In the short-term the hysteresis tends to reduce its magnitude as soon as the dynamic of the process increases, going from 10 mV (stepwise charge and discharge process at 0.5C) to 2 mV (CC charge and discharge process at 5C) after a ten hours relaxation period. In any case, the differences among the stepwise processes carried out with different current rates are limited. This behavior is in agreement with the results discussed by Roscher in [162], where the different relaxation behavior is related to the strong inhomogeneity among the particles for high current rate short-term history, which creates the transfer of lithium ions among zones at different concentrations. This produces a faster shrinking in the OCV hysteresis. Moreover, to eliminate possible errors of the SoC setting, Figure 5-33b) shows the same results but normalized with respect to the initial voltage directly after current interruption. Again the differences among the CC process and stepwise charge/discharge behavior are clearly highlighted. As the results demonstrate, the hysteresis on the tested LFP cell cannot be considered as a permanent effect, but as a phenomenon related to the short-term history and therefore to the waiting time. Nevertheless, in the limited time period, this effect cannot be ignored, especially when it comes to the on-board diagnostics of the battery, with significantly limited observation times. In this case, understanding the hysteresis phenomenon is of fundamental importance.
Figure 5-33: Different relaxation behavior after different short-term histories at 23 °C, a) absolute voltage values, b) values normalized in respect to voltage directly after the interruption of the current distinctively for the charge and discharge process.

5.6 Post-mortem analysis as application tool

A post-mortem analysis on a LiB is a process which generally involves the disassembling of a cell in order to analyze its design, the chemical and physical characteristics of the material in the actual state and to obtain an understanding of the cell processes. In this work, the analysis is carried out with two main objectives:

- Analysis of the characteristic quasi-OCV curves of the single electrodes and their performances during the lifetime in order to correctly parametrize algorithms for battery state detection (chapter 6).
- Analysis of the hysteresis effect at the electrode level, and the dependency of the minor loops with respect to the aging state.

Figure 5-34: Post-mortem analysis, cell disassembly process.
To achieve these objectives, five different cells are disassembled in a glove box under argon atmosphere. Two of these are cells in a new unused state, while the remaining three belong to the cell batch described in section 5.3. The characteristics of the mentioned cells are reported in Table 5-11.

**Table 5-11:** Overview of the characteristics of the cells which are subjected to post-mortem analysis.

<table>
<thead>
<tr>
<th>Cell name</th>
<th>Actual/Initial capacity</th>
<th>Aging history</th>
</tr>
</thead>
<tbody>
<tr>
<td>New 1 (F1)</td>
<td>8.35 Ah/8.35 Ah</td>
<td>New cell.</td>
</tr>
<tr>
<td>New 2 (F2)</td>
<td>8.23 Ah/8.2 Ah</td>
<td>Cell subjected to the capacity investigation (section 5.2.1) and to the hysteresis investigation (section 5.5).</td>
</tr>
<tr>
<td>Aged 1 (A1)</td>
<td>7.35 Ah/8.30 Ah</td>
<td>Aged cell after about 1550 EFCs at 30 °C with 50% DoD, SoC average of 50% and current rate of 1C. Afterwards subjected the hysteresis investigation (section 5.5).</td>
</tr>
<tr>
<td>Aged 2 (A2)</td>
<td>6.59 Ah/8.095 Ah</td>
<td>Aged cell after about 2400 EFCs at 30 °C with 10% DoD, SoC average of 50% and current rate of 1C.</td>
</tr>
<tr>
<td>Aged 3 (A3)</td>
<td>7.29 Ah/8.33 Ah</td>
<td>Aged cell in calendar condition at 40 °C and 50% SoC.</td>
</tr>
</tbody>
</table>

Before the post-mortem process, the cells are parametrized in terms of energy capability (measure of capacity under different current rates and ambient temperatures) and power capability (determination of the internal cell impedance by means of pulse tests and the EIS technique under different ambient temperatures). The cells are first fully discharged until the EODV and then disassembled. Afterwards, the physical parameters are measured (weight of the component and geometry) and the electrode samples are collected. Typical values of the cell’s characteristics are reported in Table 5-12 for *Cell A3*. Similar values are obtained for the other cells. The negative electrode always presents a surface which cannot be used for the cell operation, due to the lack of direct contact with the positive electrode. According to the measured values, taking into account that both electrodes are coated in both the current collector surface, the thickness of the positive electrode is between 58 and 72 μm, while that of the negative electrode is between 38 and 40 μm. For each disassembled cell, circular samples of 16 mm diameter are collected on the surface of both electrodes. In order to carry out a spatially resolved analysis of the results and to consider the possible cell inhomogeneity, five samples are collected on each electrode: one exactly in the center (named in the following “middle”), two in the first 20 cm of the electrode, which is positioned in the internal part of the jelly roll, one near the tabs (named “Int. Up”) and one on the bottom of the electrode (“Int. Down”), and the other two in the first 20 cm of the electrode, which is positioned in the outer part of the jelly roll, positioned as before (named “Ext. Up” and “Ext. Down”).

---

8 The results relative to this cell for the investigation of the hysteresis are not reported in this work.
Table 5-12: Geometric characteristics of Cell A3.

<table>
<thead>
<tr>
<th></th>
<th>Value cathode</th>
<th>Value anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode length (only active material)</td>
<td>367.5 cm</td>
<td>363 cm</td>
</tr>
<tr>
<td>Electrode total length</td>
<td>367.5 cm</td>
<td>376 cm</td>
</tr>
<tr>
<td>Electrode height</td>
<td>9.7 cm</td>
<td>9.8 cm</td>
</tr>
<tr>
<td>Total area active material</td>
<td>712,950 mm²</td>
<td>704,220 mm²</td>
</tr>
<tr>
<td>Total thickness</td>
<td>0.123 mm</td>
<td>0.075 mm</td>
</tr>
<tr>
<td>Current collector thickness</td>
<td>0.021 mm</td>
<td>0.008 mm</td>
</tr>
<tr>
<td>Current collector + electrode layer (1)</td>
<td>0.079 mm</td>
<td>0.046 mm</td>
</tr>
<tr>
<td>Current collector + electrode layer (2)</td>
<td>0.093 mm</td>
<td>0.048 mm</td>
</tr>
<tr>
<td>Electrode + current collector weight</td>
<td>64.53 g</td>
<td>74.55 g</td>
</tr>
<tr>
<td>Total cell weight</td>
<td>330.54 g</td>
<td></td>
</tr>
<tr>
<td>Separator weight</td>
<td>22.53 g</td>
<td></td>
</tr>
<tr>
<td>Electrolyte weight</td>
<td>63.64 g</td>
<td></td>
</tr>
</tbody>
</table>

For each of the collected samples, coin half-cells using pure metallic lithium as a reference counter electrode are built. The next sections describe the measurement results of the electrode performance in terms of quasi-OCV curves and in terms of hysteresis behavior.

5.6.1 Quasi-OCV curve of single electrodes

The first series of tests study the quasi-OCV behavior of the single electrodes and their current rate dependency. These results will be useful when pursuing the thesis for the development of algorithms for battery state detection, introduced in chapter 6. The tests are carried out for all built coin cells for all five disassembled cells. The procedure starts with the complete deintercalation of the lithium from the electrode with a CCCV charge process. The CC process is carried out with a current rate of 0.1C. The subsequent processes consist of CCCV discharge followed by a CCCV charge process, each carried out with the current rates of 0.1C, 0.2C, 0.3C and 0.5C. In this case, the meaning of the term charge on the electrode level refers to the deintercalation of the lithium from the electrode. This is in contrast to the standard terms referring to the full cell, where during the charging process lithium is intercalated in the anode and deintercalated from the cathode. Furthermore, the value of the current rates used to measure the quasi-OCV curves are calculated in a way that each electrode is loaded with the same current per unit of area that would see in the full cell. Thus, electrode voltage curves of anode and cathode, which can be directly subtracted and directly compared with the full voltage curve of the cell for the same current rate, can be obtained. This operation is of fundamental importance for the methodology explained in chapter 6, and therefore the concept will become clearer later on in this work. The scaling of the current rate from the cell level to the electrode level is carried out according to equation (5.2):

\[ I_{\text{elect}} = \frac{A_{\text{coin}}}{A_{\text{elect}}} I_{\text{full}} \]  (5.2)
where the current in A for the considered electrode \((I_{\text{elect}})\) depends on the total coin cell area \((A_{\text{coin}})\), on the total area of the electrode \((A_{\text{elect}})\) and on the current in Ampere at the full cell level \((I_{\text{full}})\). A typical value of the coin cell area is 201.06 mm\(^2\), while currents in the range of 2.2 mA at electrode level correspond to a current of 8 A (1C) at full cell level. In this sense it is important to highlight that full cells and coin cells present some differences in their construction and operating conditions. Electrolytes and separators employed in half cells may not coincide with those used by the manufacturer for the full cell. Moreover, pressure and temperature may also present evident differences between the two cell constructions. These factors may be the cause of small deviations between the full cell and the modeled behavior through half-cell data. Nevertheless, as it is demonstrated in chapter 6, and appendix 10.6, the modeled behavior is still acceptable and allows the proper reproduction of the full cell behavior.

As known [183], in LFP cells the amount of lithium present on the cathode when the cell is in a fully discharged state gives a direct indication of the battery’s SoH. In fact, these cells are designed in a way that the iron phosphate electrode can be fully utilized during the intercalation/deintercalation process [19][60], without the danger of creating instability in the active material related to the present amount of lithium, as happens for other LiB chemistries [184]. In this sense, Figure 5-35 shows the analysis of the first lithium deintercalation process for Cell A2 and Cell A3 and compares it with the actual battery’s SoH. The equivalent SoH for a coin cell is calculated by the relation between the total amount of lithium first deintercalated from the cathode and the total capacity of the coin cell during charge or discharge with CCCV process, in both cases with 0.1C rate. The SoH value for the full cell is calculated in relation to the maximum total capacity, which was detected during the battery lifetime. As can be noticed, a significant discrepancy exists between the values calculated for the single coin cells and the actual SoH of the full cell. This is mainly due to the initial LLI employed for the initial formation of the SEI. As it is discussed in section 6.1.2.2, values around 10% of LLI are in a reasonable range for this kind of cell, and they are able to clarify the discrepancy. Additional reasons can explain this deviation too. A new SEI formation process on the negative electrode side (pure lithium) on the coin cell might have taken place. However, this would not modify the amount of lithium which would be measured during the first deintercalation process from the cathode. Moreover, the balancing (stoichiometry) of the cell may also have some influence: for all the opened cells subjected to the post-mortem analysis, the results have shown the same trend, which might be possibly related to the fact that the cells are designed so that the available cathode active material is not fully utilized during the normal operation (less lithium is present compared to the total amount which can be stored). Other causes may be related to the possible damage of some part of the collected sample during the disassembling operation: this would explain the variation of the results among the different samples. High variability, as the one shown for Cell A3 in Figure 5-35b) (e.g. for the sample Int. Up and Int. Down) are more related to the non-homogeneous aging, which takes place during battery lifetime. This kind of behavior is also visible for Cell A1 but not in the case of Cell F1 (results not reported in this work). Only further investigations quantifying the amount of lithium present in the collected samples (for example through the
use of the inductively coupled plasma optical emission spectroscopy) could clarify the cell behavior. However, this is beyond the scope of this work.

Figure 5-35: Comparison of the rest lithium measured during the first deintercalation process of the cathode in the coin cells and the actual battery’s SoH (full cell), a) for Cell A3 and b) for Cell A2.

Figure 5-36 shows the rate dependency of the five cathode and anode cells for Cell A3. Figure 5-36a) shows the dependency for the cathodes while Figure 5-36b) for the anodes. Similar trends are observed for the five analyzed cells. The cathode cells show a clear dependency on the current rate, which is maintained both during the intercalation and deintercalation process. With an increase in current rate the electrode capacity falls exponentially. Small differences in the measured capacities are well explained by the handmade production of the test coin cells. A completely different trend is observed for the anode cells, as shown in Figure 5-36b): during the discharge process (intercalation) the capacity falls with an increasing current rate, while during the charge process (deintercalation) it remains rather constant until a current rate of 0.5C.

Figure 5-36: Dependency of the coin cell capacity on the current rate for Cell A3 at ambient temperature, a) for the cathode and b) for the anode.
This behavior has already been reported in literature [183][184]. During the intercalation, the limiting factor is represented by the diffusion in the high SoC range, while the opposite happens during the deintercalation: for the graphite in the first case the diffusion coefficient assumes values which are smaller than the ones in the second case (lower diffusion coefficient means slower diffusion kinetic). Another possible cause of this effect may be due to the fact that the last part of the intercalation process takes place in a two-phase transition with voltage values approximately near to zero. Therefore, a smaller rise of the current rate can produce the necessary polarization earlier which determines the consequent interruption of the test (cutoff voltage reached) [185]. Moreover, Figure 5-36 delivers a hint of the differences between the samples collected in the same electrode, and gives an indication of the homogeneity of the degradation inside the cells throughout the entire active material surface. The results of Cell A3 show that in the analyzed battery the built coin cells present the same performances regardless of where the samples were collected. Similar results are obtained for Cell F1 and Cell F2, while for Cell A1 and Cell A2 a scattering in the measured capacities is observed, particularly visible on the anode side. This is in agreement with the literature by date, which describes that in LFP cells the main degradation in terms of active material is generally associated with the negative electrode [35][133][60].

Figure 5-37 compares the quasi-OCV curves of anode and cathode for coin cells collected in the middle of the electrodes in different batteries. The figure compares both anode and cathode quasi-OCV curves at 0.1C during lithium intercalation and deintercalation (note the different scale of the x-axis and y-axis).

**Figure 5-37:** Comparison of the quasi-OCV curves at 0.1C rate for Cell F1, Cell A1, Cell A2 and Cell A3 at ambient temperature for the coin cell in the middle of the electrodes, a) for the cathodes during discharge and b) charge, c) for the anodes during charge and d) discharge.
Figure 5-37a) and b) show that the quasi-OCV curves on the cathode for different aged battery do not differ significantly in terms of polarization and final delivered capacity. The difference between the maximum and minimum capacity is approx. 0.226 mAh during discharge and 0.242 mAh during charge (7.8% and 8.3% of the maximum capacity respectively). On the other hand, a higher difference is observed Figure 5-37c) and d) for the anode. The difference between the maximum and minimum capacity is approx. 0.689 mAh during discharge and 0.777 mAh during charge (19% and 21% of the maximum capacity respectively). This again indicates a higher impact of the degradation on the anode compared to the cathode side.

5.6.2 OCV curve of single electrodes

As mentioned in section 5.5, the investigation of the hysteresis of the OCV has prompted thoughts as to whether the change of the minor loops in the full cell with the aging is related to the change of the hysteresis characteristics in the cathode. Moreover, the question that may also arise is, whether in the anode a particular hysteresis phenomenon appears with the degradation. Therefore, for Cell F1 and Cell A1 of Table 5-11, the characteristic of the OCV and of some of the minor loops are investigated. The investigation lasted approx. one month. During this time, checkup tests were conducted to track the degradation of the single built half-cells in terms of total capacity. The half-cells relative to the cathode electrodes showed a limited degradation (between 0% and 1.6% of capacity fade in respect to the initial value), while half-cells relative to the anode electrodes showed a significant capacity decrease (up to 11% for Cell F2 and up to 8% for Cell A1).

Firstly the OCV of cathode and anode are measured for all five built coin cells, according to the procedure shown in section 5.5.1. In this case, the reference capacity to calculate the SoC is the one measured during the intercalation with a current rate of 0.1C. The results for the half-cells relative to Cell A1 are depicted in Figure 5-38a) and c) for the cathode and in Figure 5-38b) and d) for the anode. As can be observed, an evident hysteresis is visible on the cathode and on the anode: the difference among the charge and discharge curve is approximately 17 mV at 10% SoC and decreases continuously reaching about 6 mV at 95% SoC. In contrast, the hysteresis on the anode is between 4 mV and 5 mV in the SoC range 10%-40%, and increases reaching 8 mV at 70% SoC and around 25 mV at 75% SoC (considering the scattering between the five coin cells). Similar results are obtained for Cell A1, although a slightly larger hysteresis is observed in the high SoC for the anode. On the one hand, the values related to the hysteresis of the cathode can be considered reliable and are not affected by errors due to SoC calculation, thanks to the flatness of the voltage curve. On the other hand, the values measured for the anode might be affected by possible displacement on the x-axis, especially in correspondence to the voltage stages (e.g. in the SoC range between 70% and 90%). Therefore, the hysteresis obtained in these regions should be treated considering a higher uncertainty. Based on the measured OCV curves, three minor loops are measured for both anode and cathode, with the same procedure and criteria as described in section 5.5.1. The main results are reported in Table 5-13, and are valid for all five half-cells built for each electrode for both Cell F2 and Cell A1.
Figure 5-38: Hysteresis of the OCV measured with 5% SoC step after 3 h relaxations at ambient temperature for Cell A1, a) OCV of the cathode and b) of the anode, c) hysteresis of the cathode and d) of the anode. View the different scale of the y-axis between figure a) and b).

Table 5-13: Resume of the results for the minor loop identification for Cell F2 and Cell A1 for anode and cathode.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Anode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test</td>
<td>ΔSoC [%] to enclose the loop</td>
</tr>
<tr>
<td>20→30→20</td>
<td>10%</td>
</tr>
<tr>
<td>40→60→40</td>
<td>20%</td>
</tr>
<tr>
<td>60→75→60</td>
<td>15%</td>
</tr>
</tbody>
</table>

Exemplary results are shown in Figure 5-39 for cathode and anode for one of the investigated minor loop.
Figure 5-39: Example of the measured minor loops for the coin cells Ext. Up at ambient temperature, a) cathode for Cell F2 and b) for Cell A1, c) anode for Cell F2 and d) for Cell A1.

Additional results can be found in appendix 10.6. As is mentioned in section 5.5.3 and shown in Table 5-13, no difference is found between the behaviors of the single electrodes built from cells in different aging states. This again proves that the change of the hysteresis behavior of the OCV during its lifetime is not directly related to the change of the electrode characteristics. Some additional hints of these deductions can be found in the data reported in appendix 10.6.

5.7 Summary

LFP-based cells are characterized by particular features currently making them nowadays one of the favorite choices worldwide among the available LiB chemistries. In addition to the excellent performance and intrinsic safe structure, an evident hysteresis and a flatness characteristic of the OCV make them unique. In this chapter, the results of the characterization of a HP LFP-based battery are presented. The tests are mainly based on the investigation of the rate capability (i.e. the behavior in terms of battery total capacity under different operating conditions) and on the characteristics of the OCV (flatness and hysteresis). In particular, the observation of the quasi-OCV and OCV behavior during normal operations and during lifetime delivered important information related to the battery performance and degradation mechanisms. Cells in different aging states present a different behavior in terms of major OCV hysteresis boundaries and minor hysteresis loops. The post-mortem analysis
proved that this behavior cannot be attributed to a change in the single electrode characteristics, but to a change in the cell stoichiometry, and more specifically to a change in the plateaus’ characteristics of the OCV curve. Extended tests, which were carried out to observe the hysteresis behavior, have highlighted that this phenomenon is not a permanent effect, but tends to disappear after a longer relaxation period. The evidences are of fundamental importance for the development of new algorithms which can be employed for the on-board diagnostic of LFP cells. These are the main focus of the next chapter.
6 Diagnostic of LiFePO₄ cells

BMS algorithms for battery state detection are a key component in battery systems. On the one hand they facilitate the complete exploitation of the battery performance, while guaranteeing a defined safety margin. On the other hand, they allow the delivery of information to external actors for the optimized use of the battery and its energy.

This chapter presents novel approaches for battery state detection for LFP cells. As mentioned earlier, the methodologies introduced in this work focus on the estimation of the actual battery capacity and on the determination of the battery SoC. The developed algorithms take advantage of the aforementioned particular characteristics of LFP cells, i.e. the flatness and the hysteresis of the OCV curve. In both cases, the presented approaches are completely new developments. Therefore the focal point of this work is mainly the testing and validation phase of these algorithms, i.e. the verification of their working principles. A discussion on the implementation on µC and related problems is given. The content of this chapter are partially based on [186][187].

6.1 A novel approach for on-board capacity estimation in LiFePO₄ cells

The on-board estimation of the actual battery capacity in BEVs and PHEVs is a challenging task for a BMS. The capacity must be calculated without the need to discharge the battery completely and starting from a fully charged state. Moreover, the discharge process is often carried out in dynamic conditions under variable temperatures. As introduced by Farman et al. [94], the on-board estimation of the total battery capacity for LiBs can be carried out mainly in four different ways. Often the selected approach calculates the total capacity according to equation (6.1) (Coulomb counting method):

\[ Q_{\text{actual}} = \frac{\int_{t_0}^{t_1} i(t) \cdot dt}{S_0 C_{t_1} - S_0 C_{t_0}} \cdot 100 \] (6.1)

Once the value of the Ah-throughput between two SoC values is tracked, the actual capacity can be calculated by estimating the value of the SoC within the same time period independently from the capacity itself. One of the ways to achieve this is using the OCV, based on the knowledge of the relation “OCV-SoC”. Two conditions are required: i) this relationship has to be known and strictly monotonous, and ii) it has to remain unchanged during battery lifetime (or at least its changes must be tracked). This methodology is presented in the literature published to date by Einhorn et al. [95] and by Plett [96] with satisfactory results, even though the issue regarding the change of the OCV curve due to
aging is not considered by the authors. The use of the OCV-SoC relation of equation (6.1) for capacity estimation becomes more complicated in LFP cells. In fact, the flatness of the OCV curve and its remarkable hysteresis behavior make the diagnostic of this cell particularly difficult. Moreover, as mentioned in chapter 5, the aging mechanisms have an evident impact on the OCV curve, changing its characteristics noticeably. Thus, such easy methodology cannot be used for LFP cells and a new approach is needed. In current studies several authors have presented attempts to estimate the battery capacity by means of filter approaches applied for the parametrization of equivalent battery circuit models. Waag [72] presents a method for the estimation of the electromotive force during battery voltage relaxation and uses this to estimate the SoC and the battery’s capacity according to equation (6.1). However, the method is not feasible for LFP cells, due to their mentioned features. Methods based on filtering approaches [90][175][188] generally present promising results, although they can be hardly implemented using low-cost μC. In another approach, the researchers concentrated on the observation of the quasi-OCV curves, studying their characteristics with the differential analysis (ICA and DVA). Some authors attempt use these methods onboard for capacity estimation [135][189][190]. Unfortunately the derivative operation in signals with superimposed noise can lead to the amplification of this noise, and, in some cases, to the misinterpretation of the processed information. Using the ICA and DVA as offline tools, Dubarry et al. [44][134] and Groot [92] analyzed the behavior of the quasi-OCV curve during battery lifetime and use simple equations to model the relation among the aging mechanisms (or degradation modes DMs) and the characteristics of the electrode voltage curves. A similar approach is also used by Han et al. [60] for different lithium-ion chemistries, and by Wang in [191] for LFP cells. This method is a promising approach which can be used as a baseline for the development of algorithms for the on-board capacity estimation for LFP cells. Schmidt et al. [192] use this approach for the offline analysis of the open circuit potential with the goal of identifying the composition of blended cathodes and their degradation modes. In [193] the authors present an algorithm for capacity estimation based on half-cell curves. However, this method is applied on NMC cells and is based on the assumption that the electrode characteristics do not change during battery lifetime, an assumption which introduces significant errors when applied to LFP cells [44].

Based on these research lines, this chapter proposes a novel algorithm for battery capacity estimation in LFP cells. The algorithm is based on the online estimation of the single DMs and on the determination of the characteristics of the electrode curves. This process is carried out based on the information in terms of plateau lengths present in the full voltage curves. Knowing the width of the plateaus, the corresponding DMs can be estimated in order to find the correct position and dimension of the single electrode voltage curve. Therefore, the full cell curve can be reconstructed and the total battery capacity calculated. The next sections are structured as follows. Firstly the characteristics of the voltage curves of LFP cells and the impact of aging on their shape are recalled briefly, with the introduction of a model which describes these phenomena. Secondly, a new BMS structure is presented, with the implemented algorithm for capacity estimation. Finally the results are shown, and the ensuing
problems regarding the implementation of the algorithm and the merits of the presented approach discussed.

6.1.1 Degradation model for LiFePO$_4$ cells

The description of the impact of the so-called degradation modes on the characteristic of the full voltage curve of an LFP cell is reported by Dubarry et al. in [35][44]. These effects are again proposed and reproduced in this work in Figure 6-1. Additional information can be obtained in appendix 10.7 in Figure 10-25.

Figure 6-1: Representation of the DM effect on the voltage curve of LFP cells, a) cell in a new state, b) effect of LLI, c) effect of LAM in the positive electrode in delithiated state, d) effect of LAM in the positive electrode in lithiated state, e) effect of LAM in the negative electrode in delithiated state, f) effect of LAM in the negative electrode in lithiated state (based on [44]).

Figure 6-1a) shows the trend of the cell’s full voltage curve. As already reported in section 3.4, this is obtained by subtracting the anode from the cathode voltage curve. The resulting full voltage curve is characterized by the plateaus IA, IIA and VA. As can be observed, the lengths of the cathode and anode curves (amount of Ah which can be delivered
under the same current per surface unit) are not equal, since usually the anode is slightly oversized to avoid lithium plating [35]. Moreover, in the new state, the starting point of the anode and cathode curves are slightly shifted by an offset, which means that during the operation of the cell the two electrodes are not wholly used. The characteristics of the single plateaus in terms of length and position change during the lifetime affected by the single aging mechanisms. As introduced in section 3.3, the division of the aging mechanisms according to their consequences results in two main DMs, the LLI and the LAM. The effect of the LLI on the full voltage curve is depicted in Figure 6-1b), and represented by a left shift of the cathode curve in respect to the anode curve. As a consequence, the length of plateau IA is reduced and the battery capacity decreased. The LAM can take place in both the positive and the negative electrode, and it can be distinguished in a lithiated or in a delithiated phase depending on the cases in which this mechanism take places. Therefore four different cases can be identified, as depicted in Figure 6-1c-f). For all of the them, LAM is defined as the shrinkage of the considered electrode curve while maintaining it fixed on the point relative to the lithiated/delithiated phase. For example the LAM on the negative electrode in lithiated phase (Figure 6-1f) can be modeled as the shrinkage of the anode curve maintaining it fixed in the point relative to the lithiated phase. As a consequence, width and position of the three plateaus change depending on the degradation modes and on their magnitude. During battery lifetime, the cell will be affected by a combination of all of them, depending on the operating conditions which the battery is subjected to. At this point it is clear that the characteristics of the plateaus in terms of length can be read as a “book of the battery aging” and can deliver direct information about the battery’s SoH and therefore on its capacity.

Based on the described mechanisms, a degradation model is developed and presented. The model is based on the equations presented by Dubarry in [44] and Groot in [92], and presented in equations (6.2)-(6.5). The model describes the change of the characteristics of the starts and end points of the electrode capacity depending on the single DM (LLI and the four types of LAM) and on the initial electrode capacity.

\[
Q_{\text{Ne, start}} = -LAM_{\text{Pe,De}} \cdot Q_{\text{Pe,BOL}} \tag{6.2}
\]

\[
Q_{\text{Ne, end}} = Q_{\text{Ne,BOL}} - LAM_{\text{Ne,De}} \cdot Q_{\text{Ne,BOL}} - LAM_{\text{Ne, Li}} \cdot Q_{\text{Ne,BOL}} - LAM_{\text{Pe,De}} \cdot Q_{\text{Pe,BOL}} \tag{6.3}
\]

\[
Q_{\text{Pe, start}} = -LAM_{\text{Ne, Li}} \cdot Q_{\text{Ne,BOL}} - LLI \cdot Q_{\text{Pe,BOL}} \tag{6.4}
\]

\[
Q_{\text{Pe, end}} = Q_{\text{Pe,BOL}} - LAM_{\text{Pe, Li}} \cdot Q_{\text{Pe,BOL}} - LAM_{\text{Pe,De}} \cdot Q_{\text{Pe,BOL}} - LAM_{\text{Ne, Li}} \cdot Q_{\text{Ne,BOL}} - LLI \cdot Q_{\text{Pe,BOL}} \tag{6.5}
\]

In equation (6.2)-(6.5) the terms \( Q_{\text{start}} \) and \( Q_{\text{end}} \) represent the starting and ending points respectively of the electrode in the Ah scale. Their meaning is depicted in Figure 6-1a); the indexes Ne and Pe mean negative and positive electrode respectively, the indexes De and Li denote the delithiated and lithiated state respectively. The DMs are expressed in equation (6.2)-(6.5) in percent. The Ah scale is normalized in respect to the total capacity of
the positive electrode in a new state. This means that in a new state, \( Q_{\text{Pe,BOL}} \) is equal to one, while \( Q_{\text{Ne,BOL}} \) is normally bigger than one. For the sake of clarification, considering the cell in a new state (case of Figure 6-1a), the value of \( Q_{\text{Ne,start}} \) is zero, which corresponds also to the fully discharged state of the full cell; \( Q_{\text{Pe,start}} \) is smaller than zero, with a value depending on the initial offset. The value of the \( Q_{\text{Pe,end}} \) is then smaller than one. The resulting full voltage range, which goes from \( Q_{\text{Ne,start}} \) to \( Q_{\text{Pe,end}} \) is considered the reference value for a cell in a new state, i.e. in the normalized reference system the new cell has a full capacity equal to one (see Figure 10-25 in appendix 10.7). As soon as the cell ages, the value of the capacity terms in equations (6.2)-(6.5) change based on the DMs. Therefore, the total capacity of the two electrodes in relative terms can be calculated according to Groot [92] following equations (6.6)-(6.7):

\[
Q_{\text{Ne,EOL}} = Q_{\text{Ne,BOL}} \cdot (1 - LAM_{\text{Ne}}) \tag{6.6}
\]

\[
Q_{\text{Pe,EOL}} = Q_{\text{Pe,BOL}} \cdot (1 - LAM_{\text{Pe}}) \tag{6.7}
\]

In equations (6.6)-(6.7) the values of the capacity of the electrodes \( Q_{\text{Ne,BOL}} \) and \( Q_{\text{Pe,BOL}} \) (expressed in relative terms) can be calculated as the difference \( Q_{\text{end}} - Q_{\text{start}} \) employing the respective values assumed by each electrode at the BOL. Therefore, the electrode capacities \( Q_{\text{Ne}} \) and \( Q_{\text{Pe}} \), in whichever point of the lifetime, can be calculated in the same manner using the respective values of \( Q_{\text{end}} \) and \( Q_{\text{start}} \) at the point of the battery life by using equations (6.2)-(6.5). The value of the full cell capacity in relative terms is calculated according to equation (6.8):

\[
Q_{\text{full cell,EOL}} = \min(Q_{\text{Ne,end}}, Q_{\text{Pe,end}}) - \max(Q_{\text{Ne,start}}, Q_{\text{Pe,start}}) \tag{6.8}
\]

The introduced model can be employed for the analysis of the results obtained during accelerated aging tests for the identification of the DMs. An example is given in Figure 6-2. An LFP cell of the same type as the one investigated in this work was aged under cycling conditions with a 2C current rate, 50% DoD, 50% SoC average at 40 °C ambient temperature. The capacity values measured during the checkups are depicted in Figure 6-2d) (cross points). According to this data, the model introduced in equations (6.2)-(6.5) is used to reproduce the degradation during battery lifetime. Figure 6-2a) shows the evolution of the quasi-OCV curves modelled with the identified DMs with the arrow indicating the direction of the aging. Figure 6-2b) and c) depicts the voltage analysis of the quasi-OCV and the evolution of the two peaks respectively. Figure 6-2d) compares the relative values of the capacity obtained through the model and the measurement. On the same plot, the evolution of the distance between the peaks \( P_1 \) and \( P_2 \), and of the distance between \( P_2 \) and the origin of the axes are also reported. The evolution of the DMs and their values in % is reported in Figure 6-3. As can be observed, the model can reproduce the effect due to the contemporary interaction of different effects, and can therefore describe the complete battery degradation. Additional examples of
the analysis, which can be conducted with the presented model, can be found in appendix 10.7.1.

**Figure 6-2:** Reproduction of the degradation of the 8 Ah HP LFP cell aged under cycling conditions with 2C current rate, 50% DoD, 50% SoC average at 40 °C, a) modelling of the evolution of the quasi-OCV curves during aging (arrow direction), b) resulting dV analysis, c) evolution of the two identified peaks, d) comparison between the measured capacity fade and the one obtained by the model for the different checkups, evolution of the distance between the peaks P₁ and P₂ (P₁-P₂), evolution of the distance between P₂ and the origin of the axes (P₂).

**Figure 6-3:** DMs obtained by the modelling of the capacity fade data reported in Figure 6-2.
6.1.2 Novel BMS structure for SoC and SoH estimation

Due to the different characteristics of the OCV curve presented by LFP cells in respect to other LiB chemistries, a new BMS structure for aging estimation is proposed, which differs from the traditional one [66]. A scheme of the novel BMS concept is depicted in Figure 6-4. The architecture can be divided into two parts. The first part is the online estimation of the single plateau characteristics. As will be demonstrated later, only the plateau length contains necessary and sufficient information for the detection of the battery’s SoH. The plateau information can be gathered during a charging process or during a normal driving operation. Regarding the charging process, the observation of the battery behavior for the collection of the plateau information can be carried out during a CC charging process with a limited current rate (currents smaller than 0.3C are sufficient). These conditions can be easily satisfied in EVs and PHEVs. The second method is the observation of the battery behavior under load and its modeling through an EECEM. Once the passive parameters (resistances and capacitances) are adapted online according to the operating conditions and to the actual aging, the value of the OCV can be tracked and used to reconstruct the actual plateaus’ characteristics. In this work, the method developed by Waag et al. in [89] is employed for this task. Once enough information is gathered, this data is pre-processed in order to normalize the collected values to the chosen standard conditions (current rate and ambient temperature).

![Diagram of Novel BMS structure for DM estimation and actual battery capacity determination.](image)

**Figure 6-4:** Novel structure of BMS for DM estimation and actual battery capacity determination.
Afterwards the information is ready to be processed in the offline part of the BMS (not real-time calculation). At this point it is important to underline that not real-time/offline calculation is referred to the possibility for the μC in the BMS to not carry out the requested operation in real time. This allows the distribution of the computational effort over a longer time period, thus reducing the load of the BMS μC.

6.1.2.1 Working principle of the algorithm

The calculation of the degradation modes and therefore of the actual battery capacity is carried out following the scheme presented in Figure 6-5. The process starts at step a), where different groups of \( P_i = \{LLI; LAM_{Fe}; LAM_{Ne} \} \) parameter sets are generated, each one containing different values of the degradation modes \( LLI \), \( LAM_{Fe} \) and \( LAM_{Ne} \) in the lithiated and delithiated phase. Each parameter set is then applied to equations (6.2)-(6.5) and the characteristics of the modified cathode and anode electrode are calculated.

![Diagram of the working principle](Figure 6-5: Working principle of the “not real-time” calculation block.)

The new characteristic values are applied at step b) to the measured anode and cathode voltage curve of a new cell (step c)). The new curves obtained at step b) are summed up and the “simulated“ full voltage curve is obtained at step d). At step e) the curve is processed and the lengths of the plateaus are measured. These results are compared with the one collected online (as described above) at step g) and the actual error is calculated at step f). The calculated error is compared with a defined threshold \( \varepsilon \) at step h). If the error is bigger than \( \varepsilon \), new sets of degradation modes are generated and the process takes place again starting at step a). If the error is smaller than \( \varepsilon \), the reconstructed voltage curve represents the actual battery
SoH state, and its dimension in terms of Ah represents the actual battery capacity (step \( i \)). The entire procedure is carried out separately for the charge and for the discharge process, so that the capacities during both charge and discharge are calculated.

### 6.1.2.2 Identification of the stoichiometry of a new cell

The two electrode voltage curves available at step \( c \) have to be measured on a sample at the BOL. This can be carried out, for example, through a post-mortem analysis. For this, the results collected during the post-mortem analysis introduced in section 5.6 are employed. In particular, the measurements at electrode level with scaled current (see section 5.6.1 and equation (5.2)) allow the direct comparison between i) the quasi-OCV curve measured at full cell level with 0.1C (CC charge and discharge) and ii) the difference between the quasi-OCV of the anode and cathode measured with the correspondent scaled current of 0.1C (under CC charge and discharge). This comparison is carried out in a way that the three plateaus identified on the two curves (measured on the full cell and reconstructed from the single electrode measurements) are characterized by the same lengths. This length is considered in relative terms as explained in section 6.1.1. The results of the obtained stoichiometry for the charge and discharge process are depicted in Figure 6-6.

**Figure 6-6:** Representation of the stoichiometry of the LFP cell for the CC charge and discharge process at 0.1C, a) offset between cathode and anode voltage curves during charge, b) corresponding full voltage curve during charge, c) offset between cathode and anode voltage curves during discharge, d) corresponding full voltage curve during discharge.

---

\( ^9 \) The overvoltage effect cannot be compared, due to the different conditions between the full cell and the coin cells, in terms of internal cell pressure, different electrolyte and separator etc.
These values are of key importance, in order to distinguish the effect of the LLI on the electrode curves from the initial stoichiometry of a cell in a pristine state (i.e. when the formation process of the SEI can be considered concluded). In quantitative terms, the obtained offset during the charge and discharge process differ slightly, with a value of approx. 12.46% and 7.66% respectively. Although both values fall in a range which is in agreement with what contemporary literature specifies for the same type of cell [44][183][194][195], the difference may be considered excessive. The reason may lie in the fact that in this work the parametrization process of the full cell is done with a series of CC charge and discharge processes, where only the charging phase terminates with a CV phase. This means that while the discharge process starts with the battery in a physically fully charged state, the charge process starts when the battery is not totally empty. Therefore a bigger offset is identified between the anode and cathode curves for the charge process. Nevertheless, the different values are used for the implementation of the algorithm, although only the offset found for the discharge process may represent the real cell stoichiometry.

6.1.2.3 Identification of the plateaus’ lengths

The detection of the plateaus on the collected data during the online and the offline procedure takes place without the need of any differentiation. The lengths of plateaus VA and IIA are estimated by saving the data in a vector of limited length and fitting the data with a linear function with constrained dependency, as explained in [196]. The beginning and end of a plateau is determined by fixing the pendency of the respective fitting linear function during the recalibration process of the algorithm. The length of plateau IA, however, is estimated by fitting the data with a so-called sigmoid function [197], by using the Nelder-Mead method [198]. This allows the correct identification of the precise point where the single phase region is placed. In fact, in this region the growth of the battery’s internal resistance can create some difficulties, and can deliver imprecise information on the plateau’s length. Exemplary results of the two used methods are shown in Figure 6-7a) for the plateaus VA and IIA and Figure 6-7b) for the plateau IA.

![Figure 6-7: Identification algorithms of the plateaus’ lengths, a) identification of the length of plateau VA and IIA, b) identification of the length of plateau IA.](image-url)
6.1.2.4 Error function and fitting strategy

The algorithm employed at step a) to generate the new parameter sets $P_i$ is the VPA. This method has been successfully used by Waag et al. in [66][89] and modified to be used for the presented research. The error at step f) is calculated considering that one of all available errors that shows the highest value with the actual degradation modes, as shown in equation (6.9):

$$\text{Error}_{\text{actual}} = \max(LP_{i,\text{measured}} - LP_{i,\text{fitted}})$$  \hspace{1cm} (6.9)

where $LP_i$ represents the length of the $i^{th}$ plateau expressed in Ah. In this way, it is not necessary to gather the information about all the existing plateaus online. The algorithm will proceed in order to minimize the single error related to the available plateaus (the one measured online).

First attempts of algorithm implementation have shown that the use of all five DMs reported in equations (6.2)-(6.5) did not deliver satisfactory results. The algorithm was not able to converge, and often not able to reduce the error to a negligible value. This was probably due to the high amount of variables in respect of the amount of available information. A first way to improve algorithm convergence is based on the reduction of the unknown variables, in a way that the tracked mechanisms still maintain a physical meaning. Therefore, the results which are shown in the following section are obtained under the assumption that during the lifetime only the DMs $LLI$ and $LAM_{Ne}$ take place. This is in agreement with the current literature, in which the post-mortem analysis of disassembled LFP cells has demonstrated that the battery degradation can be explained by only these two DMs [35][199][200], and in some extreme cases by only $LLI$ [183]. When studying singularly the impact of the two possible different types of $LAM$ on the negative electrode (lithiated and delithiated) on the plateaus’ lengths, the obtained results are rather comparable. Therefore, this work chooses only the $LAM_{Ne,De}$ from the two possible $LAM_{Ne}$, for estimating of the battery capacity. This assumption is also in agreement with recent studies [35] and is thus considered feasible. Moreover, all these hypotheses are based on the fact that the main goal of the presented method is the estimation of the total battery capacity. The correct determination of all DMs which physically perfectly reflect the actual battery aging state is beyond the scope of this work.

Based on this postulate, the fitting algorithm proceeds in tracking only one of the DMs per time based on the actual error. In detail, if the actual error is relative to the plateaus VA or IIA, only the $LAM_{Ne,De}$ is changed, while in case of plateau IA only the $LLI$ is changed. The tracking process takes place in two steps. In the first step the two modes are adjusted following the aforementioned rule, according to the parameter set for the VPA. The second step takes place when the sum of the actual single plateau errors is below a defined threshold. As the method approaches the found minima (global or local), the generation of the new
parameter set $P_i$ occurs with a smaller interval\textsuperscript{10} compared to the first step. As long as the stop criteria is not yet satisfied and the error is still considerable but constant for a certain number of iterations, the single DMs are forced to change with a value proportional to the actual error in order to force the convergence. In particular, if the actual error is negative, the length of the considered plateau in the reconstructed curve is bigger than the length of the measured plateau; therefore the considered DM must be increased. It happens vice versa if the error is positive.

6.1.3 Actual battery capacity estimation

In this section the online estimation of the plateaus and the scaling process are shown. Furthermore, the results regarding the offline estimation of the total battery capacity are shown. Finally, the problems found in the development phase of the proposed methodology are discussed. For the sake of clarification, in this section the capacity measured with CC charge or discharge with a current rate of 0.1C under an ambient temperature of 23 °C is defined as the standard capacity.

6.1.3.1 Detection of plateau during the charging phase

As already mentioned, the plateau of the quasi-OCV curve can be estimated during a constant current discharge process with limited current rate. The conditions under which the process takes place might differ from the standard conditions used to define the total battery capacity. Figure 6-8 presents exemplary results for the scalability of two plateaus for different current rates and ambient temperatures. Figure 6-8a) and b) present the relation between the lengths measured under an ambient temperature of 23 °C and under different ambient temperatures for the plateaus IA and IIA respectively. The same analysis is carried out in Figure 6-8c) and d), which show the relation between the plateau’s lengths measured with a current rate of 0.1C and for different current rates. Each point represents a cell in different aging state. The plateaus’ lengths are measured using the methods mentioned in section 6.1.2.3. As can be observed, it is possible to find a nearly linear relationship between the plateaus measured in standard conditions and the plateaus measured in different conditions. Regarding the plateaus VA (results not reported in this work), a similar conclusion can be drawn, although a clear linear correlation cannot be found as for the case of the other two plateaus. This is due to the greater difficulty in clearly identifying plateau VA, as is shown in Figure 6-7a). Nevertheless, the plateau VA does not play a fundamental role, so that its correct identification is not a necessary condition for a correct SoH estimation as the next sections demonstrates. The established linear relationships are only semi-empirical: this means that they have to be measured for each LFP cell. This constitutes a huge drawback of the presented methodology and whose solution is not investigated in detail in this work.

\textsuperscript{10} For a better understanding and full comprehension of the methodology the reader is advised to the references [66][89].
Figure 6-8: Scalability of the plateaus’ length for different charging conditions, a) relation between the length of a plateau measured at 23 °C and at different temperatures for the case of plateau IIA and b) plateau IA, c) relation between the length of a plateau measured with a current rate of 0.1C and at different current rates for the case of plateau IIA and d) plateau IA. Each point represents a cell in different aging state.

A potential answer to the problem is to investigate the possible physical phenomenon which regulates these dependencies in order to avoid expensive tests and to stipulate universal rules valid for all cells of the same types. It must be stated here that depending on the type of cell, current rates above 0.2-0.3C are not sufficient to clearly distinguish the plateaus.

6.1.3.2 Detection of plateau during the driving phase

As mentioned earlier, the detection of the plateaus is implemented with an EECM: after the passive parameters are tracked, the value of the OCV can be estimated backwards and it can be used to estimate the plateaus’ lengths. Figure 6-9 shows an exemplary result obtained during a driving operation. Figure 6-9a) shows the current profile of the driving cycle scaled for the tested cell and repeated in sequence. Figure 6-9b) shows different voltage trends:

- “Quasi-CV 0.1C”; in red with continuous line the quasi-OCV curve, i.e. the voltage curve measured in a laboratory test with a constant current discharge process with a current rate of 0.1C (measurement procedure can be found in section 5.5.1). The
process starts with a cell in a fully charged state and ends when the cutoff voltage value is reached.

- “Tracked OCV”: in blue with dotted line the OCV estimated with the EECM, as already described in section 6.1.2.
- “Tracked and filtered OCV”: in green with a dashed/dotted line the filtered OCV signal from the previously estimated (blue dotted line) OCV. This signal is obtained from the “tracked OCV” by means of different infinite impulse response filters which consider the information in terms of OCV as valid only in an operating range in which the current rate is limited (below 1C).
- “Measured OCV”: with brown crosses the measured OCV curve in a laboratory test by means of the galvanostatic intermittent titration technique (GITT). Measurements methods and characteristics of the OCV curve can be found in section 5.5.1.

**Figure 6-9:** Online detection of the plateaus during driving phase at 23 °C, a) current profile of a repeated partially FTP75 driving cycle, b) comparison among the offline measured OCV and quasi-OCV curve and the tracked and filtered OCV values by means of an equivalent electrical circuit model.

The squares and circles in Figure 6-9b) indicate the estimation of the end point of the plateaus carried out in the quasi-OCV and in the tracked and filtered OCV respectively, with the methods mentioned in section 6.1.2.3. As demonstrated it is possible to estimate the length of the single plateaus (in particular of plateau IA and IIA) correctly without tracking the OCV precisely. In fact, the tracked OCV is still affected by an error, due to the overvoltage phenomena that the chosen EECM is not able to reproduce. Nevertheless, even if affected by negligible errors, the different two-phase transitions, and therefore the plateaus’ lengths can
still be clearly identified. As shown from Marongiu et al. in [201], the addition of a new simple \( R||C \) branch in the EECM, which describes the diffusion mechanisms, does not deliver impressive enhancements. For a better and more precise estimation of the OCV, the additional diffusion branch should also be temperature and current dependent. This could help correctly estimate of the OCV for phase with prolonged higher current rates (e.g. prolonged highway paths) which would involve the implementation of complex equations. However, such a procedure would result in a higher computational effort for the \( \mu C \), which is, in most cases, not needed. In fact, as already mentioned, the simple used circuit is able to deliver sufficient information in terms of plateaus’ lengths in the majority of the cases in which EVs are used (urban paths or limited highway distances), although the OCV is not estimated accurately. Moreover, the presence of small deviations between the points estimated in the quasi-OCV and in the tracked OCV and its effect on the estimation of the battery capacity can be limited by collecting plateau information in subsequent driving cycles and averaging them, together with a plausibility analysis. Additional results can be found in appendix 10.7.2.

### 6.1.3.3 Offline estimation of total battery capacity

As shown in Figure 6-4, once the online information is gathered, it can be pre-processed and then used for the offline calculation of the total battery capacity. In order to validate the proposed methodology, different samples from the cell batch presented in section 5.3 are selected after a defined storage time or Ah-throughput. The main goal is to test if the algorithm is able to detect the battery capacity even though the aging conditions (and therefore the different aging mechanisms) may be different and unknown. The characteristics of the tested cells are reported in Table 6-1. In order to properly validate the working principle of the proposed methodology and the convergence of the algorithm, three different scenarios are viewed. In the first scenario all the information relative to the length of the three plateaus (IA, IIA and VA) is collected online, both during charge and during discharge processes. In the second scenario only the information of two plateaus, namely plateau IA and IIA, is collected online. Finally, in the third scenario only information relative to one plateau, namely plateau IA, is gathered. The study establishes whether only the plateaus’ lengths provide sufficient information to estimate the battery SoH, and how much information is necessary. The results shown are obtained after the information is processed and scaled to the standard conditions. Figure 6-10 shows an example of the DM tracking process. Figure 6-10a) and b) show the evolution of \( LLI \) and \( LAM_{Ne,De} \) in respect to the iteration number, while Figure 6-10c) and d) show the evolution of the total error and of the single plateau’s error. One iteration is represented by the tracking process of DMs which goes from step \( a \) to step \( h \) in Figure 6-5 for all the generated parameter sets \( Pi \) at step \( a \). As shown on the left side of the figure, the value of the total error is first reduced after a few iterations after a strong change of the \( LAM_{Ne,De} \) value and a second time after approx. 21 iterations after the change of the \( LLI \) value. Subsequently the values are changed only slightly in order to reduce the error as much as possible.
As mentioned above, the DMs $LAM_{Pe, Li}$, $LAM_{Pe, De}$ and $LAM_{Ne, Li}$ are not tracked and they are kept to zero for all the adaptation processes. The graphic exemplifies that the algorithm is able to reduce the error to a negligible value in a limited number of iterations. As shown in Figure 6-10, the change of the initial conditions does not prevent the algorithm from converging to similar values. In both case, when three (left side) or two (right side) plateaus are known, the tracked DMs fall at the end of the process in the same range. Moreover, setting the starting value of $LLI = 7.54\%$ and $LAM_{Ne, De} = 20\%$ in case three plateaus are known, brings the two DMs to converge to 11.20\% and 17.20\% respectively, again assuring the stability of the implemented method (results reported in appendix 10.7.2 on Figure 10-34). Figure 6-11 depicts the results for the capacity estimation in the offline process. The results of the calculated average error and standard deviation are reported for all batteries introduced in Table 6-1. Figure 6-11a) shows the results for the charge process, Figure 6-11b) for the discharge process. Of the three scenarios mentioned earlier, the case containing the information regarding plateau IA is evaluated with two different start values of the $LAM_{Ne, De}$.

Table 6-1: Characteristics of the cells used for the algorithm validation.

| Cell name | Aging history | Actual SoH / %
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>New</td>
<td>Cell in a pristine/unused state</td>
<td>100</td>
</tr>
<tr>
<td>Cal. 1</td>
<td>Calendar aging at ambient temperature of 40 °C and at SoC of 50%</td>
<td>85.78</td>
</tr>
<tr>
<td>Cal. 2</td>
<td>Calendar aging at ambient temperature of 50 °C and at SoC of 20%</td>
<td>82.30</td>
</tr>
<tr>
<td>Cal. 3</td>
<td>Calendar aging at ambient temperature of 50 °C and at SoC of 50%</td>
<td>76.77</td>
</tr>
<tr>
<td>Cyc. 1</td>
<td>Cycle with a constant current of 1C during charge/discharge with a SoC span of 10% between 45% and 55% SoC at ambient temperature of 30 °C</td>
<td>81.53</td>
</tr>
<tr>
<td>Cyc. 2</td>
<td>Cycle with a constant current of 1C during charge/discharge with a SoC span of 10% between 25% and 75% SoC at ambient temperature of 30 °C</td>
<td>88.91</td>
</tr>
<tr>
<td>Cyc. 3</td>
<td>Cycle with a constant current of 1C during charge/discharge with a SoC span of 10% between 10% and 90% SoC at ambient temperature of 30 °C</td>
<td>84.15</td>
</tr>
<tr>
<td>Cyc. 4</td>
<td>Cycle with a constant current of 6C during charge/discharge with a SoC span of 10% between 45% and 55% SoC at ambient temperature of 30 °C</td>
<td>83.47</td>
</tr>
</tbody>
</table>

As mentioned above, the DMs $LAM_{Pe, Li}$, $LAM_{Pe, De}$ and $LAM_{Ne, Li}$ are not tracked and they are kept to zero for all the adaptation processes. The graphic exemplifies that the algorithm is able to reduce the error to a negligible value in a limited number of iterations. As shown in Figure 6-10, the change of the initial conditions does not prevent the algorithm from converging to similar values. In both case, when three (left side) or two (right side) plateaus are known, the tracked DMs fall at the end of the process in the same range. Moreover, setting the starting value of $LLI = 7.54\%$ and $LAM_{Ne, De} = 20\%$ in case three plateaus are known, brings the two DMs to converge to 11.20\% and 17.20\% respectively, again assuring the stability of the implemented method (results reported in appendix 10.7.2 on Figure 10-34). Figure 6-11 depicts the results for the capacity estimation in the offline process. The results of the calculated average error and standard deviation are reported for all batteries introduced in Table 6-1. Figure 6-11a) shows the results for the charge process, Figure 6-11b) for the discharge process. Of the three scenarios mentioned earlier, the case containing the information regarding plateau IA is evaluated with two different start values of the $LAM_{Ne, De}$.

$^{11}$ The value of the SoH is defined as the ratio between the value of the total actual capacity measured with 0.1C constant current discharge and the value of the same capacity for the new cell in the same condition.
Figure 6-10: Example of the evolution of the parameters during the offline aging estimation for the charge process, left in case three plateaus are known and right in case only two plateaus are known, a) evolution of the LLI, b) evolution of the LAM on the negative electrode in the delithiated phase, c) evolution of the total error, d) evolution of the error related to the single plateaus, where $L_1 \rightarrow VA$ and $L_3 \rightarrow IA$. On the top of each plot, the initial conditions of the simulation are reported.

The results obtained are reported separately in Table 6-2 and Table 6-3 respectively for the charge and discharge process. The value of the percent error is calculated according to equation (6.10):

$$\text{Error} = \frac{Q_{\text{real}} - Q_{\text{calc}}}{Q_{\text{real}}} \cdot 100$$  \hspace{1cm} (6.10)$$

where $Q_{\text{real}}$ is the value of the actual battery capacity and $Q_{\text{calc}}$ is the capacity value calculated by the algorithm. As can be observed, the information from all three plateaus assures the convergence of the algorithm in all the cases studied. The average error is 0.98% for the charge process and 1.10% for the discharge process. The standard deviation is for both cases around 0.7%. As expected, the same trend can be observed when only the information of two plateaus is collected. Both for the charge and discharge process the average error remains below 1% (around 0.8%) while the standard deviation remains limited to approx. 0.5%-0.6%. The limited error for both the scenarios with the knowledge of three and two plateaus is related to the characteristics of the plateaus VA and IIA in the full cell curve. These result
from the characteristics of the anode curve. Thus if the length of one of the two plateaus decreases during the battery lifetime, the other plateau will decrease proportionally.\textsuperscript{12}

\textbf{Figure 6-11:} Results of the offline estimation of the total capacity for the different considered scenarios, a) for the charge process and b) for the discharge process.

Therefore it is sufficient to gain information on only plateau IIA in order to correctly estimate and track the DMs. Furthermore, one can expect that with more information (namely on all three plateaus’ lengths) a more precise value of the battery capacity is delivered.

\textbf{Table 6-2:} Capacity estimation error in \% for the tested aged cells for the charge process. The maximum and minimum errors are highlighted in red and green respectively.

<table>
<thead>
<tr>
<th>Cell name</th>
<th>3 plateaus available</th>
<th>2 plateaus available</th>
<th>1 plateau available (\text{LAM}\text{start} = 10%)</th>
<th>1 plateau available (\text{LAM}\text{start} = 0%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal. 1</td>
<td>0.76</td>
<td>1.01</td>
<td>6.28</td>
<td>16.49</td>
</tr>
<tr>
<td>Cal. 2</td>
<td>1.10</td>
<td>0.74</td>
<td>\textbf{10.85}</td>
<td>\textbf{21.50}</td>
</tr>
<tr>
<td>Cal. 3</td>
<td>\textbf{2.66}</td>
<td>0.39</td>
<td>1.70</td>
<td>10.90</td>
</tr>
<tr>
<td>Cyc. 1</td>
<td>0.61</td>
<td>\textbf{1.64}</td>
<td>6.29</td>
<td>14.83</td>
</tr>
<tr>
<td>Cyc. 2</td>
<td>0.51</td>
<td>0.34</td>
<td>5.06</td>
<td>\textbf{4.06}</td>
</tr>
<tr>
<td>Cyc. 3</td>
<td>0.77</td>
<td>\textbf{0.13}</td>
<td>4.89</td>
<td>14.44</td>
</tr>
<tr>
<td>Cyc. 4</td>
<td>\textbf{0.42}</td>
<td>1.20</td>
<td>9.59</td>
<td>19.02</td>
</tr>
</tbody>
</table>

This is valid as a general rule, as can be seen in Table 6-2 and Table 6-3. However, in two cases the error for the first scenario rises to 2.66\% for the charge process and to 2.71\% for the discharge process, thereby generating a higher standard deviation. This trend can be explained by the fact that knowledge of all three plateaus can create problems in the algorithm’s convergence. In some cases the algorithm has difficulties to converge to a correct solution, i.e. to a proper value of the degradation modes which simultaneously reduce the error for the

\textsuperscript{12} This assumption is valid in case \text{LAM}_{Pe} does not take place during the battery lifetime, therefore \text{LLI} and \text{LAM}_{Ne} can be considered as the dominant mechanisms.
three plateaus according to equation (6.9). In fact, sometimes the change of one of the DMs generates a reduction of the error related to a single plateau but the increase of the others.

**Table 6-3:** Capacity estimation error in % for the tested aged cells for the discharge process. The maximum and minimum errors are highlighted in red and green respectively.

<table>
<thead>
<tr>
<th>Cell name</th>
<th>3 plateaus available</th>
<th>2 plateaus available</th>
<th>1 plateau available (LAM&lt;sub&gt;start&lt;/sub&gt; = 10%)</th>
<th>1 plateau available (LAM&lt;sub&gt;start&lt;/sub&gt; = 0%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal. 1</td>
<td>0.93</td>
<td>0.70</td>
<td>5.74</td>
<td>15.76</td>
</tr>
<tr>
<td>Cal. 2</td>
<td><strong>0.23</strong></td>
<td><strong>0.06</strong></td>
<td>6.41</td>
<td><strong>19.11</strong></td>
</tr>
<tr>
<td>Cal. 3</td>
<td>1.26</td>
<td>1.26</td>
<td>3.86</td>
<td>14.15</td>
</tr>
<tr>
<td>Cyc. 1</td>
<td>0.82</td>
<td>0.25</td>
<td><strong>0.22</strong></td>
<td>9.70</td>
</tr>
<tr>
<td>Cyc. 2</td>
<td>0.87</td>
<td>0.32</td>
<td><strong>6.74</strong></td>
<td>1.96</td>
</tr>
<tr>
<td>Cyc. 3</td>
<td><strong>2.71</strong></td>
<td>0.64</td>
<td>2.95</td>
<td>12.72</td>
</tr>
<tr>
<td>Cyc. 4</td>
<td>0.91</td>
<td><strong>1.69</strong></td>
<td>4.39</td>
<td>14.17</td>
</tr>
</tbody>
</table>

Therefore, following this process the algorithm enters a closed loop and converges to an imprecise solution. In contrast, the knowledge of only two plateaus assures the reduction of the global error in a more efficient manner and guarantees a faster convergence to more precise solutions. If only one of the plateaus is known (namely IA), the error in the estimation of the capacity increases dramatically reaching a value of 6.38% (charge) and 4.33% (discharge) when LAM<sub>Ne</sub> has a starting value of 10%, and a value of 14.46% (charge) and 12.51% (discharge) when LAM<sub>Ne</sub> has a starting value of 0%. The standard deviation is in one case above 2% and in the other case above 5%. The knowledge of the length of only plateau IA is not sufficient to properly track the degradation modes. In fact, the knowledge of the last plateau contains insufficient information regarding the entire voltage curve, and therefore the battery capacity cannot be calculated correctly. The evident highest error in the second case is related to the smaller initial value of the LAM<sub>Ne</sub> which is kept for the final calculation of the battery capacity due to a lack of tracking information on this mechanism.

### 6.1.3.4 Merging approach between charge and discharge process

The question which arises at this point is whether it is necessary to measure plateaus IA and IIA during charge (or discharge) to estimate the battery capacity correctly during charge (or discharge), or whether it suffices to measure one of the two plateaus during the charge process and the other during the driving operation. For example: is it possible to calculate both the total battery capacity during charge and discharge if the plateau IIA is measured during the charge process, and the plateau IA is estimated during the driving operation? A first attempt at answering this question is carried out by analysing the values of the DMs obtained by the algorithm and comparing them with the charge and discharge process estimation. In fact, if the DMs assume the same values, they could be used interchangeable, regardless of the process in which they were estimated. On the one hand, the analysis proves that the value of the obtained LLI is in all cases nearly identical for the same battery between the one estimated during charge and the one estimated during discharge. The difference between the two values delivered from the algorithm for the investigated cells oscillates between 2.2% and 0.3%
Diagnosis of LiFePO4 cells (average of 0.9%). On the other hand, taking a look at the obtained values of the $LAM_{Ne,De}$, the difference oscillates between 7.5% and 0.15% (average of 4%). In reality, the values of the obtained DMs for the charge and discharge process should almost coincide, as the analysis carried out on the two curves measured for the same battery should reflect the same aging state, irrespective of the analysed process (charge or discharge). The fact that in some cases a vast difference is found for the $LAM_{Ne,De}$ indicates that the use of only this DM plus the $LLI$ is sufficient to estimate the battery capacity, but insufficient to describes comprehensively the physic of the actual aging state of the battery. Probably, all DMs should be part of the aging, as only the right mix of them can describe the actual aging state correctly which can then be observed equally in both the charge and the discharge curve.

To overcome this problem, a second attempt is undertaken to observe whether a particular relationship can be found between the plateaus measured during charge and discharge, as already shown in Figure 5-18. In particular if the plateaus are again calculated following the methods introduced in section 6.1.2.3 $DOLQHDUUHODWLRQFDQEHIRXQGEHWZHHQWKHSODWHDXV¶$ length measured during charge and discharge during the battery lifetime. The relations which are discovered are shown in equations (6.11)-(6.12) for the plateaus IIA and IA respectively.

\[
Length_{IIA, DCH} = 1.9107 \cdot Length_{IIA,CHA} - 0.6408 \quad (6.11)
\]

\[
Length_{IIA, DCH} = 0.9201 \cdot Length_{IIA,CHA} - 0.0128 \quad (6.12)
\]

In equations (6.11)-(6.12) the terms “Length” is normalized in respect to the respective plateaus’ lengths measured for a cell in a pristine state. By using these relationships it is possible to obtain comprehensive information on the battery capacity (charge and discharge) only measuring two different plateaus, independently from the process they are measured. An example of the results obtained for two aged cells for all possible cases is listed in Table 6-4.

Table 6-4: Exemplary results of the estimation of the capacity through mixed plateaus’ information between charge and discharge process.

<table>
<thead>
<tr>
<th>Cell name</th>
<th>Process</th>
<th>Available plateau</th>
<th>Capacity / Ah</th>
<th>Error / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyc. 2</td>
<td>Charge</td>
<td>IIA from discharge</td>
<td>7.24</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IA from discharge</td>
<td>7.29</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Discharge</td>
<td>IIA from charge</td>
<td>7.67</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IA from charge</td>
<td>7.63</td>
<td>1.13</td>
</tr>
<tr>
<td>Cal. 1</td>
<td>Charge</td>
<td>IIA from discharge</td>
<td>7.09</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IA from discharge</td>
<td>7.25</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>Discharge</td>
<td>IIA from charge</td>
<td>7.52</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IA from charge</td>
<td>7.52</td>
<td>1.01</td>
</tr>
</tbody>
</table>

The limited error again proves the correctness of the working principle of the method. However, the necessity to measure the relationships shown in equations (6.11)-(6.12)
6 Diagnostic of LiFePO4 cells

represents a significant drawback. As mentioned in section 6.1.3.1, these relationships should be based partially on physical laws, which exclude the necessity of new and expensive parametrization routines each time the algorithm is adapted for a different cell type.

6.1.3.5 Continuous tracking of the capacity during driving

Another key aspect which should be analyzed is the stability of the calculated battery capacity. This refers to the variability of the measured battery capacity when the measurement is repeated several times in series. As mentioned by Waag in [66], in some cells the deviation between two consecutive measurements executed in a laboratory environment can reach 0.6%. Therefore, the question is how this behavior can influence the on-board estimation of the capacity also related to the measurement of the single plateaus. Measurements carried out in a laboratory with a CC discharge of 0.1C at 23 °C for the cell Cal. 1 have shown variations within 0.32% over a period of two months. This gives an indication of the correct reproducibility of the measured capacities and of the cell stability. In order to analyze the consequence of this effect on the results obtained by the algorithm, the cell Cal. 1 is discharged by employing different driving profiles based on the FTP75 and on real drive EV paths. The determined voltage behavior is then given to the plateau estimation approach introduced in section 6.1.3.2, and the results are used to estimate the total battery capacity for each one of the recorded profiles. For some of the profiles the estimation of the plateaus’ lengths cannot be considered valid: this is indicated by the large divergence in respect to the values estimated with other profiles. This may be related to the possible high and prolonged current rates occurring during a stage transition in the voltage curve, which makes the estimation of the exact plateau’s length difficult. The remaining values, which are considered correct, produce values of actual battery capacity with estimation errors of between 3.4% and 0.4%, with an average value of 1.95%. The high variation in the obtained capacity values can be related to:

1- The inaccuracy of the used EECM, which allows the correct estimation of the plateaus’ lengths only when the stage transitions can be clearly reconstructed (for example by using an additional diffusion branch which is current and temperature dependent).

2- The frequent presence during the driving operations of phases with high current rates, which may reduce the available reversible capacity and therefore falsify the estimation of the plateaus’ length.

Nevertheless, even though these effects have still not been investigated in detail, the employment of simple methods obtains reasonable results with limited and acceptable errors.

6.1.3.6 Merits and drawbacks

The presented method for on-board estimation of the battery capacity in LFP cells presents some clear merits which can be summarized as follows:
1- In order to calculate the battery capacity, it is not necessary to discharge the cell completely. The information contained in the plateaus is adequate. In particular, only the length of the plateau represents sufficient information.

2- Not all the plateaus are needed: the knowledge of three or two plateaus’ lengths is necessary and sufficient to correctly calculate the battery capacity. An average error of 0.98% (charge) and 1.10% (discharge) is obtained when three plateaus are known, and of 0.78% (charge) and 0.70% (discharge) when two plateaus are known. The knowledge of only one plateau does not assure the correct tracking of the degradation modes and therefore the proper estimation of the battery capacity.

3- Not all the information needs to be collected at the same time. This means that for example the information on plateau IIA can be collected during charge and on plateau IA during discharge. Nevertheless it must be assured that not much time passed between the collections of the different information.\(^{13}\)

4- Part of the proposed methodology can run offline. The term offline means that the approach is implemented in the microcontroller but does not need to be executed in real time. The estimation of the actual battery capacity can be done over a longer and extended rest period, for example, at night when the vehicle is parked. By this, the computational effort of the BMS microcontroller can be reduced and a less powerful and thus cheaper controller may be used.

5- The algorithm is easy to parametrize: only the characteristics of the cell in a new state are needed, in terms of stoichiometry and half-cell voltage curve. Some additional tests are needed in order to scale the collected plateaus correctly to the standard temperature and current rate conditions. The implementation of this dependency based on physical laws, which describe the phenomena, may save additional effort.

6- The method is valid for LFP vs. graphite cells, mainly due to the need of collecting information on plateaus. Nevertheless, the proposed model and the approach have a general formulation, which can also be used for other LiB chemistries. It is clear that in the specific case the formulation of the error necessary to track the degradation modes should be changed.

However, despite these merits, some drawbacks still remain:

1- The most important information resides in the plateaus’ lengths. Therefore it is necessary to measure a plateau without interruption. This means that occasionally it is necessary to discharge the battery during a normal driving operation to 30%-40% SoC.

2- When plateau IA is almost absent in the OCV curve due to degradation and is no longer evidently visible (its length cannot be defined clearly), some difficulties arise in the estimation of the capacity. The same happens when plateau IIA and IA cannot be

\(^{13}\) This period of time is related mainly to the ambient conditions and to the operation of the vehicle. In standard conditions (25 °C and daily driving operation of 40-60 km) a period not longer than 4-6 months should be considered.
6 Diagnostic of LiFePO4 cells

exactly distinguished, due to inhomogeneous aging or an excessive increase in the battery impedance, which makes it difficult to identify the respective stage transition.

3- In case the model presented in equations (6.2)-(6.5) has to be used to reproduce the battery voltage, the contribution of the impedance and its variation mechanisms during lifetime should also be included, especially for HE cells, where the contributions cannot be neglected even if the current rates are small.

6.2 Hysteresis model for SoC estimation

The estimation and determination of the SoC is one of the main tasks of a BMS. As discussed in chapter 4, different techniques exist for SoC estimation. Many of these methods are based on the knowledge of the relationship OCV-SoC. As discussed in detail in this work, in the case of LFP cells, this relationship is non-monotonous while the OCV itself presents an evident hysteresis. Moreover, as introduced in section 5.5, there is an extreme change in the relationship during battery lifetime, depending on DMs. This means that many of the methods presented in recent literature (such as [170][174]), which are based on complex filtering approaches but still relay on the OCV-SoC knowledge, are valid only for new cells, when the change of this relationship is not tracked during battery lifetime. This section presents an easy method for estimating the SoC in LFP cells based on the Coulomb counting approach. The method is able to determine the correct SoC value with limited errors without the need of complex filtering even when the initial SoC is unknown. Moreover, with the help of the novel approach for capacity estimation presented in the previous section, the relationship OCV-SoC can be easily adapted during battery lifetime.

6.2.1 Modeling of the hysteresis minor loops for online estimation

The model which is presented in this section for SoC estimation is based on the reproduction of the voltage behavior of the LFP cell in terms of OCV. This means that the voltage is modeled both in terms of major hysteresis boundaries and minor hysteresis loops. One of the possible manners to achieve this was already presented in section 5.5.4. However, the presented modeling approach may be too complex for implementation in a µC, due to the high amount of information which must be stored in the form of coefficients and lookup tables. Moreover, such accuracy may not be needed either, if compared with the number of experiments conducted to obtain sufficient knowledge of the modeled phenomena. Therefore, in the following an easier approach is shown, which assures a compromise between accuracy and parametrization effort. The model of the OCV is based again on the equation (5.1) presented in section 5.5 (Roscher et al. [177]). According to this relationship, the hysteresis factor $Ψ$ can be calculated following equation (6.13):

$$Ψ = \frac{OCV(SoC) - OCV_{Dch}(SoC)}{OCV_{Chg}(SoC) - OCV_{Dch}(SoC)}$$

(6.13)

Now, if the hysteresis factor is calculated for all the minor loops parametrized for new and aged samples, a clear trend can be detected. Figure 6-12 shows as example the coefficient $Ψ$.
plotted for all the loops identified for Cell A and Cell B reported in Table 5-8. The coefficient \( \Psi \) is plotted versus the \( \Delta \text{SoC} \) required in order to enclose the minor loops, and normalized with regard to the initial SoC. For the charge process of the minor loops shown in Figure 6-12a), a steep increase of the hysteresis factor during the first 5% of charge throughput and a subsequent slower increase are observed.

**Figure 6-12:** Hysteresis factor plotted for the minor loops identified for a new and aged cell, a) for the charge steps of the minor loops, b) for the discharge steps.

According to this behavior, an exponential function can be used for the description of \( \Psi \) in the form of equation (6.14):

\[
\Psi = 1 - e^{-k_{\text{Cha}} \Delta \text{SoC}}
\]  

(6.14)

The value of \( k_{\text{Cha}} \) is a factor which describes how steep the increase of the hysteresis factor is. As for the identified loops, the value of \( \Psi \) reaches a value around 0.5 after a \( \Delta \text{SoC} \) of 5% in the entire SoC range. According to this criterion, the value of \( k_{\text{Cha}} \) can be obtained according to equation (6.15):

\[
k_{\text{Cha}} = \frac{\ln(1 - 0.5)}{0.05} = 13.86
\]  

(6.15)

A similar discussion deals with the behavior of the minor loops for the discharge steps. Therefore a \( k_{\text{Dch}} \) factor can be defined according to equation (6.16):

\[
\Psi = e^{-k_{\text{Dch}} \Delta \text{SoC}}
\]  

(6.16)
which value can be obtained according to equation (6.17) setting a value of the hysteresis factor of approx. 0.35 at 5% ΔSoC.

\[ k_{\text{Dch}} = \frac{\ln(0.35)}{0.05} = 20.99 \approx 21 \]  

With this easy formulation, a limited computational effort in the calculation of the hysteresis factor can be assured, together with a limited parametrization effort. Nevertheless, as will be demonstrated, sufficient accuracy is obtained in the OCV modeling and SoC estimation.

### 6.2.2 Working principle of the algorithm for SoC estimation

Based on the values obtained in the previous section, the OCV can be calculated by just knowing the SoC (Ampere-hour counting based), the actual major hysteresis boundary curves and, in the case of partial charge or discharge events, the charge throughput. The major hysteresis boundaries are stored in the form of lookup tables, and are adapted during battery lifetime due to the information derived from the capacity estimation algorithm introduced in section 6.1. The recalibration of these curves is presented in section 6.2.4. In order to calculate the behavior of the OCV between the major hysteresis boundaries, the hysteresis factor has to be estimated. This is only calculated by the exponential functions when the OCV does not lie on the charge or discharge hysteresis boundaries. Summarizing, the hysteresis factor \( \Psi \) works according to the following rules:

- \( \Psi \) is zero and still discharging \( \rightarrow \) \( \Psi \) remains zero;
- \( \Psi \) is one and still charging \( \rightarrow \) \( \Psi \) remains one;
- \( \Psi \) is zero and the process change from discharge to charge \( \rightarrow \Delta \text{SoC} \) is initialized to zero and calculation of \( \Psi \) according to equation (6.14);
- \( \Psi \) is one and the process change from charge to discharge \( \rightarrow \Delta \text{SoC} \) is initialized to zero and calculation of \( \Psi \) according to equation (6.16).

If the current sign changes during a partial charge or discharge cycle, it is assumed that \( \Delta \text{SoC} \) changes as if the same point was reached by a charge or discharge event starting from one of the corresponding boundary curves (charge boundary in case of current sign change from positive to negative and vice versa). Moreover, a complete recalibration of \( \Psi \) is made when the cell is either fully charged or empty.

The modeling approach for the OCV is used as a means to estimate the battery SoC correctly. As mentioned, to estimate the OCV in a defined operating condition, the value of the SoC must be known, so that the equation (5.1) can be correctly employed. The SoC is calculated with a simple Coulomb counting method. If the starting or the actual value of the SoC is false, the calculated OCV is incorrect and does not match the real value. Therefore, every time that an OCV value is measured between the battery’s poles after a sufficiently long rest period, the predicted and measured values can be compared and the remaining error can be used to recalibrate the SoC. A schematic representation of the working principle of the entire SoC
estimation algorithm is shown in Figure 6-13 and Figure 6-14. Figure 6-13 describes the implemented approach for SoC estimation, highlighting the initialization mechanism of the SoC and the calculation of the SoC based on the Ampere-hour counting and on the use of the OCV model. Figure 6-14 shows the recalibration methods of the SoC based on the possible measured OCV. Moreover, as introduced in both pictures and explained in detail in sections 6.2.2.1 and 6.2.2.2, two different approaches are implemented and tested.

**Figure 6-13:** Working principle of the SoC estimation algorithm.

The term “recursive approach” refers to the capability to recalibrate the SoC continuously during a relaxation period until the error between measured and predicted voltage is below a defined threshold. The term “non-recursive approach” refers to the possibility of recalibrating the SoC during each relaxation period only once after the waiting time has passed. The initialization process and the correction of the SoC value for the two approaches are described in the next sections.
Figure 6-14: Recalibration of the SoC Coulomb counting based method with two different approaches.

6.2.2.1 Algorithm initialization
The proposed algorithm is able to estimate the SoC correctly without knowing its initial value. This is done by means of the available OCV value at the initialization of the algorithm, even though the OCV of the tested cell presents flatness features with evident hysteresis. By starting with an initial measured OCV, the charge boundary is used to find the minimal SoC by using the following criteria:

\[ OCV_{cha}(SoC_{min}) \geq OCV_{initial} \] (6.18)

Equation (6.18) relies on the fact that a given OCV always lies between the boundary curves. Following equation (6.19)

\[ OCV_{dch}(SoC_{max}) \leq OCV_{initial} \] (6.19)

the error band in which the real SoC lies can be defined as:
Following this criteria, the initialization process of the SOC for the non-recursive and recursive approach is slightly different, as depicted in Figure 6-15.

**Figure 6-15:** Initialization process of the SoC algorithm.

For the non-recursive method, the initial SoC is chosen exactly in the middle of the SoC error band. By doing so the average error is always assumed to be minimal.

\[
SoC_{\text{initial}} = 0.5 \cdot (SoC_{\text{max}} - SoC_{\text{min}})
\]  
(6.21)

The maximal SoC error (width of the SoC band) can be calculated as follows:

\[
Error_{SoC} = SoC_{\text{initial}} - SoC_{\text{min}}
\]  
(6.22)

For the recursive approach, the initial SoC is set to the calculated minimum SoC. This represents the worst case SoC.

\[
SoC_{\text{initial}} = SoC_{\text{min}}
\]  
(6.23)

The maximum SoC error (band gap of SoC) is bigger than the one for the non-recursive version:
Generally speaking, the SoC error can be significantly higher when the initial measured OCV lies in a plateau region or small if it lies in a stage transition. Moreover, the initial SoC error of the non-recursive version is always smaller than the one of the recursive version. The initial value of $\Psi$ is calculated by using equation (6.13) for both versions.

6.2.2.2 SoC recalibration

The correction of the SoC is done when a measured OCV value is available after a minimum of three hours rest. The resulting OCV error is calculated and subsequently minimized by using the non-recursive or recursive approach according to equation (6.25):

$$\text{Error}_{OCV} = OCV_{\text{measured}} - OCV_{\text{modeled}}$$  \hspace{1cm} (6.25)

In case the actual SoC is too small, the resulting error will be negative, and vice versa. Moreover, since the proposed approach with the exponential function does not reconstruct the OCV precisely and due to the long plateau phases present in the OCV curve, the SoC correction is only conducted if the OCV error is greater than the intrinsic error of the model (around 5 mV). By doing this, the stability of the algorithm is ensured. As the hysteresis factor does not rely on the actual SoC but only on the charge throughput between a charging and discharging event, $\Psi$ remains unchanged during the SoC adaption.

For the non-recursive approach, one adaption step is done during every pause interval greater than three hours. The SoC is corrected by adding or subtracting half of the actual SoC error band:

$$\text{SoC}_i = \text{SoC}_{i-1} \pm 0.5 \cdot \text{Error}_{\text{SoC}}$$  \hspace{1cm} (6.26)

where the index $i$ defines the current time step. The SoC error is added if the calculated OCV error is greater than zero and subtracted if it is smaller than zero. Afterwards the new SoC error is calculated for the next correction step. The OCV is then calculated according to equation (5.1) with the new SoC. With this method the SoC band gap is minimized until it is close to zero. In this condition, to be able to correct the SoC, a minimum SoC error can be set to an arbitrarily chosen value (e.g. 1%). This may be necessary in order to correct the error generated by the additionally used Coulomb counting algorithm.

For the recursive approach, the SoC is adapted continuously in every pause interval greater than three hours until the OCV error is smaller than the intrinsic OCV error of the model. This is achieved by adding a certain SoC value to the current SoC (in this case a step of 0.1% is used):
The OCV is then calculated according to equation (5.1) with the new SoC.

### 6.2.3 OCV modeling and SoC tracking

An exemplary validation of the modeling of the OCV behavior is depicted in Figure 6-16. The data refers to Cell B of Table 5-8. In this case the value of the initial SoC is specified as known, as the goal is to observe if the model is able to reproduce the OCV behavior properly.

![Figure 6-16](image.png)

**Figure 6-16**: Exemplary validation of the voltage modelling for Cell B of Table 5-8 for ambient temperature of 23 °C. a) SoC and Ψ profiles, b) measured voltage and modelled OCV, c) OCV error, d) comparison between measured and modeled OCV points represented in form of minor loop.

Figure 6-16 demonstrates the validity of the model approach even if based on simple assumptions. The modeled OCV mirrors in almost the entire SoC range the measured relaxed voltage, as depicted in Figure 6-16c) and d). Only after 20 h does the voltage error increase to 7.4 mV, due to the fact that the model is able to reproduce only voltage points which are within the major hysteresis boundaries. This is not the case in the points measured after 20 h, as shown in Figure 6-19d).
An exemplary validation of the two SoC approaches is shown in Figure 6-17. The data refers to Cell F2 of Table 5-11 and are obtained testing the cell with a mix of driving profiles (FTP75), charging phases and pauses.

![Figure 6-17](image)

**Figure 6-17:** Exemplary validation of the two SoC estimation approaches for a mixed profile for Cell F2 of Table 5-11 for an ambient temperature of 23 °C, a) measured and estimated SoC, b) measured voltage and modelled OCV, c) OCV errors, d) SoC errors.

As can be observed, even without knowing it, in both cases (non-recursive and recursive method) the initial SoC is set in a proper range, so that the initial SoC error is limited within 2%. During each pause the SoC is corrected based on the voltage error and adapted in order to reduce it. Figure 6-17d) shows that the error band for the SoC for the non-recursive method is reduced from approximately 2% to 1% while the error remains at around 0.5%. Considering the recursive approach, only the reference error and the maximum error are shown, as
described in section 6.2.3. In particular, the maximum SoC has to be read as difference with the reference error. In this case it is also apparent that the error band is reduced during the profile, going from approx. 3% at around 10 h up to 1% after 15 h until the end. One might assume that this kind of approach is not able to properly detect the battery SoC if the cell is currently cycled in a plateau and if the initial SoC value is unknown. To observe this behavior the two methods are tested with the profile shown in Figure 6-18. The data refers to Cell B of Table 5-8.

Figure 6-18: Exemplary validation of the two SoC estimation approaches for profile obtained in the middle SoC range for Cell B of Table 5-8, a) measured and estimated SoC, b) measured voltage and modelled OCV, c) OCV errors, d) SoC errors.

One can see that the value of the initial SoC selected from the algorithms is wrong for both approaches: the real SoC value is approx. 60% while the selected value is 80%. During the first 10 h both methods are not able to correct the SoC, as the error between measured and
predicted voltage is smaller than 5 mV (the cell is cycled in the middle of plateau IIA). As soon as the real SoC moves outside of the plateau (after approx. 12.5 h), the modeled OCV no longer matches the measured OCV due to the SoC error. Therefore a correction can take place. Because the non-recursive method only carries out one correction, the complete elimination of the error is not guaranteed when the cell returns to the plateau region again during the cycle. With the recursive method, on the other hand, the one measured OCV value outside of the plateau is sufficient to reduce the error from 20% to 3.6% with a reduction of the band gap from 40% to 7.2%.

6.2.4 Recalibration of the hysteresis model

Once the offline algorithm has tracked the DMs and calculated the total battery capacity, this information can be used by the BMS to recalibrate the hysteresis model which might be employed for battery modeling or for SoC determination. The recalibration is applied to the OCV hysteresis boundaries for the charge and discharge process in the BMS in the form of lookup tables. In this case the OCV values are stored in a range between 10% and 90% SoC with steps of 5%. To adapt each single value, the actual quasi-OCV curves for the charge and discharge process can be reconstructed due to the recovered DMs. These curves are compared with the quasi-OCV curves of the cell in a new state, and the differences of voltage are calculated. The obtained values are normalized following equation (6.28):

\[
\Delta V_{\text{Hyst}} = \frac{\Delta V_{\text{qOCV}}}{\Delta V_{\text{qOCV}}} \cdot \Delta V_{\text{Hyst}}
\]

In equation (6.28), \(\Delta V_{\text{Hyst}}\) and \(\Delta V_{\text{qOCV}}\) represent the voltage difference between the new and the aged cell for each SoC point for the OCV and quasi-OCV curves respectively; \(\Delta V_{\text{Hyst}}\) represents the difference between the maximum and minimum voltage in the SoC range for each of hysteresis curves (charge and discharge), while \(\Delta V_{\text{qOCV}}\) has the same meaning but for the quasi-OCV curves. The \(\Delta V_{\text{Hyst}}\) values obtained for each SoC are then added to the actual OCV values in the lookup table. An example of the recalibration effect is shown in Figure 6-19. Figure 6-19a) shows again the effects of the DMs on the shape of the OCV hysteresis curve. Figure 6-19c) depicts the error in Volts among the two curves both for the charge and discharge. The error is substantial especially in the low and high SoC range. In the middle SoC range it remains limited, due to the flatness of the OCV curve. The results of the recalibration are shown in Figure 6-19b) and in d). The plot shows that the error is reduced to 20 mV for almost the entire SoC range, especially in the high and low SoC range, for both charge and discharge. This again validates the presented method and assures correctness of the tracked aging mechanisms.
Figure 6.19: Recalibration of OCV hysteresis model by means of tracked degradation modes, a) OCV hysteresis measured for a new (blue circles) and for an aged cell (red rhombus) during charge and discharge, b) OCV hysteresis of the aged cell (red rhombus) and hysteresis of the new cell (green squares) after recalibration, c) error between OCV of a new and aged cell, d) error between OCV of an aged and a new cell after recalibration.

6.3 Further system development towards microcontroller implementation

The next step, which follows the proof of concept of a diagnostic algorithm, is its complete “translation”, i.e. the preparation of the developed methods for complete implementation and integration in μC and their validation in the field. In this work, some suggestions are provided on how the presented methods can be prepared for field testing and where difficulties and problems might arise. It must be pointed out that the methods presented in this chapter have already been partially designed in a simple way in order to reduce the steps to the μC implementation as much as possible.

Concerning the SoC estimation methods described in section 6.2, the need for a high amount of storage memory can be attributed to the lookup tables for the storage of the OCV curves (charge and discharge) and of their temperature dependency. Regarding the rest of the procedure used in the implemented algorithm, this does not require any vectors, so that the implementation is possible with a μC with limited memory (in the order of tens of kByte). Regarding the complex functions, such as exponential calculation, these can be implemented in form of lookup tables.
The method presented in section 6.1 for the on-board estimation of the total battery capacity may present some other difficulties. As mentioned, the way the method is designed is already an additional step towards field testing. In fact, the main calculation of the DMs can be carried out offline (VPA algorithm), giving the possibility to employ the full potentiality of the μC only for the DMs tracking process in a period when the car is not in operation. The biggest effort must be undertaken in the detection of the plateaus’ lengths during the driving operation, during a CC charge process or during the offline DMs tracking process. In this case the methods used to evaluate the concept phase must use vectors, in which to store the voltage and charge throughput samples. The optimization process, which delivers the optimal length of these vectors, is related to the accuracy of the voltage measurement, the sample rate and the desired accuracy in the estimation of the actual battery capacity. Nevertheless, limiting the number of samples per vector to 10-20 values should guarantee an acceptable compromise between accuracy and memory. The other main issue concerns the data which has to be stored in the μC memory related to the quasi-OCV curves of anode and cathode for a new cell. It would be simpler to store them in form of lookup tables in the EEPROM of the master board. This would involve a large storage capacity depending on how many samples are saved. For instance, if the voltage curve of anode and cathode are stored with vectors of approx. 50,000 samples, both for the charge and discharge process (four curves), together with an Ah-throughput vector, by using a float32 format for each value, a storage memory of approx. 1 MB is needed. The size of these vectors can be simply reduced by storing a defined value of the voltage curve only if there is a remarkable difference with the previous sample. In this case, by using vectors of only 500 samples, the needed storage memory is reduced to approx. 9 kB. However, some tests have shown that reducing the amount of saved samples by eliminating values in the flat regions of the curves can have a significant impact on the calculation of the plateaus’ lengths, which ultimately has an indirect influence on the finally acquired capacity. Therefore, it is pivotal for correct calculation, that these curves are accurate (i.e. limited interpolation operations). Substituting the mentioned electrode curves with fitting functions would be a further possibility. This operation also poses various problems, mainly due to the operations with huge numbers (coefficient of the fitting functions) which should be avoided in the μC environment, in addition to the exactitude these curves should have. For these reasons, the best and most feasible solution is to store the detected curves in a large memory EEPROM. The accuracy of the voltage sensor placed in the battery packs, i.e. the influence of the measurement accuracy on the detection of the plateaus’ lengths and therefore on the final capacity is another fundamental issue. This issue cannot be evaluated without any real data. However, for a proper estimation of single cells and pack state with LFP batteries, a measurement accuracy of the voltage within 2-3 mV must be guaranteed. This is the price to pay for the use of this particular LiB chemistry. Accuracy below these values may be harmful even if complex diagnostic methods are used, because the physico-chemical features of the cell cannot be changed.
6.4 Summary

Even today, the diagnostic of LFP cells remains a big challenge, due to the particular features of LFP cells. In this chapter, a chain of novel methods for the estimation of the actual state of LFP cells is presented. The estimation of the actual battery capacity is carried out by detecting the actual DMs which took place in the cell during its lifetime. These are estimated by observing the behavior of the voltage plateaus and comparing their lengths with the ones of a new cell. With this information, the actual quasi-OCV can be reconstructed and the total capacity estimated with an error within 2%. The obtained information can be used for the recalibration of the OCV curves presented in the BMS for battery modeling or SoC estimation. Two simple approaches are presented, which calculate the SoC of LFP cells precisely and correct possible errors for cells in different aging conditions. As demonstrated, the initial incorrect estimation of the SoC due to the presence of flat regions can be corrected instantaneously and accurately as soon as the flat regions are abandoned, regardless of the aging state of the cell. The connections and iterations of the presented methods is at the base of the presented new BMS structure, which highlights again the importance of understanding the intrinsic physico-chemical behavior of the cell and using the obtained knowledge for correct state detection during the entire battery lifetime.
7 Aging of Lithium-Ion batteries in a V2G scenario

The vehicle-to-grid concept, indicated usually with the abbreviation V2G, is one of the possible ways to realize the integration of PHEVs and BEVs in the energy system completely. Moreover, its implementation may be of fundamental importance because if the EVs can be used as a profitable source this might promote acceptance of new vehicles concepts. However, the double use of batteries, i.e. for driving and for electric grid services, produces additional aging effects in the cells and therefore a shortening of their lifetime.

In this chapter, the behavior of a V2G system composed by several EVs is analyzed. The goal is to analyze the behavior of the battery packs of EVs as soon as the additional cycle operation due to the V2G services is requested. A strategy to optimize the use of the EV fleet is implemented and tested, in order to choose the best combination of vehicles which would limit overall aging and would return the best economic profit. In order to investigate this effect, the battery packs are modeled through battery electric and aging models of two different LiB chemistries, in order to reproduce the different characteristics which EVs may have in the near future. The implemented strategy is compared with a random allocation of vehicles for grid services. The results show that the fleet utilization in terms of battery lifetime is improved, even though similar batteries age differently (e.g. due to variability caused by cell production). Eventually, the presented model can be used as a tool to test different vehicle utilization strategies based on the requested grid power profile. The content of this chapter are partially based on [179].

7.1 Batteries in the V2G system

As mentioned earlier, the use of PHEVs and EVs for V2G services implies an additional cycling of the car battery packs, and therefore a reduction in the battery lifetime, which is presently the most expensive component in a vehicle. Thus, strategies which limit this additional effect must be developed in order to use the vehicle as an additional energy source, thereby gaining acceptance on the market. Recent literature has only marginally dealt with this important aspect and if, the results are often only a simplified representation of the reality and they may no longer be reliable. As mentioned in section 4.2, fundamentals of V2G can be found in [108][109]. Different V2G applications and particular scenarios are referenced in [202][203][204][205]. Talebizadeh et al. in [202] study which impact the connected vehicles have on the grid in a V2G system with regard to the standard IEEE 10-unit. The influence of 50,000 EVs on the cost of the unit commitment problem is scrutinized, without considering the effect of aging the strategy has in each battery pack. In [203] and [204] attention is again focused on the operation principle of the grid strategy and how the charging strategy can be shifted for an optimal and economical use of the energy in the vehicles. The studies cited in
the literature suggest that the combined V2G-battery aging effect is limited. Valuable information can be found in references [206][207][208][209]. Peterson et al. [206] systematically aged thirteen cells with a combination of drive profiles and V2G operations, showing the real effect that the V2G strategy has in cell lifetime. The investigation does not take into account that in reality the condition under which the battery is subjected might vary hugely, in terms of temperature and power requested from the grid. Bashash et al. [207] consider the effect that the V2G strategy might have on the grid if the charging process is scheduled in order to limit battery aging. A similar study which investigates different scenario and showing the economic advantages for customers was carried out by Lunz et al. [208]. Guenther et al. [209] have made remarkable contributions in this direction: they studied the impact of grid service activities on EV battery lifetime under different scenario over a period of approx. ten years. The simulation was carried out for one vehicle only but in different scenarios, presuming again that the battery is subjected to the same condition throughout the observed time frame. Only the ambient temperature varied throughout the year. This is a parameter which may under no circumstances be neglected, when the aging mechanisms in lithium battery in a long-term is considered. The analysis of the state-of-the-art makes it clear that the presented models and investigations do not represent reality comprehensively, as some important and fundamental key factors always are missing. Therefore, a tool, which simulates the impact of the V2G operation on vehicle batteries, must be developed in order to reflect as much as possible real operating conditions.

7.2 Model of aging in a V2G environment

The general idea of the proposed model is schematically presented in Figure 7-1.

![Figure 7-1: General structure of a V2G scenario from the view of the EVs. The picture highlights the fundamental differences in the battery type and SoH with which each EV can be equipped.](image_url)

The main components are the grid and the EVs as energy storage systems. The following exchange of information between the two actors takes place in form of:

- Power, which the grid needs to satisfy the momentary requirements.
- The value of the battery SoH variation that each power profile requested from the grid will cause in the battery pack.

In order to maintain a high variability of the different participants (i.e. EVs), one must remember that the batteries in the different vehicles contain different cell chemistries. Moreover, if one individual vehicle is compared with to another, the actual battery SoH is different, as each battery had its own history, and thus has aged differently during its lifetime. These two factors play an important role, especially in terms of grid decisions, because the initial battery investment depends on the single battery type (chemistry and manufacturer), as well as on the aging kinetics which depend also on the actual battery SoH.

The communication between grid and cars in the proposed V2G systems takes place according to the mechanisms depicted in Figure 7-2, following four steps:

**Figure 7-2:** Scheme of the communication procedure between EVs and grid in a V2G scenario in which the battery SoH is considered as a fundamental factor.

1. The grid collects all the information from the available EVs, i.e. the cars that are connected to the net and not in the charging process at a defined moment. This information might, for example, consist of the actual battery SoC and SoH. At this moment in time the grid also knows the power requests in the near future.

2. The grid can propose and send information to each available car in form of a package with $N$ different load profiles (each one with different value of peak power), fulfilling the following condition:

$$\sum_{i=1}^{m} P_{n,m} = P_{req} \rightarrow n = 1,2 \ldots N$$  \hspace{1cm} (1)
where \( m \) is the number of cars, \( N \) is the total number of the transmitted usage profiles, and \( P_{\text{req}} \) is the power requested from the grid in the moment in which the communication takes place (from the grid side, the value of the power can be positive or negative, in case of battery discharge or charge respectively).

3. For each of the \( N \) usage profiles proposed, the BMS of each vehicle has to predict the possible SoH variation that every profile would generate on the battery pack. In order to accomplish this, the BMS has to be equipped with aging prediction models able to prognosticate the battery lifetime depending on the future short term conditions, in terms of environment (ambient temperature) and operation (battery current rate).

4. The grid receives the whole information from each EV and calculates which is the best combination of load profiles that can be used to:
   a. Satisfy the grid requirement in terms of power;
   b. Limit as much as possible the SoH variation of the entire available EVs.

The question which may arise is what the near future means, and how often the communication process should take place. A possible solution proposes the definition of a time window as a fundamental element of the system; for example, the window can have duration of one hour. Inside each window, the communication process between EVs and grid takes place in the early stage. Thereafter and until the end of the time window each available EV is either i) cycled with the specified load profile, or ii) in standby or idle mode, because the grid has come to the conclusion that is not economically convenient to cycle a defined car in this time window in respect to other cars.

The entire system is implemented in Matlab/Simulink©. Figure 7-3 shows the diagram of the implemented structure. The three main components, i.e. battery models, time manager system algorithm and business model algorithm are introduced in the next sections.

**Figure 7-3:** Simulation setup, with the subsystems that compose the environment, and with the communication between the different components.
7 Aging of Lithium-Ion batteries in a V2G scenario

7.2.1 Battery models

Two different LiB chemistries are considered to model the battery packs of the single EVs. One of the two selected batteries is the LFP cell presented in detail in chapter 5. For the sake of simplicity, this cell type is named as Cell LFP in the following, as indicated in Figure 7-3. General characteristic of the cell can be found in Table 5-1. The second type of battery is an NMC-based LiB. From now on, this cell type is named Cell NMC, and its characteristics are reported in Table 7-1.

Table 7-1: General characteristics of the considered NMC-based cells.

<table>
<thead>
<tr>
<th>Type</th>
<th>SLPB100216216HR2 (HP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Graphite</td>
</tr>
<tr>
<td>Cathode</td>
<td>LiNi$<em>{1/3}$Mn$</em>{1/3}$Co$_{1/3}$O$_2$</td>
</tr>
<tr>
<td>Nominal capacity</td>
<td>40 Ah</td>
</tr>
<tr>
<td>Nominal voltage</td>
<td>3.7 V</td>
</tr>
<tr>
<td>Shape</td>
<td>Pouch-bag</td>
</tr>
</tbody>
</table>

For each of the two selected cells, 50 battery models are considered. In this way, the differences between the EVs can be defined not only through the cell chemistry, but also through the actual SoC and SoH. Each battery model is composed of an EECM and an aging prediction model. The EECM employed is the typical model presented in Figure 3-4, and its parametrization for the two selected cells is carried out by the measurement of the OCV behavior and by EIS. The latter is executed in a frequency range of 2 mHz – 5 kHz, for five different ambient temperatures (-10, 0, 10, 25 and 40 °C) and for seven SoC values (100%, 90%, 70%, 50%, 30%, 20% and 10%). Refer to [29][210] for typical procedures and approaches used for parametrizing a battery EECM based on EIS. The information is stored in the model as lookup tables and linearly interpolated for values which fall within the mentioned ranges. The aging prediction models implemented to simulate the degradation and to predict battery aging in V2G systems are based on semi-empirical approaches obtained by accelerated aging tests. Accelerated aging tests for the Cell LFP were already presented in section 5.3. An identical procedure is followed for the Cell NMC, with some small change both for the calendar and for the cycle tests$^{14}$. Results for the capacity fade trend are reported in Figure 7-4a) for the calendar conditions and Figure 7-4b) for the cycling conditions. Data related to the evolution of the internal resistance during lifetime can be found in appendix 10.9.1. Figure 7-4 shows that while similar conclusion can be drawn for the calendar aging conditions as the ones obtained for the Cell LFP, apparent differences can be observed for cycle conditions. In detail, Figure 7-4b) illustrates a non-dependency from the

---

$^{14}$ The calendar tests are carried out for 40, 50 and 70 °C ambient temperature, while for 50 °C the SoC 20%, 50%, 80% and 100% are investigated. For the cycle tests the current rate 1C, 1.5C and 2C for the DoD 10%, 50% and 80% are investigated.
current rate keeping constant the DoD, even though the used values are not very high (CC discharge up to 12C are allowed according to the manufacturer). Such behavior has not yet been documented in contemporary literature. This behavior facilitates the modeling of degradation during cycle aging, as the factor current rate does not need to be treated. The data obtained from the accelerated aging tests is used to parameterize degradation models for both cell types. The model is implemented in such a way that the total aging of the cell is obtained considering the contribution of the calendar and the cycle aging separately. In this manner, the overall degradation of the battery can be calculated as the sum of the cycle (when present) and calendar (always present) contributions in each moment in time. Therefore a fitting process is carried out separately on the results from the calendar and from the cycle tests, as shown exemplarily by Ecker et al. in [120].

![Graph](image)

**Figure 7-4:** Evolution of the capacity fade (a) during the calendar aging tests and (b) during the cycle aging tests for the overall cell batch for the Cell NMC.

Two different degradation models are generated. One is for the capacity fade and one for the resistance increase. During the tests it has been observed that for the tested cells (HP) the capacity fade takes place for each investigated conditions with a higher rate than the increase of resistance. Therefore, the total SoH (defined as the lowest value between actual relative capacity and resistance) always coincides with the actual capacity value, which also determines the EOL criterion. Thus, in the following, only the parameters obtained for the capacity degradation model are introduced. Moreover, this also allows a better understanding of the results of the optimization strategy, as only dependent on one degradation parameter. Two different model formulations are tested. In this chapter only one is presented, while the remaining is reported in appendix 10.9.2 together with the corresponding results. For both cells, the calendar aging model takes into account the effect of time, temperature and SoC (voltage), as shown in equation (7.1) for the Cell LFP and in equation (7.2) for the Cell NMC:

\[
\Delta Q_{\text{cal}} = \left(a_1 \cdot a_2 \frac{(\text{Temperature} - 23)}{10}\right) \cdot e^{(a_3 \cdot \text{Voltage})} \cdot \sqrt{\text{time}}
\]  

(7.1)

\[
\Delta Q_{\text{cal}} = \left(a_1 \cdot a_2 \frac{(\text{Temperature} - 23)}{10}\right) \cdot e^{(a_3 \cdot \text{Voltage})} \cdot \text{time}
\]  

(7.2)
where $\Delta Q_{\text{cal}}$ represents the variation of the normalized battery capacity (in respect to the initial capacity) due to calendar aging and $a_i$ the fitted coefficients. The cycle model takes into account the DoD and current rate for the Cell LFP and only the DoD for the Cell NMC in form of a Wöhler curve, as shown in equation (7.3) and (7.4) respectively:

$$EFC = b_1 \cdot I^{b_2} \cdot b_3 \cdot DOD^{b_4} \quad (7.3)$$

$$EFC = b_1 \cdot DOD^{b_2} + b_3 \quad (7.4)$$

where $b_i$ is the fitting coefficient for the cycle model and $I$ is the current rate. The value of the equivalent loss of capacity is calculated according to equation (7.5) for both cell types:

$$\Delta Q_{\text{cyc}} = \frac{0.2}{EFC} \quad (7.5)$$

where $\Delta Q_{\text{cyc}}$ represents the variation of the normalized battery capacity due to cycle aging, while the coefficient 0.2 represents the normalized 20% of capacity fade necessary to reach the EOL criterion. The final value of normalized actual capacity is obtained by summing up the contribution of the calendar and cycle aging and subtracting them to the value at the BOL, as shown in equation (7.6):

$$Q_{\text{actual}} = 1 - (\Delta Q_{\text{cal}} + \Delta Q_{\text{cyc}}) \quad (7.6)$$

Finally, the value of the actual SoH is calculated according to equation (7.7):

$$SoH = \frac{Q_{\text{actual}} - Q_{\text{EOL}}}{Q_{\text{BOL}} - Q_{\text{EOL}}} \cdot 100 \quad (7.7)$$

A value of SoH of 100% indicates a new cell, a value of SOH of 0% indicates a cell that has reached the EOL criterion. The obtained fitting coefficient for the calendar and cycle model for both cell types are reported in Table 7-2. Exemplary validation of the fitted models with the measured degradation data for both cell types are depicted in Figure 7-5 both for capacity fade, for calendar models and for cycle models. While the calendar model for the Cell LFP reproduces the measured data correctly in most conditions, the calendar model for the Cell NMC reproduces only qualitatively the capacity behavior. The first reason can be found in the increase of capacity at the beginning of the lifetime for some conditions, a phenomenon which cannot be reproduced by the proposed model approach and which makes the prediction imprecise. The second reason is related to the necessity of limiting the total lifetime of the battery to a reasonable value (approx. 15 years at 25 °C at 50% SoC). According to this choice, the fitted model fulfills this requirement, but fails partially in the quantitative reproduction of the behavior.
Table 7-2: Coefficients obtained for the two tested LiBs for the calendar and cycle aging models.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Cell LFP</th>
<th>Cell NMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>$5.66 \times 10^{12}$</td>
<td>$2.74 \times 10^{13}$</td>
</tr>
<tr>
<td>$a_2$</td>
<td>1.61</td>
<td>2.63</td>
</tr>
<tr>
<td>$a_3$</td>
<td>6.03</td>
<td>4.78</td>
</tr>
<tr>
<td>$b_1$</td>
<td>699.99</td>
<td>$1.57 \times 10^5$</td>
</tr>
<tr>
<td>$b_2$</td>
<td>-1.19</td>
<td>-0.098</td>
</tr>
<tr>
<td>$b_3$</td>
<td>370.53</td>
<td>$-9.72 \times 10^4$</td>
</tr>
<tr>
<td>$b_4$</td>
<td>-0.57</td>
<td>-</td>
</tr>
</tbody>
</table>

Moreover, the choice of two different behaviors in respect to the time (linear for Cell NMC and exponential for Cell LFP) represents a factor which influences the chosen V2G strategy, which effect can be observed in the proposed tool.

**Figure 7-5:** Validation of the calendar and cycle aging model for the tested cells, a) calendar aging model validation for the Cell LFP and b) for the Cell NMC, c) cycle aging model validation for the Cell LFP and d) for the Cell NMC.

The same phenomenon occurs in the cycle model validation, albeit inverted. While for the Cell NMC the model reproduces the measured data perfectly (due to the single dependency from the DoD), for the Cell LFP this happens only qualitatively. In fact, as mentioned in section 5.3.2, the analysis of the data does not show any clear dependency on the investigated
parameters. Moreover, because of the non-uniform aging between the different samples, together with the sudden decline of the capacity shown under some test conditions, it is difficult to generate a model which can quantitatively reproduce the observed behaviors. Therefore, the proposed model is created only considering some test conditions with the intent of developing an approach which represents and reproduces the qualitatively battery behavior\textsuperscript{15}. It should be said that it is not the objective to develop a tool that simulates reality but one that studies the effect of operating strategies on the battery aging behavior changing the influences on defined factors. To this end, the models proposed above are more than sufficient.

### 7.2.2 Time manager subsystems

The Time Manager System (TMS) controls and leads the entire simulation environment. Therefore, the system controls each of the 100 EVs and activates/deactivates the communication with the grid throughout the simulation. For each EV, the system generates three signals that describe in detail the state of every car:

1. **Vehicle status**: a binary signal that can assume the value of one if the respective car is connected to the grid in a defined moment, and the value of zero if the car is in the driving phase;
2. **Profile signal**: a signal that can assume a value between one and six (one to four \( \rightarrow \) different driving profiles, which the car can be subjected to, if in the driving operation; five \( \rightarrow \) the car is in the V2G operation; six \( \rightarrow \) the car is in the charge process);
3. **Departure signal**: a signal that defines the departure time of each car, i.e. at which time the car starts the driving phase.

The state of each car (the three signals above mentioned) is updated by the TMS at the beginning of each time window. To ensure the highest variability of the car operation, the calculation of the EV states takes place mainly following the probability density function shown in Figure 7-6. The function defines for each hour of the day how high the probability is that a car is not connected to the grid. The probability that a car is either connected or not connected to the grid in each hour is evidently one. Using this function, the TMS can define the vehicle status and define a departure time for each EV at the beginning of each time window. Moreover, the TMS also decides with which of the available driving profiles (from one to four) cars not connected to the grid are cycled. The four available profiles are able to discharge the battery with different DoD. The decision is taken randomly, considering that a defined percent of EV not connected to the grid must be driven with the drive cycle \( N \) which causes a defined DoD in the battery, as shown in Table 7-3.

\textsuperscript{15} The obtained models limits the maximum lifetime to 15 years in calendar conditions under standard ambient temperature (23-25 °C) for the mentioned EOL criterion.
Figure 7-6: Probability function for cars to be on tour plotted vs. time used to calculate the actual EV status and the departure time. On the x-axis one means a time period between 00:00 and 01:00 am, 24 means a time period from 11:00 pm to 00:00 am.

Finally, the TMS has the task to activate and deactivate the communication between the EVs connected to the grid and the grid itself.

Table 7-3: Scheme used to define with which drive profile the cars not connected to the grid are cycled.

<table>
<thead>
<tr>
<th>$N$</th>
<th>Cycle DoD</th>
<th>% of EVs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10%</td>
<td>30%</td>
</tr>
<tr>
<td>2</td>
<td>30%</td>
<td>40%</td>
</tr>
<tr>
<td>3</td>
<td>50%</td>
<td>20%</td>
</tr>
<tr>
<td>4</td>
<td>80%</td>
<td>10%</td>
</tr>
</tbody>
</table>

7.2.3 Optimization strategy

The task of the business model algorithm shown in Figure 7-3 is to reproduce the algorithm that, in a possible V2G scenario, must operate in the central intelligent grid system, to which all the EV charging stations are connected. The system receives a request to provide a specific amount of electric energy capacity during a predetermined time period. Subsequently, an optimization strategy, which is in charge of allocating EV battery capacities available for this task and is responsible for selecting those with the lowest operating costs, is presented in this section.

First of all, once the EVs are connected to the grid, the departure time of each one is known. Knowing that for LiB low SoC are beneficial for the lifetime [208][211], the charge process is shifted an delayed until the exact time of departure. This takes place under the premise that at the time of departure the cars have to be fully charged (100% SoC) so that they can be fully utilized by their owners. In the remaining time, the EVs can be used for the V2G services. The strategy implemented in this work for the allocation of the vehicles aims to:
- Maximize the economical profit of using the vehicles, which means maximizing the difference between the profit obtained selling or buying energy from the grid and the loss in investment by the usage/cycle of the battery;
- Prolong as much as possible battery lifetime, so that at least the EOL of the battery pack does not underpass the lifetime of the car.

As already depicted in Figure 7-2, the algorithm generates $n$ different usage profile for the $m$ available cars based on the actual status of each EV (SoC, battery type and availability) and on the size of the requested time frame for the supply of electric capacity (in this case one hour). Hence, a power matrix $P_{\text{matrix}}$ [kW] is built, as shown in equation (7.8):

$$P_{\text{matrix}} = \begin{bmatrix} P_{11} & \cdots & P_{1n} \\ \vdots & \ddots & \vdots \\ P_{m1} & \cdots & P_{mn} \end{bmatrix}$$  \hspace{1cm} (7.8)

where all the terms $P_{mn}$ represent the proposed usage profiles. The profiles are sent to the BMS of each car, which uses the aging prediction model to calculate the variation of the SoH $\Delta SoH_{\text{matrix}}$ [%] that each battery will run through, if cycled with the requested profiles:

$$\Delta SoH_{\text{matrix}} = \begin{bmatrix} \Delta SoH_{11} & \cdots & \Delta SoH_{1n} \\ \vdots & \ddots & \vdots \\ \Delta SoH_{m1} & \cdots & \Delta SoH_{mn} \end{bmatrix}$$  \hspace{1cm} (7.9)

At this point, a cost function matrix $f_{\text{matrix}}$ is built for each of the obtained $\Delta SoH$ values:

$$f_{\text{matrix}} = \begin{bmatrix} f_{11} & \cdots & f_{1n} \\ \vdots & \ddots & \vdots \\ f_{m1} & \cdots & f_{mn} \end{bmatrix}$$  \hspace{1cm} (7.10)

Each of the $f_{mn}$ terms is calculated according to the following formulation:

$$f_{mn} = \frac{\text{Price}_{\text{en}} \cdot En_{\text{EV}} - \Delta SoH_{\text{profile}} \cdot Price_{\text{batt}} \cdot Q_{\text{batt}}}{P_{\text{profile}}} \cdot \frac{\text{Lifetime}}{\text{Lifetime}_{\text{avg}}}$$  \hspace{1cm} (7.11)

where $\text{Price}_{\text{en}}$ is the cost of the energy [€/kWh], or the sum which the car owner receives for participating in the V2G services; $En_{\text{EV}}$ is the amount of energy [kWh] charged into or discharged from each EV during the V2G operation; $\Delta SoH_{\text{profile}}$ is the variation of SoH [%] which corresponds to the usage profile $P_{\text{profile}}$ [kW]; $Price_{\text{batt}}$ is the price of the battery pack per energy unit [€/kWh], while $Q_{\text{batt}}$ is the capacity of the battery pack [kWh]; $\text{Lifetime}$ represents the predicted lifetime [years] based on the actual SoH and age, while $\text{Lifetime}_{\text{avg}}$ is the average of the predicted lifetime [years] of all the available EVs. The first term in the cost function is the profit made by taking part to the V2G services. This value is set against the amount of power defined for each usage profile. This allows the correct comparison among
terms obtained by different loads, as higher power means higher profit, but also higher current and DoD and therefore faster aging. The higher the difference between economic profit and loss of investment, the higher the first term is. The second term generates a more uniform aging among the EV, based on the predicted lifetime. A car with a shorter predicted lifetime is characterized by a second term with a lower value compared to a second car with a longer predicted lifetime. The introduction of the second term in equation (7.11) has the goal to obtain a degradation of the entire car fleet as shown in Figure 7-7. The idea behind this is to avoid having to replace the battery pack on the car and to try to manage the vehicles in such way that the life-cycle of the battery coincides approx. with the lifespan of the car (in the example 15 years). The vehicle chosen for V2G services is the one with a longer predicted lifetime and limited actual age which will therefore take precedence over a vehicle with a shorter predicted lifetime and limited actual age. Figure 7-7 depicts the uniform aging in a car chosen according to the specified optimized premise (dotted lines) as opposed to the aging of a car chosen randomly (lines with points). In reality, the prevailing effect will be less obvious, as the best-choice strategy only affects use during V2G operations, which only exploit a small percent of the total battery load. The calculation of the lifetime prediction takes place with a linear relationship between the actual SoH and the actual time in operation. This is a considerable simplification in the calculation, seen that most likely the degradation takes place with an exponential trend during calendar aging. Nevertheless, this assumption can be considered valid for the following reasons.

![Figure 7-7: Comparison between the degradation followed by the cars used randomly and the degradation obtained by optimal car usage for V2G services.](image)

According to the models obtained in section 7.2.1, the cycle aging is modeled with a linear relationship, and its contribution is dominant in most cases in respect to calendar aging. Moreover, only the Cell LFP is characterized by exponential calendar degradation: for this cell, the use of a more complicated lifetime prediction involving exponential formulation did
not deliver different results in respect to the assumed simplification. As the results section shows, using a linear formulation obtains a visible enhancement due to the optimization strategy, while at the same time limiting the computational effort needed for the calculation in the model.

Once the $f_{\text{matrix}}$ is built, the optimization problem can be solved by maximizing the following cost function:

$$\max_{x_{m,n} \in \{0,1\}} (x_{11} \cdot f_{11} + \cdots + x_{1n} \cdot f_{1n} + x_{m1} \cdot f_{m1} + \cdots + x_{mn} \cdot f_{mn})$$

(7.12)

$x_{m,n}$ represents a binary variable of the optimization function which must respect the two following restrictions:

$$\begin{align*}
  x_{11} + x_{12} + \cdots + x_{1n} &\leq 1 \\
  x_{21} + x_{22} + \cdots + x_{2n} &\leq 1 \\
  \vdots & \\
  x_{m1} + x_{m2} + \cdots + x_{mn} &\leq 1
\end{align*}$$

(7.13)

$$x_{11} \cdot P_{11} + \cdots + x_{1n} \cdot P_{1n} + x_{m1} \cdot P_{m1} + \cdots + x_{mn} \cdot P_{mn} \geq P_{\text{requested}}$$

(7.14)

The first requirement (equation (7.13)) ensures that an EV can only be selected for one usage profile at a time; the second requirement (equation (7.14)) ensures that the EVs selected are able to provide the regulation power requested $P_{\text{requested}}$. The problem is similar to the so-called rucksack problem [212], therefore a similar solution is used to solve it and to find the optimal car combination.

### 7.2.4 Simulation data and scenarios

In this section, the conditions under which the simulations were carried out are explained. Moreover, the important data used during the simulation is defined.

#### 7.2.4.1 EVs characteristics

The EVs are defined with an installed battery capacity of 20 kWh for both types. This capacity value falls in the typical range of capacity for battery packs which are installed in contemporary BEVs. Furthermore, during the simulation, the single EVs are reproduced with a single cell behavior (in terms of power and capacity). This implies that all the V2G usage profiles sent from the business model to the single EVs have to be scaled from the pack level to the cell level (battery models). The profiles used to excite the different vehicles to simulate the driving phase are obtained by driving different real EVs in mixed motor routes involving many different driving conditions in a city. The obtained data is then taken as a “basis element” to build the four profiles reported in Table 7-3, by scaling them to the cell level. The battery pack prices for the two technologies are $345\,€/kWh$ for $\text{Cell LFP}$ and $210\,€/kWh$ for
Cell NMC [213]. Despite the fact that LFP cells may be cheaper than other LiB chemistries (as commonly assumed), the quoted prices are only indicative and must be taken as a general parameter, which impact on the strategy can be analyzed, as shown in section 7.3.3 and in appendix 10.9.3.

7.2.4.2 Grid characteristics and V2G services

For the simulated scenarios, the size of the considered time frame in which the communication process between grid and EVs takes place is one hour. If the car is connected to the net during this time, it can be charged or it can contribute to the V2G services. Concerning the charging process, the objective is to postpone it as much as possible, in order to obtain the car ready (fully charged) at the exactly time of departure. The power used to recharge each car is limited to 3.6-3.7 kW (maximum power of a single phase transmission with 230 V and 16 A in Germany). Regarding the V2G operation, as mentioned in section 4.2, the use of an EV fleet for V2G services might be interesting for different market segments. In particular, the studied case regards the use of the EV fleet for V2G operation in a wind park in order to compensate the difference between the predicted and real energy production. Generally speaking, the usage of the EV fleet in the frequency regulation market (primary or secondary reserves) would produce a significantly higher profit due to the higher price system operators are prepared to pay for the availability of the vehicles. However, the frequency of the usage of the fleet for V2G may be in some occasion limited, so that the effect of the implemented strategy may not be apparent in the proposed model. Therefore, in spite of the modest earnings, the implemented simulation environment is tested in a scenario which involves the penetration of the renewable energy systems in the actual electric power grid. The used data is referred to a wind park and is again scaled for the 100 EVs fleet object of this study. Refer to [214] for information on this data. Figure 7-8 shows the data for a time period of six months.

![Figure 7-8: Difference between the prediction and real generation of a wind park for a time period of six months [214].](image)

Moreover, during the V2G operation, the valid SoC range is between 30% and 100%. This guarantees that a minimum amount of energy is always present in the vehicles in case of a
sudden emergency. Furthermore, it has been considered that during communication between grid and EVs, each car will receive three power profiles, with a different amount of power with a maximum value of 3.5 kW.

7.2.4.3 Ambient temperature and simulated scenarios

Four different scenarios have been simulated, considering the variation of i) ambient temperature, and ii) V2G procedure of the grid. Two different ambient conditions were studied namely the city of Aachen (Germany) and the city of Dubai (United Arab Emirates). The average temperatures for the two cities are shown in Figure 7-9 [215].

![Figure 7-9: Annual average temperature for the city of Aachen (Germany) in blue, and for the city of Dubai (United Arab Emirates) in red.](image)

The choice of these two temperature profiles allows the investigation of how the different ambient conditions influence the battery aging, even if the focus of the implemented model lies on the limitation of the cycling aging contribution. Regarding the V2G procedure, the simulations were carried out for two different cases. The first scenario used the optimization strategy described in section 7.2.3. The second scenario is used as a term of comparison. It addresses the utilization of a procedure in which the SoH of the single vehicle is not included. To fulfill the grid regulation service, the cars in this case are chosen randomly (without any rule) from those that are available for a V2G operation. The four obtained simulation scenarios are listed in Table 7-4.

<table>
<thead>
<tr>
<th>Temperature Profile</th>
<th>Aachen</th>
<th>Dubai</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random selection method</td>
<td>①</td>
<td>②</td>
</tr>
<tr>
<td>Optimization strategy</td>
<td>③</td>
<td>②</td>
</tr>
</tbody>
</table>
7.3 Results and discussion

In this section the results from the implemented scenarios are shown and discussed. Due to the limited space, only exemplary results are shown. Additional results can be found in appendix 10.9.3.

7.3.1 Improvement of the car fleet utilization by means of intelligent strategies

In the simulated scenarios, an EV number between 1 and 50 is defined for the vehicle equipped with Cell LFP, while an EV number between 51 and 100 is defined for the vehicle equipped with Cell NMC. Moreover, to ensure correct data evaluation and comparison, the starting conditions in terms of SoH, status signal of the cars and SoC for the simulated cases are the same for each of the 100 EVs. In particular, all EVs have an initial SoH different between each other, with a value included between 100% and 85%. Figure 7-10 illustrates exemplarily the trend of the vehicle status signal, the profile signal, power and SoC for the car no. 51 during the first 48 h of one of the simulated scenarios.

![Figure 7-10: Trend of the vehicle status signal, profile signal, cell power and SoC for car number 51 for the first 48 hours of one of the simulated scenario.](image)

The value of the power refers to the single cell characteristic, i.e. before the single vehicle data is processed from the business model, it is necessary to scale the power information in terms of usage profile and final decision for a V2G operation from the pack level to the cell level. The vehicle is connected to the grid (status signal equal to one) at the beginning of the simulation, and can operate in the V2G (profile signal equal to five), with a SoC value of approx. 50%. After five hours from the start, the charge process takes place (profile signal equal to six), until the SoC reaches 100%. After nine hours, the status signal goes to zero and
the vehicle is driven with the drive profile number two, which corresponds to the profile that discharge the battery with a DoD of circa 30%, as shown in Table 7-3. At the time correspondent to ten hours the car is again connected to the grid in V2G operation (profile signal equal to five) and the business model (grid) decides that the energy of the car can be used in the time window between 10 and 11 hours for a V2G operation: the battery vehicle is discharged with a constant power for one hour. The battery pack is again discharged in the V2G mode in the time window between 21 and 22 hours with a corresponding constant power. A similar behavior is obtained for all the 100 EVs: in one year all the vehicles on average drive for the same mileages, the discrepancy lies in the number of times that each car is employed for grid regulation services and with which amount of power. As a qualitative representation of the car behavior, Figure 7-11 shows the SoH trend for the entire EV fleet for the scenario no. 1 of Table 7-4.

![Figure 7-11: Trend of the SoH (in terms of capacity fading) for all 100 EVs for the entire simulation time for the scenario no. 1 in Table 7-4.](image)

Figure 7-11 shows clearly the differences in the initial SoH value. Moreover, the slightly different trend in the SoH can be observed. In fact, while a slightly exponential trend of the SoH can be detected for the cars between no. 1 and no. 50 (Cell LFP), the cars between no. 51 and no. 100 (Cell NMC) are characterized by a linear behavior, which also generates a reduction of the SoH with a faster rate.

Figure 7-12 shows the comparison between the results relative to the scenarios no. 1 and no. 3 of Table 7-4. Figure 7-12a), b) and c) refer to the random choice of the vehicles for the ambient temperature in Aachen, while Figure 7-12d), e) and f) refer to the optimized choice of the vehicles for the same weather conditions. The simulation is carried out for approx. eight years, until the first cars achieve the EOL criterion. Taking a look at Figure 7-12a), the difference between the SoH trends of the two different cells becomes apparent. Firstly, the cars equipped with the Cell NMC show a linear aging behavior in respect to the others, which
display a slightly exponential trend. Moreover, a faster degradation rate is shown from the cars between no. 51 and no. 100. Comparing the Figure 7-12a) and d) it is evident that the proposed optimization strategy has two particular effects. The first effect is the reduction of the scattering between cars of the same type, so that now EVs equipped with the same cells age more uniformly.

Figure 7-12: Comparison of the results for the scenarios no. 1 and no. 3 for the weather conditions of Aachen, a) SoH, b) predicted lifetime and c) total V2G energy for the random choice of the EVs; d) SoH, e) predicted lifetime and f) total V2G energy for the optimized choice of the EVs.
The second effect is the reduction of the difference between the lifetime of the cars with \textit{Cell NMC} and with \textit{Cell LFP}. In fact, the gap between the two different cars seems to decrease in Figure 7-12d), while the lifetime of the cars with \textit{Cell NMC} is approx. 140 months in Figure 7-12a) and rises to approx. 150 months in Figure 7-12d). This effect can also be numerically and qualitatively observed in Figure 7-12b) and e). The average lifetime of the entire fleet is marginally increased from approx. 11.8 years to 11.9 years. This is related to the increase of the lifetime of the cars with \textit{Cell NMC} in comparison with the cars with \textit{Cell LFP}. Moreover, it is clear that the difference between the two different car types decreases, while the band width of cars equipped with the same cells is also reduced. The difference behavior between the two scenarios is confirmed in Figure 7-12c) and f) which depict the total energy relative to each cars for the entire simulated time frame. The optimization strategy clearly generates a higher use of the vehicles equipped with Cell LFP in respect to the scenario with the random choice, so that a more uniform degradation can be obtained between cars with different battery packs. Finally it can be stated that the adopted strategy impacts the degradation of the fleet only minimally. This is due to the fact that the optimization can only act on the amount of power used for the V2G operation, which is only a small percentage in comparison to the entire energy used by each vehicle during its lifetime (which involves also the charging power and the driving operations). Moreover, it has to be considered that the calendar aging is still a decisive factor in battery degradation. In particular, one of the possibilities to influence and limit it lies in the control of the SoC. This would involve a strategy which attempts to keep the SoC of each vehicle as low as possible during the V2G operation. Such a strategy was also tested within the frame of this work without any evident and interesting improvements. The reason for this is the fact that the simulation tool is already implemented with approaches which attempt to maintain the battery SoC low (e.g. the shift of the charging process of each car just before the departure time). Therefore, the results shown and the obtained effects can be considered satisfactory also in quantitative terms.

A similar analysis compares the results obtained for the scenarios no. 2 and no. 4 in Figure 7-13. The simulation is carried out for approx. three years and the results apply to the weather condition in Dubai. As can be observed, the ambient temperature plays a crucial role in battery degradation and limits the effect of the introduced optimization strategy. In fact, observing the SoH trend (Figure 7-13a) and c), the differences between the trends are almost negligible. Only small variations are noticeably at the end of the lifetime of the cars equipped with \textit{Cell LFP}. The results related to the predicted lifetime (Figure 7-13b) and e) show a similar trend as the one observed for the weather condition in Aachen. Again a reduction of the total average lifetime is accompanied by an increase in the lifetime for the \textit{Cell NMC} and a decrease for the \textit{Cell LFP}, a sign that the strategy works properly in this case too. This is mainly related to the different usage of the cars between the two scenarios, as shown again in Figure 7-13c) and f). The optimization strategy tends to opt for using massively the cars equipped with \textit{Cell LFP} in order to accelerate the reduction of their lifetime and to limit the degradation of the cars with \textit{Cell NMC}. A further important factor is the analysis of the total gain or loss of investment for the four scenarios given in Table 7-4. The results are presented in Figure 7-14. For the four presented cases the y-axis represents the first term of
equation (7.11) without the normalization in respect to the used profile $P_{\text{profile}}$. Their values are denoted with the respective signs. This means that a negative cost function value constitutes a V2G usage condition in which the loss of investment on the capital (i.e. the battery pack) is higher than the profit obtained by the energy sale for V2G services.

The value used for the term $Price_{\text{en}}$ in equation (7.11) is 0.045 €/kWh, and is obtained as the average between the price given for the negative and positive error in the power prediction.

The value used for the term $Price_{\text{en}}$ in equation (7.11) is 0.045 €/kWh, and is obtained as the average between the price given for the negative and positive error in the power prediction.

Figure 7-13: Comparison of the results for the scenarios no. 2 and no. 4 for the weather conditions of Dubai, a) SoH, b) predicted lifetime and c) total V2G energy for the random choice of the EVs; d) SoH, e) predicted lifetime and f) total V2G energy for the optimized choice of the EVs.
Comparing the scenarios for the weather condition in Aachen (Figure 7-14a) and b), the additional and optimized use of the EVs has a beneficial effect on the lifetime of the fleet, but generate a loss on the investment for the vehicle equipped with Cell LFP, mainly due to the higher investment prices set for the cells, as mentioned in section 7.2.4.1. A similar and more pronounced effect is seen in Figure 7-14c) and d): due to the high battery cost and to the low price for the energy supply, the use of cars equipped with Cell LFP produces in both cases a loss of investment.

![Figure 7-14: Analysis of the total profit/loss of investment for the four scenarios of Table 7-4, a) random choice for Aachen, b) optimized choice for Aachen, c) random choice for Dubai, and d) optimized choice for Dubai.](image)

The loss increases significantly when the optimized strategy is employed instead of the random choice, while evidently an opposite trend is observed for the cars equipped with Cell NMC. This analysis highlights the fact that such a strategy and the use of EV for V2G operation in general will only become attractive if the price offered for the service covers the costs of the additional use of the battery, and therefore the resulting fall in depreciation.
7.3.2 Effect of inhomogeneous aging

In the results shown so far the assumption is that all batteries of the same type follow the same degradation model, so that starting from the same point (SoH), the cells age in the same manner, qualitatively and quantitatively. However, this does not coincide with reality, as cells of the same types produced by the same manufacturer do not always behave in the same manner, due to production differences, defects or other reasons. In order to take this factor into account and to test the proposed strategy in this condition too, the degradation is calculated based on the models presented in section 7.2.1 and by adding a defined tolerance value. This value is generated randomly once at the beginning of the simulation for each battery and continuously summed up to the total ΔSoH for the entire simulation. This means that each battery is characterized by a certain tolerance which is maintained during its lifetime, and which causes some batteries to ages faster than other cells of the same type. The employed tolerance values are shown in Figure 7-15.

![Figure 7-15: Representation of the scattering on the SoH for batteries of the same type, a) employed value, b) probability density function and cumulative distribution of the employed values.](image)

The results obtained by using the new degradation models are presented in Figure 7-16 for the weather conditions in Aachen, again comparing scenario no. 1 and no. 3. As can be observed, the degradation of the cell now takes place with a higher dispersion, so that batteries of the same type age extremely differently. In particular, if the vehicles were chosen with the random choice strategy for V2G, some of the cars equipped with Cell NMC reach the EOL criterion for the battery already after 120 months (ten years). The use of the strategy first reduces the differences in the aging of the battery of the same type and increases the lifespan of cars with fast degradation rate, as shown in Figure 7-16d). When comparing Figure 7-16b) and e) it becomes evident that the use of the proposed strategy generates an increase in the total average lifetime and in the lifetime of the Cell NMC, with a consequent decrease of the average lifetime of the Cell LFP. Again the reduction of the band width of each cell type based on the used strategy is evident. Similar conclusion but with limited effects can be drawn
by observing the results of the weather condition in Dubai, which are reported in appendix 10.9.3 in Figure 10-42.

Figure 7-16: Comparison of the results for the scenarios no. 1 and no. 3 for the weather conditions of Aachen in case of degradation with different rate of batteries of the same type, a) SoH, b) predicted lifetime and c) total V2G energy for the random choice of the EVs; d) SoH, e) predicted lifetime and f) total V2G energy for the optimized choice of the EVs.
7.3.3 Influence of the battery prices

In order to study the influence of the different battery pack prices, the optimization strategy is tested by inverting the respective prices introduced in section 7.2.4.1. The results for the weather condition in Aachen are shown in Figure 7-17.

**Figure 7-17:** Effect of the inversion of the battery price on the lifetime for the weather condition of Aachen, a) SoH, b) predicted lifetime, c) total V2G energy and d) total profit/loss of investment.

When comparing the SoH (Figure 7-17a) and the lifetime prediction (Figure 7-17b) trend with the ones shown in Figure 7-12, only minimal differences can be discovered. The predicted lifetime is almost the same, with only a small increase in the average value for the Cell LFP is obtained. Also the amount of energy for the total simulation time remains unchanged comparing Figure 7-12f) and Figure 7-17c). Evidently, the only difference can be found in the total profit which is obtained for the V2G operation. In fact, now only cars with Cell LFP are profitable, due to the lower price (now 210 €/kWh). In contrast, using cars with Cell NMC, even if limited, leads to a loss of investment in most cases. Additional results relating to the effect of the battery prices can be found in appendix 10.9.3, where the use of different models with prolonged lifetimes shows different and more pronounced effects.
7 Aging of Lithium-Ion batteries in a V2G scenario

7.4 Summary

The V2G concept is a possible solution to help boost EVs and PHEVs in the automotive market. To obtain a complete penetration of these technologies and a full integration with the actual electric grid, intelligent algorithms are needed on both sides, i.e. in the BMS of each vehicle and in the management system of the grid.

In this chapter a simulation environment with 100 EVs for the reproduction of a V2G concept is presented. The proposed tool comprises EVs with different LiB battery technologies. Each vehicle is described by an electric and an aging prediction model parametrized with real experimental data. A strategy for the choice of the EVs taking part in the V2G services is introduced. The strategy tries to choose the EVs in a way that the degradation of the entire fleet occurs in a uniform manner, with the intent, on the other side, to maximize the economical profit in the car usage. The results verify the proper working of the optimization method. As soon as the calendar aging does not play a decisive role (mainly low ambient temperature), the correct choice of the EVs can prolong the lifetime of the weaker battery going to the detriment of the stronger one. This produces a reduction of the differences in the vehicles from the fleet, even if type of LiB cells employed in the cars are different. The presented tool can be used for the implementation of new V2G operating strategies and for the correct positioning of a specific car fleet in a precise market segment.
Aging of Lithium-Ion batteries in a V2G scenario
8 Summary and Outlook

This work analyzes and investigates to a large extent a LiB type in all possible research areas of interests, starting from the basics, i.e. the analysis of the battery working principle at the material and cell level, to the top, i.e. the development of battery monitoring systems and the integration of them into the vehicle and into the electric grid. The analysis put special emphasis on studying LiB degradation during lifetime, on understanding and detecting this phenomenon, and on exploring how the loss of performance affects battery operation when the integration into a complex system takes place.

The analysis carried out within the framework of this work concentrates mainly on LFP technology. The main reason for this is due to the particular characteristics in respect to other LiBs, which makes these cells difficult to diagnose. These features are represented by the characteristic flat voltage curve and by the presence of a significant hysteresis in the OCV. The experimental investigation has shown that the hysteresis is a phenomenon related to the relaxation time, which tends to disappear over a long period of time. However, in the application such a time window is not available, so that an “application-related” hysteresis must be considered. A comprehensive study of the phenomenon shows that in addition to the major hysteresis boundaries, the single minor loops also change their characteristics with degradation. Therefore, a model which is parametrized for a new cell is no longer valid for an aged battery. It becomes apparent that a behavior change of the minor loops is mainly related to the change in the characteristics of the OCV and in particular of its plateaus’ lengths. A simple model based on the observed phenomena with a limited error can reproduce these features. The ensuing post mortem analysis shows the correctness of the assumptions, as no changes in the behavior of the single electrodes in terms of hysteresis is observed during lifetime. The experimental analysis based on the observation of the quasi-OCV curves during battery lifetime allows understanding the behavior of the single plateaus, and points to the direction of the development of novel algorithms for battery state detection. The proposed methods for the estimation of the cell SoH are based on the detection of the actual degradation modes (DM) which occurred during the lifetime. The information related to the plateaus’ lengths acquired online (either during the drive operation or during the charge process) allows the estimation of the SoH through the reconstruction of the quasi-OCV curve. Using the estimated DMs, this curve has plateaus with the same length as the ones measured during normal operation. The actual battery capacity during the charge and discharge process can be calculated with an error of approx. 1% in almost all the analyzed cases based merely on the information of two on three available plateaus. The presented model for SoH estimation is generally valid and can be employed for other LiBs. The information collected by the SoH estimation algorithm is employed for the recalibration of the hysteresis model, which can be used for the reproduction of the battery electric behavior or for SoC estimation. The simple
used algorithm calculates the value of the actual SoC with an error within 2-3% (in case the operation does not start in the middle of a plateau) with unknown initial SoC, in spite of the flatness of the OCV curve. These novel developed approaches are part of a new proposed BMS structure, with the estimation of the degradation as a fundamental factor. Such a structure is adapted to be employed in EVs used for V2G services. In this sense, this work introduces a simulation tool for V2G operation. The tool considers a car fleet with 100 EVs, with different histories and equipped with different LiB cells. The simulation environment allows testing a strategy which allocates the vehicle for V2G operation aiming at optimizing their lifetime. The results show that the presented strategy limits the degradation for cars with an expedited degradation (i.e. shorter lifetime) by substantially using vehicles with a predicted longer life. This achieves a more uniform degradation of the entire fleet, and avoids that some of the vehicles reach the EOL criterion prematurely. For weather conditions with moderate average temperatures throughout the year (e.g. Aachen), the optimized use of the vehicles increases the lifetime of the weakest cars by approx. one year. The correct working principle is also successfully tested in case of vehicles equipped with the same battery types but characterized by a very different cell behavior (i.e. same cell ages in different manner). Limited effects are observed if the calendar aging prevails, due to the reduced impact on the lifetime of the cycle aging.

Even so, a lot of work remains to be done which goes beyond this thesis. The analysis of the hysteresis clarifies the change of behavior of the single minor loops during lifetime, but the hysteresis phenomenon itself has not been fully understood. Apart from this, it may be interesting to observe if cells of the same types but from different manufacturers behave in the same manner, respecting the same rules. With different cells of the same chemistries, a broader study may provide a full comprehension of the phenomenon and its complete explanation. Furthermore, a wider post mortem analysis carried out in a whole batch of aged cells accompanied with methods which also analyze the disassembled materials at particle level may afford a complete insight into the degradation. Regarding the novel implemented battery state detection algorithms, two main drawbacks are evident. Firstly all the presented methods are tested as a proof of concept: the approaches were developed over a long time period, which prevents a real evaluation whether they could be implemented in a feasible manner in a µC environment. Hence, the requirement in terms of memory (RAM and ROM) could be evaluated. Additionally, the voltage sensor accuracy, which surely is critical for a battery with flat OCV curve, could also be evaluated. The second open point lays on the test of the developed methods for battery packs. Although a BMS can always provide a single cell voltage, the parallel connection of cells in a module might results in the fading of the plateaus in the OCV curve, when the aging is not homogeneous, and therefore it might be impossible to distinguish these plateaus precisely. Therefore it might be of interest to evaluate the minimum number of cells which has to be monitored in order to estimate (with an acceptable error) the capacity in a battery pack correctly. Eventually, the determination of the single plateaus during the driving operation should be further developed, so that they can also be estimated in case of prolonged driving phases with high current rates. Within the developed V2G environment, an additional analysis could differentiate further the characteristics of the
vehicles among each other, i.e. considering packs with different capacity, introducing other battery chemistries or considering battery packs with parallel connections of different LiB chemistries. Thus, new strategies, which may tend more to optimize profit instead of lifetime, can be tested. Further cases explore the market segment in which V2G services are sold. One example is the use of a car fleet for frequency regulation, a market segment in which the additional cycle operation may be constricted but a considerable profit increase can be generated.
Summary and Outlook
9 Bibliography


[61] L. Lu, X. Han, J. Li, J. Hua, and M. Ouyang, “A review on the key issues for lithium-ion battery management in electric vehicles,” *J. Power Sources*, vol. 226, pp. 272–288, 15 March.


presented at the European Electric Vehicle Congress, Brussels (Belgium), 2014, pp. 1–12.


10 Appendix

10.1 Constants

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$</td>
<td>Faraday’s constant, 96,485 As/mol</td>
</tr>
<tr>
<td>$R$</td>
<td>Gas constant, 8.314 J/(mol K)</td>
</tr>
</tbody>
</table>
### 10.2 Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_i$</td>
<td>-</td>
<td>Coefficients fitted for calendar degradation model (different units)</td>
</tr>
<tr>
<td>$A$</td>
<td>m²</td>
<td>Active surface area</td>
</tr>
<tr>
<td>$A_{\text{coin}}$</td>
<td>mm²</td>
<td>Area of the electrode for coin cell</td>
</tr>
<tr>
<td>$A_{\text{elect}}$</td>
<td>mm²</td>
<td>Total area of electrode in the full cell</td>
</tr>
<tr>
<td>$b_i$</td>
<td>-</td>
<td>Coefficients fitted for cycle degradation model (different units)</td>
</tr>
<tr>
<td>$D$</td>
<td>cm²/s</td>
<td>Diffusion constant</td>
</tr>
<tr>
<td>$E_{\text{En}}$</td>
<td>kWh</td>
<td>Energy requested for V2G services</td>
</tr>
<tr>
<td>$E_0$</td>
<td>V</td>
<td>Standard cell potential</td>
</tr>
<tr>
<td>$f$</td>
<td>€/kW</td>
<td>Cost function for the optimization strategy for V2G</td>
</tr>
<tr>
<td>$f_{\text{matrix}}$</td>
<td>€/kW</td>
<td>Matrix of the cost functions</td>
</tr>
<tr>
<td>$i$</td>
<td>A</td>
<td>Overall current</td>
</tr>
<tr>
<td>$i_0$</td>
<td>A</td>
<td>Exchange current density</td>
</tr>
<tr>
<td>$i_0'$</td>
<td>A/mm²</td>
<td>Specific exchange current density</td>
</tr>
<tr>
<td>$I_{\text{elect}}$</td>
<td>A</td>
<td>Current in the coin cell</td>
</tr>
<tr>
<td>$I_{\text{full}}$</td>
<td>A</td>
<td>Current in the full cell</td>
</tr>
<tr>
<td>$I$</td>
<td>-</td>
<td>Current rate (current in A/cell capacity in Ah)</td>
</tr>
<tr>
<td>$k_{\text{Cha}}$</td>
<td>-</td>
<td>Exponential coefficient for the hysteresis factor for charge</td>
</tr>
<tr>
<td>$k_{\text{Dch}}$</td>
<td>-</td>
<td>Exponential coefficient for the hysteresis factor for discharge</td>
</tr>
<tr>
<td>$\text{Lifetime}$</td>
<td>years</td>
<td>Predicted lifetime for each EV</td>
</tr>
<tr>
<td>$\text{Lifetime}_{\text{avg}}$</td>
<td>years</td>
<td>Average of the predicted lifetime for the entire EV fleet</td>
</tr>
<tr>
<td>$LP$</td>
<td>Ah</td>
<td>Plateau’ length</td>
</tr>
<tr>
<td>$P_{\text{matrix}}$</td>
<td>kW</td>
<td>Matrix of the power profile for V2G usage</td>
</tr>
<tr>
<td>$P_{\text{profile}}$</td>
<td>kW</td>
<td>Power of a V2G usage profile</td>
</tr>
<tr>
<td>$P_{\text{req}}$</td>
<td>W</td>
<td>Power requested for grid services</td>
</tr>
<tr>
<td>$P_{\text{price_batt}}$</td>
<td>€/kWh</td>
<td>Price of battery pack for energy unit</td>
</tr>
<tr>
<td>$P_{\text{price_En}}$</td>
<td>€/kWh</td>
<td>Cost/price of the V2G services</td>
</tr>
<tr>
<td>$OCV_{\text{cha}}$</td>
<td>V</td>
<td>Major hysteresis charge boundary</td>
</tr>
<tr>
<td>$OCV_{\text{dch}}$</td>
<td>V</td>
<td>Major hysteresis discharge boundary</td>
</tr>
<tr>
<td>$Q$</td>
<td>Ah</td>
<td>Capacity</td>
</tr>
<tr>
<td>$Q_{\text{activity}}$</td>
<td>-</td>
<td>Reaction quotient</td>
</tr>
<tr>
<td>$Q_{\text{actual}}$</td>
<td>-</td>
<td>Relative value of the actual battery capacity</td>
</tr>
<tr>
<td>$Q_{\text{BOL}}$</td>
<td>-</td>
<td>Relative value of the battery capacity at the beginning-of-life</td>
</tr>
<tr>
<td>$Q_{\text{calc}}$</td>
<td>Ah</td>
<td>Battery capacity calculated by the algorithm</td>
</tr>
<tr>
<td>$Q_{\text{EOL}}$</td>
<td>-</td>
<td>Relative value of the battery capacity at the end-of-life</td>
</tr>
<tr>
<td>$Q_{\text{Pe/Ne,end}}$</td>
<td>-</td>
<td>Termination point of the considered electrode in the relative Ah scale</td>
</tr>
<tr>
<td>$Q_{\text{Pe/Ne,start}}$</td>
<td>-</td>
<td>Start point of the considered electrode in the relative Ah scale</td>
</tr>
<tr>
<td>$Q_{\text{real}}$</td>
<td>Ah</td>
<td>Actual battery capacity</td>
</tr>
<tr>
<td>$Q_{\text{batt}}$</td>
<td>kWh</td>
<td>Total capacity of the battery pack</td>
</tr>
<tr>
<td>$r$</td>
<td>cm</td>
<td>Particle radius</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
<td></td>
</tr>
<tr>
<td>$R_{\text{actual}}$</td>
<td>Relative value of the actual battery resistance</td>
<td></td>
</tr>
<tr>
<td>$R_{\text{BOL}}$</td>
<td>Relative value of the battery resistance at the beginning-of-life</td>
<td></td>
</tr>
<tr>
<td>$R_{\text{EOL}}$</td>
<td>Relative value of the battery resistance at the end-of-life</td>
<td></td>
</tr>
<tr>
<td>$SoC_{\text{min}}$</td>
<td>Minimum state-of-charge</td>
<td></td>
</tr>
<tr>
<td>$SoC_{\text{max}}$</td>
<td>Maximum state-of-charge</td>
<td></td>
</tr>
<tr>
<td>$SoH_C$</td>
<td>State-of-Health related to the actual capacity</td>
<td></td>
</tr>
<tr>
<td>$SoH_R$</td>
<td>State-of-Health related to the actual resistance</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
<td></td>
</tr>
<tr>
<td>$U_{\text{EMF}}$</td>
<td>Electromotive force in a fully equilibrated state</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Symmetry coefficient</td>
<td></td>
</tr>
<tr>
<td>$\Delta V_{\text{Hyst}}$</td>
<td>Voltage difference between the OCV of a new and the aged cell for each SoC point</td>
<td></td>
</tr>
<tr>
<td>$\Delta V_{\text{qOCV}}$</td>
<td>Voltage difference between the quasi-OCV of a new and the aged cell for each SoC point</td>
<td></td>
</tr>
<tr>
<td>$\Delta V_{\text{Hyst}}$</td>
<td>Difference between the maximum and minimum voltage in the SoC range for OCV curve</td>
<td></td>
</tr>
<tr>
<td>$\Delta V_{\text{qOCV}}$</td>
<td>Difference between the maximum and minimum voltage in the SoC range for quasi-OCV curve</td>
<td></td>
</tr>
<tr>
<td>$\Delta Q_{\text{cal}}$</td>
<td>Variation of the relative battery capacity due to calendar aging</td>
<td></td>
</tr>
<tr>
<td>$\Delta Q_{\text{cyc}}$</td>
<td>Variation of the relative battery capacity due to cycle aging</td>
<td></td>
</tr>
<tr>
<td>$\Delta SoH_{\text{matrix}}$</td>
<td>Matrix of the variation of SoH for each of the proposed V2G usage profiles</td>
<td></td>
</tr>
<tr>
<td>$\Delta SoH_{\text{profile}}$</td>
<td>Variation of SoH for a V2G usage profile</td>
<td></td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Error threshold / Exit criteria for capacity estimation algorithm</td>
<td></td>
</tr>
<tr>
<td>$\eta_{\text{act}}$</td>
<td>Generic activation overpotential</td>
<td></td>
</tr>
<tr>
<td>$\eta_{\text{act,neg}}$</td>
<td>Polarization voltage from the interfacial charge-transfer reactions on the negative electrode</td>
<td></td>
</tr>
<tr>
<td>$\eta_{\text{act, pos}}$</td>
<td>Polarization voltage from the interfacial charge-transfer reactions on the positive electrode</td>
<td></td>
</tr>
<tr>
<td>$\eta_{\text{f,neg}}$</td>
<td>Polarization voltage due to passivation layers on the negative electrode</td>
<td></td>
</tr>
<tr>
<td>$\eta_{\text{f,pos}}$</td>
<td>Polarization voltage due to passivation layers on the positive electrode</td>
<td></td>
</tr>
<tr>
<td>$\eta_{\text{ohmic}}$</td>
<td>ohmic overpotential</td>
<td></td>
</tr>
<tr>
<td>$\Psi$</td>
<td>Hysteresis factor</td>
<td></td>
</tr>
</tbody>
</table>
10.3 Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEV</td>
<td>Battery Electric Vehicle</td>
</tr>
<tr>
<td>BMS</td>
<td>Battery Management System</td>
</tr>
<tr>
<td>BOL</td>
<td>Beginning-of-Life</td>
</tr>
<tr>
<td>CC</td>
<td>Constant Current</td>
</tr>
<tr>
<td>CHA</td>
<td>Charge</td>
</tr>
<tr>
<td>CV</td>
<td>Constant Voltage</td>
</tr>
<tr>
<td>DCH</td>
<td>Discharge</td>
</tr>
<tr>
<td>De</td>
<td>Delithiated phase</td>
</tr>
<tr>
<td>DM</td>
<td>Degradation Modes</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl Carbonate</td>
</tr>
<tr>
<td>DoD</td>
<td>Depth-of-Discharge</td>
</tr>
<tr>
<td>DVA</td>
<td>Differential Voltage Analysis</td>
</tr>
<tr>
<td>EC</td>
<td>Ethyl Carbonate</td>
</tr>
<tr>
<td>EECM</td>
<td>Equivalent Electric Circuit Model</td>
</tr>
<tr>
<td>EESS</td>
<td>Electrochemical Energy Storage System</td>
</tr>
<tr>
<td>EFC</td>
<td>Equivalent Full Cycle</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>EMF</td>
<td>Electromotive Force</td>
</tr>
<tr>
<td>EMS</td>
<td>Energy Management System</td>
</tr>
<tr>
<td>EOCV</td>
<td>End-Of-Charge Voltage</td>
</tr>
<tr>
<td>EODV</td>
<td>End-Of-Discharge Voltage</td>
</tr>
<tr>
<td>EOL</td>
<td>End-of-Life</td>
</tr>
<tr>
<td>EV</td>
<td>Electric Vehicle</td>
</tr>
<tr>
<td>HE</td>
<td>High Energy</td>
</tr>
<tr>
<td>HEV</td>
<td>Hybrid Electric Vehicle</td>
</tr>
<tr>
<td>HP</td>
<td>High Power</td>
</tr>
<tr>
<td>ICA</td>
<td>Incremental Capacity Analysis</td>
</tr>
<tr>
<td>( I_n )</td>
<td>Nominal current</td>
</tr>
<tr>
<td>LFP/LiFePO(_4)</td>
<td>Lithium iron phosphate based materials</td>
</tr>
<tr>
<td>Li</td>
<td>Lithiated phase</td>
</tr>
<tr>
<td>LiB</td>
<td>Lithium-ion Battery</td>
</tr>
<tr>
<td>LiCoO(_2)</td>
<td>Lithium Cobalt oxide based materials</td>
</tr>
<tr>
<td>LiPF(_6)</td>
<td>Lithium hexafluorophosphate</td>
</tr>
<tr>
<td>LMO</td>
<td>Lithium manganese oxide based materials</td>
</tr>
<tr>
<td>LAM</td>
<td>Loss of Active Material</td>
</tr>
<tr>
<td>LLI</td>
<td>Loss of Lithium Inventory</td>
</tr>
<tr>
<td>NCA</td>
<td>Lithium Nickel Cobalt Aluminum oxide based materials</td>
</tr>
<tr>
<td>Ne</td>
<td>Negative electrode</td>
</tr>
<tr>
<td>NiCad</td>
<td>Nickel Cadmium</td>
</tr>
<tr>
<td>NiMH</td>
<td>Nickel Metal Hydride</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>NMC</td>
<td>Lithium Nickel Manganese Cobalt oxide based materials</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>OEM</td>
<td>Original Equipment Manufacturers</td>
</tr>
<tr>
<td>PbA</td>
<td>Lead-acid battery</td>
</tr>
<tr>
<td>Pe</td>
<td>Positive electrode</td>
</tr>
<tr>
<td>PHEV</td>
<td>Plug-in Hybrid Electric Vehicle</td>
</tr>
<tr>
<td>RUL</td>
<td>Remaining Useful Life</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid Electrolyte Interphase</td>
</tr>
<tr>
<td>SLI</td>
<td>Starting, Lightning and Ignition</td>
</tr>
<tr>
<td>SoC</td>
<td>State-of-Charge</td>
</tr>
<tr>
<td>SoF</td>
<td>State-of-Function</td>
</tr>
<tr>
<td>SoH</td>
<td>State-of-Health</td>
</tr>
<tr>
<td>TMS</td>
<td>Time Manager System</td>
</tr>
<tr>
<td>$U_n$</td>
<td>Nominal voltage</td>
</tr>
<tr>
<td>VPA</td>
<td>Varied-Parameters Approach</td>
</tr>
<tr>
<td>$\mu$C</td>
<td>Microcontroller</td>
</tr>
</tbody>
</table>
10.4 Influence of current, temperature and rest period on the total capacity

The additional data reported in this section refers to the investigation of the current rate effect on the total battery capacity introduced in section 5.2.1.

10.4.1 Temperature variation dependency

The tests investigate the influence of the temperature variation during the discharge process on the total capacity delivered by the battery and demonstrate if this variation influences only the last part or the entire discharge process. Table 10-1 shows a resume of the tests.

Table 10-1: Test matrix for temperature variation investigation with two temperature steps and a 6 h pause in between. The tests are done with a current rate of 1C.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Temperature / °C</th>
<th>Temperature / °C</th>
<th>Pause</th>
<th>50%→EODV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100%→50% SoC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td></td>
<td>6 h</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>23</td>
<td></td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0</td>
<td></td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>23</td>
<td></td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

During each process, the battery starts in a fully charged state (CCCV), then it is discharged from 100% to 50% SoC with a current rate of 1C at ambient temperature $T_1$, and from 50% SoC until the empty state with the same current, but a temperature $T_2$ different from $T_1$. The test is repeated by inverting the two temperature values. The tests are carried out for three different temperatures (0 °C – 23 °C – 40 °C). Between the two steps of the discharge process, a pause of 6 h is set up, to temper the cell to the defined ambient temperature. Figure 10-1 shows the values of the total capacity for both cells.

Figure 10-1: Trend of the normalized available capacity for temperature influence investigation test for a) new cell and b) aged cell.
The differences in the final capacity values appear for the test where the last part of the discharge process is carried out with a temperature of 0 °C (no. 25, 29 and 30). Between these tests, the difference in the capacity is due to the value of the cell temperature when the discharge process is firstly stopped (50% SoC): the biggest capacity is for both cells the one obtained in the test where the batteries are discharged from 100% to 50% SoC at 40 °C, followed by the one at 23 °C. In the other six tests (the group no. 26, 28 and 33, and the group no. 27, 30 and 32) the battery temperature seems to not influence the final capacity value for both cells. By this, the temperature variation during the discharge process influences the final battery capacity only if the difference between the two temperatures is significant. Further investigations with frequent changes in the ambient temperature during the discharge process could give a better understanding of the phenomenon.

10.4.2 Presence of rest periods

The tests investigate the presence of pauses of different length during the discharge process on the total cell capacity and particularly demonstrate if the interruption length is a critical factor. Table 10-2 shows a resume of the tests.

Table 10-2: Test matrix for the investigation of the pause duration. The tests are done at ambient temperature of 23 °C.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Rest period length</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2C</td>
<td>1C</td>
</tr>
<tr>
<td>34</td>
<td>40</td>
</tr>
<tr>
<td>35</td>
<td>41</td>
</tr>
<tr>
<td>36</td>
<td>42</td>
</tr>
<tr>
<td>37</td>
<td>43</td>
</tr>
<tr>
<td>38</td>
<td>44</td>
</tr>
<tr>
<td>39</td>
<td>45</td>
</tr>
</tbody>
</table>

During each process, the battery starts in a fully charged state (CCCV charge process), then it is discharged from 100% to 50% SoC with a current \(I_1\), and after an interruption of a defined duration (no load current), from 50% SoC to the empty state with the same current rate. The tests are carried out for six different pause durations, and each one for three different current rates \(0.2C \pm 1C \pm 5C\). During all the tests, the climate chamber is set with an ambient temperature of 23 °C. Figure 10-2 shows the value of the final capacity for both cells. The presence of a break of a different length (from 0 to 360 min) during the discharge process does not particularly influence the final capacity for both cells for a current rate of 0.2C. For the new cell no big variation in terms of capacity is detected also for 1C current rate, while already small differences can be noted for the aged cell: the presence of a pause seems to provoke a worsening in performance (test No. 40→no pause, test No. 45→6 h pause). This can be seen more clearly in the tests done with a 5C current rate for both cells, where the discharging done without a break shows always a higher final capacity. One might assume that the presence of a pause, allowing the completion of the diffusion processes in the cell,
could be favorable for battery performance, but in this case the tests have shown an opposite behavior, especially for high current rates.

Figure 10-2: Trend of the normalized available capacity for the investigation of the pause duration for a) new cell and b) aged cell.

This effect is probably related to the maintained high temperature in the cell reached with a current rate of 5C when no interruption is set during the discharge process: the reached temperature allows releasing part of the available reversible capacity. Since an interruption is set, the decrease of the temperature during the pause reduces the amount of capacity which is available at the end of the process.
10.5 Investigation and modelling of the hysteresis of the open circuit voltage: additional tests results

In this section additional results obtained during the investigation of the hysteresis of the OCV for the analyzed LFP cell are presented. Description of the investigated phenomena can be found in section 5.5.

![Figure 10-3: Comparison between the OCV curves obtained for the investigated cells of Table 5-8 at begin-of-test measured every 5% SoC during charge and discharge at an ambient temperature of 23 °C.](image-url)
10.5.1 Minor loops identification

**Figure 10-4:** Comparison between the major hysteresis boundaries and the investigated minor loops starting from 20% SoC, a) New cells, b) Cell B, c) Cell C and d) Cell D. The loops are parameterized starting from a fully charged state. The OCV is measured with a stepwise process of 5% SoC at 23 °C. View the different scale of the axes. Cell data reported in Table 5-8.
Figure 10-5: Comparison between the major hysteresis boundaries and the investigated minor loops starting from 30% SoC, a) New cells, b) Cell B, c) Cell C and d) Cell D. The loops are parameterized starting from a fully charged state. The OCV is measured with a stepwise process of 5% SoC at 23 °C. View the different scale of the axes. Cell data reported in Table 5-8.
Figure 10-6: Comparison between the major hysteresis boundaries and the investigated minor loops starting from 40% SoC, a) New cells, b) Cell B, c) Cell C and d) Cell D. The loops are parameterized starting from a fully charged state. The OCV is measured with a stepwise process of 5% SoC at 23 °C. View the different scale of the axes. Cell data reported in Table 5-8.
Figure 10-7: Comparison between the major hysteresis boundaries and the investigated minor loops starting from 60% SoC, a) New cells, b) Cell B (no loop can be parametrized), c) Cell C and d) Cell D. The loops are parameterized starting from a fully charged state. The OCV is measured with a stepwise process of 5% SoC at 23 °C. View the different scale of the axes. Cell data reported in Table 5-8.
10.5.2 Current dependency of the minor loops

**Figure 10-8:** Investigation of the current dependency for one of the three investigated minor loops for a new cell of Table 5-8 (test carried out according to the test part no. 6 of Figure 5-19). The compared loops are parameterized starting from a fully charged cell.

**Figure 10-9:** Investigation of the current dependency for one of the three investigated minor loops for the aged Cell B of Table 5-8 (test carried out according to the test part no. 6 of Figure 5-19). The compared loops are parameterized starting from a fully charged cell.
10.5.3 Temperature behavior of the OCV and of the minor loops

Figure 10-10: Dependency of the hysteresis curves on the ambient temperature for Cell B of Table 5-8 (test carried out according to the test part no. 3 of Figure 5-19), a) OCV curves measured every 5% SoC during charge and discharge at ambient temperature of 0 °C, 23 °C and 40 °C, b) difference between the OCV curve measured at x °C (OCV\textsubscript{x}) and the OCV curve measured at 23 °C (OCV\textsubscript{23}).
Figure 10-11: Dependency of the hysteresis curves on the ambient temperature for Cell D of Table 5-8 (test carried out according to the test part no. 3 of Figure 5-19), a) OCV curves measured every 5% SoC during charge and discharge at ambient temperature of 0 °C, 23 °C and 40 °C, b) difference between the OCV curve measured at x °C (OCV_x) and the OCV curve measured at 23 °C (OCV_{23}).
Figure 10-12: Investigation of the temperature dependency for one of the three investigated minor loops for a new cell of Table 5-8 for ambient temperatures of 0 °C, 23 °C and 40 °C (test carried out according to the test part no. 7 of Figure 5-19). a) 0 °C, 23 °C and 40 °C, b) 23 °C, c) 0 °C and d) 40 °C. The loops are parameterized starting from a cell in a fully charged state.
Figure 10-13: Investigation of the temperature dependency for one of the three investigated minor loops for Cell B of Table 5-8 for ambient temperatures of 0 °C, 23 °C and 40 °C (test carried out according to the test part no. 7 of Figure 5-19). a) 0 °C, 23 °C and 40 °C, b) 23 °C, c) 0 °C and d) 40 °C. The loops are parameterized starting from a cell in a fully charged state.
The temperature dependency of the OCV curves can be analyzed with a different method than described in this work, as discussed by Nieto et al. in [216]. The test procedure of the mentioned method for the investigated LFP cell is presented in Figure 10-14 and Figure 10-15. The procedure is similar to the one presented in section 5.5.1 (test part no. 3) for the determination of the OCV major hysteresis boundaries, with the difference that the ambient temperature is not kept constant for the entire test procedure. After the cell is brought to a defined SoC level, the value of the OCV for that temperature is recorded after a rest period (quasi-steady state). Then, the ambient temperature is set to a chosen value and the OCV is again recorded after a rest period. The procedure is repeated for all the chosen temperature values and the single values of the OCV (relative to the set SoC) are recorded. At the end of the process, the ambient temperature is set to the initial value and the SoC is set to the next level. The process is then repeated for the other SoC values. Results for the method for the investigated LFP cell are presented in Figure 10-16.

**Figure 10-14:** Test procedure for the investigation of the ambient temperature on the hysteresis of the OCV in a single test. The procedure is reproduced according to Nieto et al. [216].
Figure 10-15: Extract of the data set of the test procedure depicted in Figure 10-15 between 5 and 5.5 days.

Figure 10-16: Comparison of the OCV curves for different ambient temperature obtained through the test procedure shown in Figure 10-14 and Figure 10-15.
10.5.4 OCV modeling

Figure 10-17: Validation of the semi-empirical approach for hysteresis modelling, a) comparison between measured and modelled minor loops (starting from 50% SoC) for Cell B, b) corresponding error, c) comparison of measured and modelled minor loops (starting from 30% SoC) for Cell D, b) corresponding error. Data referred to section 5.5.4.
10.5.5 Hysteresis after long relaxation behavior

![Graph showing hysteresis behavior](image)

**Figure 10-18:** Investigation of the long-term hysteresis behavior at an ambient temperature of 23 °C, hysteresis during the relaxation after charge and discharge short-term history for the Cell C of Table 5-8.

10.6 OCV evaluation for single electrodes

Figure 10-19, 20, 21 and 22 present the additional minor loops measured for the investigated cells of Table 5-11.

![Graph showing OCV for single electrodes](image)

**Figure 10-19:** Measured minor loops (start SoC of 20%) for the coin cells Ext. Up at ambient temperature for the anode, a) *Cell F2* and b) *Cell A1*. 
Figure 10-20: Measured minor loops (start SoC of 50%) for the coin cells Ext. Up at ambient temperature for the anode, a) Cell F2 and b) Cell A1.

Figure 10-21: Measured minor loops (start SoC of 20%) for the coin cells Ext. Up at ambient temperature for the cathode, a) Cell F2 and b) Cell A1.

Figure 10-22: Measured minor loops (start SoC of 60%) for the coin cells Ext. Up at ambient temperature for the cathode, a) Cell F2 and b) Cell A1.
Figure 10-23 and Figure 10-24 present the comparison between the measured (blue circles) and the modeled (red crosses) charge and discharge hysteresis boundary for the Cell A1 of Table 5-11 respectively. The modeled OCV is obtained subtracting OCV measured for the cathode and for the anode electrode (results shown in Figure 5-38).

![Figure 10-23: Comparison of the measured (blue circles) and the modeled (red crosses) charge hysteresis boundary for the Cell A1 of Table 5-11.](image1)

![Figure 10-24: Comparison of the measured (blue circles) and the modeled (red crosses) discharge hysteresis boundary for the Cell A1 of Table 5-11.](image2)
10.7 Estimation of the battery capacity: additional results

**Figure 10-25:** Detailed representation of the meaning of the terms employed in equation (6.2)-(6.5) for the description of the relation between the capacity of the electrodes and the capacity of the full cell (referred to the new state). For a full representation of the different aging mechanisms the reader is addressed to Figure 6-1.
10.7.1 Simulation of aging through a mix of DMs

Introduction and explanation of the following results can be found in section 6.1.1.

Figure 10-26: Reproduction of the degradation of the 8 Ah HP LFP cell aged for a LLI of 30%, a) modeling of the evolution of the quasi-OCV curves during aging (arrow direction), b) resulting dV analysis, c) evolution of the two identified peaks, d) evolution of the cell capacity and of the two identified peaks, evolution of the distance between the peaks P₁ and P₂ (P₁-P₂), evolution of the of the distance between P₂ and the origin of the axes (P₂).
Figure 10-27: Reproduction of the degradation of the 8 Ah HP LFP cell aged for a LAM$_{NeLi}$ of 30%, a) modeling of the evolution of the quasi-OCV curves during aging (arrow direction), b) resulting dV analysis, c) evolution of the two identified peaks, d) evolution of the cell capacity and of the two identified peaks, evolution of the distance between the peaks P$_1$ and P$_2$ (P$_1$-P$_2$), evolution of the distance between P$_2$ and the origin of the axes (P$_2$).
Figure 10-28: Reproduction of the degradation of the 8 Ah HP LFP cell aged for a LAM$_{NeDe}$ of 30%, a) modeling of the evolution of the quasi-OCV curves during aging (arrow direction), b) resulting dV analysis, c) evolution of the two identified peaks, d) evolution of the cell capacity and of the two identified peaks, evolution of the distance between the peaks P$_1$ and P$_2$ (P$_1$-P$_2$), evolution of the of the distance between P$_2$ and the origin of the axes (P$_2$).
Figure 10-29: Reproduction of the degradation of the 8 Ah HP LFP cell aged for a $\text{LAM}_{\text{NeDe}}$ of 30% and a LLI of 10%, a) modeling of the evolution of the quasi-OCV curves during aging (arrow direction), b) resulting $dV$ analysis, c) evolution of the two identified peaks, d) evolution of the cell capacity and of the two identified peaks, evolution of the distance between the peaks $P_1$ and $P_2$ ($P_1-P_2$), evolution of the of the distance between $P_2$ and the origin of the axes ($P_2$).
Figure 10-30: Reproduction of the degradation of the 8 Ah HP LFP cell aged for a LAM_{NeDe} of 10% and a LLI of 30%, a) modeling of the evolution of the quasi-OCV curves during aging (arrow direction), b) resulting dV analysis, c) evolution of the two identified peaks, d) evolution of the cell capacity and of the two identified peaks, evolution of the distance between the peaks P₁ and P₂ (P₁-P₂), evolution of the of the distance between P₂ and the origin of the axes (P₂).
10.7.2 Capacity estimation results and plateaus scalability

**Figure 10-31:** Online detection of the plateaus during a driving phase at 23 °C, a) current profile of a part of a repeated FTP75 driving cycle, b) comparison of the offline measured OCV and quasi-OCV curve and the tracked and filtered OCV values by means of an equivalent electrical circuit model. Data relative to the *Cell Cal.1* of Table 6-1.
Figure 10-32: Online detection of the plateaus during a driving phase at 23 °C, a) current profile of a part of a repeated FTP75 driving cycle, b) comparison of the offline measured OCV and quasi-OCV curve and the tracked and filtered OCV values by means of an equivalent electrical circuit model. Data relative to the Cell Cal.1 of Table 6-1.
Figure 10-33: Online detection of the plateaus during a driving phase at 23 °C, a) current profile of a part of a repeated FTP75 driving cycle, b) comparison of the offline measured OCV and quasi-OCV curve and the tracked and filtered OCV values by means of an equivalent electrical circuit model. Data relative to the Cell Cyc.1 of Table 6-1.
**Figure 10-34:** Example of the evolution of the parameters during the offline aging estimation for the charge process in case three plateaus are known, a) evolution of the LLI, b) evolution of the LAM on the negative electrode in the delithiated phase, c) evolution of the total error, d) evolution of the error related to the single plateaus, where \( L_1 \rightarrow VA \) and \( L_3 \rightarrow IA \) (referred to Figure 3-12). On the top of the plot, the initial conditions of the simulation are reported.

**Figure 10-35:** Comparison of the total battery capacity measured for a current rate of 1C and for a current rate of 0.1C for the cell listed in Table 6-1, a) for the charge and b) for the discharge process. In both cases (charge and discharge) the capacity is calculated with a CC process with the indicated current rate, starting from an empty (for the charge) or fully charged (for the discharge) state.
10.8 SoC estimation: additional results

**Figure 10-36:** Exemplary validation of the voltage modeling for *Cell B* of Table 5-8 for an ambient temperature of 40 °C, a) SoC and $\Psi$ profiles, b) measured voltage and modelled OCV, c) OCV error, d) comparison of measured and modeled OCV points represented in form of minor loop.
Figure 10-37: Exemplary validation of the two SoC estimation approaches for a mixed profile for Cell F2 of Table 5-11 for an ambient temperature of 15 °C, a) measured and estimated SoC, b) measured voltage and modelled OCV, c) OCV errors, d) SoC errors.
10.9 Additional results of V2G scenarios

10.9.1 Resistance degradation for the **Cell NMC**

![Graphs showing resistance degradation over time and cycles for different conditions.]

**Figure 10.38:** Evolution of the resistance increase (a) during the calendar aging tests and (b) during the cycle aging tests for the overall cell batch for the **Cell NMC.** The value of the resistance is measured through a pulse of duration of 2 s with 1C current rate for SoC of 50%. Capacity degradation can be found in Figure 7-4.

10.9.2 Supplementary calendar aging models employed for V2G simulations

A supplementary aging model was developed in the frame of this work. For both cells, the calendar aging model takes into account the effect of time, temperature and SoC (voltage), as shown in equation (10.1) for the **Cell LFP** and in equation (10.2) for the **Cell NMC**:

\[
\Delta Q_{\text{cal}} = \left( a_1 \cdot e^{\left(\frac{-a_2}{\text{Temperature}}\right)} \cdot e^{(a_3 \cdot \text{Voltage})} \right) \cdot \sqrt{\text{time}} \quad (10.1)
\]

\[
\Delta Q_{\text{cal}} = \left( a_1 \cdot e^{\left(\frac{-a_2}{\text{Temperature}}\right)} \cdot e^{(a_3 \cdot \text{Voltage})} \right) \cdot \text{time} \quad (10.2)
\]

The cycle aging model remains unchanged, and follows equation (7.3) and equations (7.4). The values of the coefficients for the calendar and cycle model are reported in Table 10-3.
Table 10-3: Coefficients obtained for the two tested LiBs for the supplementary calendar and cycle aging models.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Cell LFP</th>
<th>Cell NMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_1$</td>
<td>$5.71 \times 10^9$</td>
<td>$1.60 \times 10^{10}$</td>
</tr>
<tr>
<td>$a_2$</td>
<td>154.92</td>
<td>216.18</td>
</tr>
<tr>
<td>$a_3$</td>
<td>5.28</td>
<td>4.92</td>
</tr>
<tr>
<td>$b_1$</td>
<td>229.82</td>
<td>$1.57 \times 10^3$</td>
</tr>
<tr>
<td>$b_2$</td>
<td>-0.92</td>
<td>-0.098</td>
</tr>
<tr>
<td>$b_3$</td>
<td>292.77</td>
<td>$-9.72 \times 10^4$</td>
</tr>
<tr>
<td>$b_4$</td>
<td>-0.42</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 10-39 shows the validation of the supplementary develop aging models for the Cell LFP and Cell NMC.

Figure 10-39: Validation of the supplementary calendar and cycle aging model for the tested cells, a) calendar aging model validation for the Cell LFP and b) for the Cell NMC, c) cycle aging model validation for the Cell LFP and d) for the Cell NMC.
10.9.3 Additional results by means of the supplementary aging model

**Figure 10-40**: Comparison of the results for the scenarios no. 1 and no. 3 of Table 7-4 (weather condition of Aachen) for the aging model presented in appendix 10.9.2, a) SoH, b) predicted lifetime and c) total V2G energy for the random choice of the EVs; d) SoH, e) predicted lifetime and f) total V2G energy for the optimized choice of the EVs.
Figure 10-41: Comparison of the results for the scenarios no. 2 and no. 4 of Table 7-4 (weather condition of Dubai) for the aging model presented in appendix 10.9.2, a) SoH, b) predicted lifetime and c) total V2G energy for the random choice of the EVs; d) SoH, e) predicted lifetime and f) total V2G energy for the optimized choice of the EVs.
Figure 10-42: Comparison of the results for the scenarios no. 2 and no. 4 of Table 7-4 (weather condition of Dubai) in case of degradation with different rate of batteries of the same type for the aging model of section 7.2.1, a) SoH, b) predicted lifetime and c) total V2G energy for the random choice of the EVs; d) SoH, e) predicted lifetime and f) total V2G energy for the optimized choice of the EVs. For better understanding see section 7.3.2.
Figure 10.43: Effect of the inversion of the battery price on the lifetime for the weather condition in Aachen for the aging model presented in appendix 10.9.2, a) SoH, b) predicted lifetime (refer to section 7.3.3).
11 List of publications

Within the frame of this work several publications have been prepared which are listed below. Content from these publications is used for this thesis. This is in line with the rules for dissertation of the faculty for Electrical Engineering and Information Technology at RWTH Aachen University and has been agreed with Prof. Dirk Uwe Sauer, the supervisor of this thesis. Text elements, graphs, pictures or tables from these publications are not explicitly cited within the thesis as far as they are mainly created by the author of this work. If such elements in the listed publications are mainly created by the co-authors, a direct link to the publication is given.

In particular:
- Chapter 3 is based with modification on a publication that is published during the thesis. Reprinted from [22] with permission from Elsevier.
- Chapter 4 is based with modification on a publication that is published during the thesis. Reprinted from [94] with permission from Elsevier.
- Chapter 5 is based with modification on a publication that is published during the thesis. Reprinted from [113] with permission from Elsevier.
- Chapter 6 is based with modification on a publication that is published during the thesis. Reprinted from [186] with permission from Elsevier.
- Chapter 7 is based with modification on a publication that is published during the thesis. Reprinted from [179] with permission from Elsevier.

11.1 Journal Articles


### 11.2 Conference Proceedings

1. Andrea Marongiu, Wladislaw Waag, Madeleine Ecker, Patrick Borycka, Dirk Uwe Sauer, *A battery management system for LiFePO$_4$ battery in a vehicle to grid scenario*, Advanced Automotive Battery Conference, Pasadena, California, 2013.


<table>
<thead>
<tr>
<th>ABISEA Band</th>
<th>Author</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Eßer, A.</td>
<td>Berührungslose, kombinierte Energie- und Informationsübertragung für bewegliche Systeme</td>
</tr>
<tr>
<td>2</td>
<td>Vogel, U.</td>
<td>Entwurf und Beurteilung von Verfahren zur Hochausnutzung des Rad-Schiene-Kraftschlusses durch Triebfahrzeuge</td>
</tr>
<tr>
<td>3</td>
<td>Redehorn, Th.</td>
<td>Stromeinprägendes Antriebsystem mit fremderregter Synchronmaschine</td>
</tr>
<tr>
<td>4</td>
<td>Ackva, A.</td>
<td>Spannungseinprägendes Antriebssystem mit Synchronmaschine und direkter Stromregelung</td>
</tr>
<tr>
<td>5</td>
<td>Mertens, A.</td>
<td>Analyse des Oberschwingungsverhaltens von taksynchronen Delta-Modulationsverfahren zur Steuerung von Pulsstromrichtern bei hoher Taktzahl</td>
</tr>
<tr>
<td>6</td>
<td>Geuer, W.</td>
<td>Untersuchungen über das Alterungsverhalten von Bleiakkumulatoren</td>
</tr>
<tr>
<td>7</td>
<td>Langheim, J.</td>
<td>Einzelradantrieb für Elektrostraßenfahrzeuge</td>
</tr>
<tr>
<td>8</td>
<td>Fetz, J.</td>
<td>Fehlertolerante Regelung eines Asynchron-Doppelantriebes für ein Elektroroboterfahrzeug</td>
</tr>
<tr>
<td>9</td>
<td>Schütting, L.</td>
<td>Optimierte Auslegung induktiver Bauelemente für den Mittelfrequenzbereich</td>
</tr>
<tr>
<td>10</td>
<td>Skudelny, H.-Ch.</td>
<td>Stromrichtertechnik</td>
</tr>
<tr>
<td>11</td>
<td>Skudelny, Ch.</td>
<td>Elektrische Antriebe</td>
</tr>
<tr>
<td>12</td>
<td>Schönke, F.</td>
<td>Batterie-Management für Nickel-Cadmium Akkumulatoren</td>
</tr>
<tr>
<td>13</td>
<td>v. d. Weem, J.</td>
<td>Schmalbandige aktive Filter für Schienentriebfahrzeuge am Gleichspannungs-fahrdraht</td>
</tr>
<tr>
<td>14</td>
<td>Backhaus, K.</td>
<td>Spannungseinprägendes Direktantriebssystem mit schnelllaufender geschalteter Reluktanzmaschine</td>
</tr>
<tr>
<td>15</td>
<td>Reinold, H.</td>
<td>Optimierung dreiphasiger Pulsdauermodulationsverfahren</td>
</tr>
<tr>
<td>16</td>
<td>Köpken, H.-G.</td>
<td>Regelverfahren für Parallelschwingkreisumrichter</td>
</tr>
<tr>
<td>17</td>
<td>Mauracher, P.</td>
<td>Modellbildung und Verbundoptimierung bei Elektrostraßenfahrzeugen</td>
</tr>
<tr>
<td>18</td>
<td>Protiva, F.-F.</td>
<td>Vergleich dreiphasiger Resonanz-Wechselrichter in Simulation und Messung</td>
</tr>
<tr>
<td>19</td>
<td>Brockmeyer, A.</td>
<td>Dimensionierungswerkzeug für magnetische Baulemente in Stromrichteranwendungen</td>
</tr>
<tr>
<td>20</td>
<td>Apeldoorn, O.</td>
<td>Simulationsgestützte Bewertung von Steuerverfahren für netzgeführte Stromrichter mit verringertem Netzrückwirkung</td>
</tr>
</tbody>
</table>
ABISEA Band 21
Lohner, A.
Batteriemanagement für verschlossene Blei-Batterien am Beispiel von Unterbrechungsfreien Stromversorgungen
1. Auflage 1998, 144 Seiten
ISBN 3-86073-681-7

ABISEA Band 22
Reinert, J.
Optimierung der Betriebs- eigenschaften von Antrieben mit geschalteter Reluktanzmaschine
1. Auflage 1998, 168 Seiten
ISBN 3-86073-682-5

ABISEA Band 23
Nagel, A.
Leitungsgebundene Störungen in der Leistungselektronik: Entstehung, Ausbreitung und Filterung
1. Auflage 1999, 160 Seiten
ISBN 3-86073-683-3

ABISEA Band 24
Menne, M.
Drehschwingungen im Antriebsstrang von Elektrostraßenfahrzeugen - Analyse und aktive Dämpfung
1. Auflage 2001, 192 Seiten
ISBN 3-86073-684-1

ABISEA Band 25
von Bloh, J.
Multilevel-Umrichter zum Einsatz in Mittelspannungs-Gleichspannungsübertragungen
1. Auflage 2001, 152 Seiten
ISBN 3-86073-685-X

ABISEA Band 26
Karden, E.
Using low-frequency impedance spectroscopy for characterization, monitoring, and modeling of industrial batteries
1. Auflage 2002, 154 Seiten
ISBN 3-8265-9766-4

ABISEA Band 27
Karipidis, C.-U.
A Versatile DSP/ FPGA Structure optimized for Rapid Prototyping and Digital Real-Time Simulation of Power Electronic and Electrical Drive Systems
1. Auflage 2001, 164 Seiten
ISBN 3-8265-9738-9

ABISEA Band 28
Kahlen, K.
Regelungsstrategien für permanentmagnetische Direktantriebe mit mehreren Freiheitsgraden
1. Auflage 2003, 158 Seiten
ISBN 3-8322-1222-1

ABISEA Band 29
Inderka, R.
Direkte Drehmomentregelung Geschalteter Reluktanzantriebe
1. Auflage 2003, 190 Seiten
ISBN 3-8322-1175-6

ABISEA Band 30
Schröder, S.
Circuit-Simulation Models of High-Power Devices Based on Semiconductor Physics
1. Auflage 2003, 124 Seiten
ISBN 3-8322-1250-7

ABISEA Band 31
Buller, S.
Impedance-Based Simulation Models for Energy Storage Devices in Advanced Automotive Power Systems
1. Auflage 2003, 136 Seiten
ISBN 3-8322-1225-6

ABISEA Band 32
Schönknecht, A.
Topologien und Regelungsstrategien für das induktive Erwärmen mit hohen Frequenz-Leistungsprodukten
1. Auflage 2004, 170 Seiten
ISBN 3-8322-2408-4

ABISEA Band 33
Tolle, T.
Konvertiertopologien für ein aufwandsarmes, zweistufiges Schaltnetzteil zum Laden von Batterien aus dem Netz
1. Auflage 2004, 150 Seiten
ISBN 3-8322-2676-1

ABISEA Band 34
Götting, G.
Dynamische Antriebsregelung von Elektrostraßenfahrzeugen unter Berücksichtigung eines schwingungsfähigen Antriebsstrangs
1. Auflage 2004, 166 Seiten
ISBN 3-8322-2804-7

ABISEA Band 35
Dieckerhoff, S.
Transformerlose Stromrichterschaltungen für Bahnfahrzeuge am 16 2/3 Hz Netz
1. Auflage 2004, 158 Seiten
ISBN 3-8322-3094-7

ABISEA Band 36
Hu, J.
Bewertung von DC-DC-Topologien und Optimierung eines DC-DC-Leistungsmoduls für das 42-V-Kfz-Bordnetz
1. Auflage 2004, 156 Seiten
ISBN 3-8322-3201-X

ABISEA Band 37
Detjen, D.-O.
Characterization and Modeling of Si-Si Bonded Hydrophobie Interfaces for Novel High-Power BIMOS Devices
1. Auflage 2004, 146 Seiten
ISBN 3-8322-2963-9

ABISEA Band 38
Walter, J.
Simulationsbasierte Zuverlässigkeitssimulation in der modernen Leistungselektronik
1. Auflage 2004, 134 Seiten
ISBN 3-8322-3481-0
Aachener Beiträge des ISEA

**ABISEA Band 39**
Schwarzer, U.
IGBT versus GCT in der Mittelspannungsanwendung - ein experimenteller und simulativer Vergleich
1. Auflage 2005, 184 Seiten
ISBN 3-8322-4489-1

**ABISEA Band 40**
Bartram, M.
IGBT-Umrichtersysteme für Windkraftanlagen: Analyse der Zyklenbelastung, Modellbildung, Optimierung und Lebensdauervorhersage
1. Auflage 2006, 195 Seiten
ISBN 3-8322-5039-5

**ABISEA Band 41**
Ponnaluri, S.
Generalized Design, Analysis and Control of Grid side converters with integrated UPS or Islanding functionality
1. Auflage 2006, 163 Seiten
ISBN 3-8322-5281-9

**ABISEA Band 42**
Jacobs, J.
Multi-Phase Series Resonant DC-to-DC Converters
1. Auflage 2006, 185 Seiten
ISBN 3-8322-5532-X

**ABISEA Band 43**
Linzen, D.
Impedance-Based Loss Calculation and Thermal Modeling of Electrochemical Energy Storage Devices for Design Considerations of Automotive Power Systems
1. Auflage 2006, 150 Seiten
ISBN 3-8322-5706-3

**ABISEA Band 44**
Fiedler, J.
Design of Low-Noise Switched Reluctance Drives
1. Auflage 2007, 183 Seiten
ISBN 978-3-8322-5864-1

**ABISEA Band 45**
Fuengwarodsakul, N.
Predictive PWM-based Direct Instantaneous Torque Control for Switched Reluctance Machines
1. Auflage 2007, 150 Seiten

**ABISEA Band 46**
Meyer, C.
Key Components for Future Offshore DC Grids
1. Auflage 2007, 196 Seiten
ISBN 978-3-8322-6571-7

**ABISEA Band 47**
Fujii, K.
Characterization and Optimization of Soft-Switched Multi-Level Converters for STATCOMs
1. Auflage 2008, 206 Seiten
ISBN 978-3-8322-6981-4

**ABISEA Band 48**
Carstensen, C.
Eddy Currents in Windings of Switched Reluctance Machines
1. Auflage 2008, 190 Seiten
ISBN 978-3-8322-7118-3

**ABISEA Band 49**
Bohien, O.
Impedance-based battery monitoring
1. Auflage 2008, 200 Seiten

**ABISEA Band 50**
Thele, M.
A contribution to the modelling of the charge acceptance of lead-acid batteries - using frequency and time domain based concepts
1. Auflage 2008, 168 Seiten
ISBN 978-3-8322-7659-1

**ABISEA Band 51**
König, A.
High Temperature DC-to-DC Converters for Downhole Applications
1. Auflage 2009, 160 Seiten
ISBN 978-3-8322-8489-3

**ABISEA Band 52**
Dick, C. P.
Multi-Resonant Converters as Photovoltaic Module-Integrated Maximum Power Point Tracker
1. Auflage 2010, 192 Seiten
ISBN 978-3-8322-9199-0

**ABISEA Band 53**
Kowal, J.
Spatially-resolved impedance of nonlinear inhomogeneous devices - using the example of lead-acid batteries
1. Auflage 2010, 214 Seiten
ISBN 978-3-8322-9483-0

**ABISEA Band 54**
Roscher, M.
Zustandserkennung von LiFeP04-Batterien für Hybrid- und Elektrofahrzeuge
1. Auflage 2011, 194 Seiten
ISBN 978-3-8322-9738-1

**ABISEA Band 55**
Hirschmann, D.
Highly Dynamic Piezoelectric Positioning
1. Auflage 2011, 156 Seiten
ISBN 978-3-8322-9746-6

**ABISEA Band 56**
Rigbers, K.
Highly Efficient Inverter Architectures for Three-Phase Grid Connection of Photovoltaic Generators
1. Auflage 2011, 254 Seiten
ISBN 978-3-8322-9816-9

**ABISEA Band 57**
Kasper, K.
Analysis and Control of the Acoustic Behavior of Switched Reluctance Drives
1. Auflage 2011, 214 Seiten
ISBN 978-3-8322-9869-2

**ABISEA Band 58**
Köllensperger, P.
The Internally Commutated Thyristor - Concept, Design and Application
1. Auflage 201 J, 212 Seiten
ISBN 978-3-8322-9909-5
Aachener Beiträge des ISEA

ABISEA Band 59
Schoenen, T.
Einsatz eines DC/DC-Wandlers zur Spannungsanpassung zwischen Antrieb und Energiespeicher in Elektro- und Hybridfahrzeugen
1. Auflage 2011, 138 Seiten
ISBN 978-3-8440-0622-3

ABISEA Band 60
Hennen, M.
Switched Reluctance Direct Drive with Integrated Distributed Inverter
1. Auflage 2012, 150 Seiten

ABISEA Band 61
van Treek, D.
Position Sensorless Torque Control of Switched Reluctance Machines
1. Auflage 2012, 144 Seiten
ISBN 978-3-8440-1152-4

ABISEA Band 62
Bragard, M.
Integrated Emitter Turn-Off Thyristor. An Innovative MOS-Gated High-Power Device
1. Auflage 2012, 172 Seiten
ISBN 978-3-8440-1152-4

ABISEA Band 63
Gerschler, J. B.
Ortsaufgelöste Modellbildung von Lithium-Ionen-Systemen unter spezieller Berücksichtigung der Batteriealterung
1. Auflage 2012, 350 Seiten
ISBN 978-3-8440-1307-8

ABISEA Band 64
Neuhaus, C.
Schaltstrategien für Geschaltete Reluktanzantriebe mit kleinem Zwischenkreis
1. Auflage 2012, 144 Seiten
ISBN 978-3-8440-1487-7

ABISEA Band 65
Butschen, T.
Dual-ICT- A Clever Way to Unite Conduction and Switching Optimized Properties in a Single Wafer
1. Auflage 2012, 178 Seiten
ISBN 978-3-8440-1771-7

ABISEA Band 66
Plum, T.
Design and Realization of High-Power MOS Turn-Off Thyristors
1. Auflage 2013, 130 Seiten
ISBN 978-3-8440-1884-4

ABISEA Band 67
Kiel, M.
Impedanzspektroskopie an Batterien unter besonderer Berücksichtigung von Batteriesensoren für den Feldeinsatz
1. Auflage 2013, 232 Seiten

ABISEA Band 68
Brauer, H.
Schneiddrehender Geschalteter Reluktanzantrieb mit extremem Längendurchmesserverhältnis
1. Auflage 2013, 202 Seiten
ISBN 978-3-8440-2345-9

ABISEA Band 69
Thomas, S.
A Medium-Voltage Multi-Level DC/DC Converter with High Voltage Transformation Ratio
1. Auflage 2014, 236 Seiten
ISBN 978-3-8440-2605-4

ABISEA Band 70
Richter, S.
Digitale Regelung von PWM Wechselrichtern mit niedrigen Trägerfrequenzen
1. Auflage 2014, 134 Seiten
ISBN 978-3-8440-2641-2

ABISEA Band 71
Bösing, M.
Acoustic Modeling of Electrical Drives - Noise and Vibration Synthesis based on Force Response Superposition
1. Auflage 2014, 208 Seiten

ABISEA Band 72
Waag, W.
Adaptive algorithms for monitoring of lithium-ion batteries in electric vehicles
1. Auflage 2014, 242 Seiten
ISBN 978-3-8440-2976-5

ABISEA Band 73
Sanders, T.
Spatially Resolved Electrical In-Situ Measurement Techniques for Fuel Cells
1. Auflage 2014, 138 Seiten
ISBN 978-3-8440-3121-8

ABISEA Band 74
Baumhöfer, T.
Statistische Betrachtung experimenteller Alterungsuntersuchungen an Lithium-Ionen Batterien
1. Auflage 2015, 174 Seiten
ISBN 978-3-8440-3423-3

ABISEA Band 75
Andre, D.
Systematic Characterization of Ageing Factors for High-Energy Lithium-Ion Cells and Approaches for Lifetime Modelling Regarding an Optimized Operating Strategy in Automotive Applications
1. Auflage 2015, 210 Seiten
ISBN 978-3-8440-3587-2

ABISEA Band 76
Merei, G.
Optimization of off-grid hybrid PV-wind-diesel power supplies with multi-technology battery systems taking into account battery aging
1. Auflage 2015, 194 Seiten
ISBN 978-3-8440-4148-4
ABISEA Band 77
Schulte, D.
Modellierung und experimentelle Validierung der Alterung von Blei-Säure Batterien durch inhomogene Stromverteilung und Säureschichtung

ABISEA Band 78
Schenk, M.
Simulative Untersuchung der Wicklungsverluste in Geschalteten Reluktanzmaschinen

ABISEA Band 79
Wang, Y.
Development of Dynamic Models with Spatial Resolution for Electrochemical Energy Converters as Basis for Control and Management Strategies

ABISEA Band 80
Ecker, M.
Lithium Plating in Lithium-Ion Batteries: An Experimental and Simulation Approach

ABISEA Band 81
Zhou, W.
Modellbasierte Auslegungsmethode von Temperierungsanlagen für Hochvolt-Batterien in Personenkraftfahrzeugen

ABISEA Band 82
Lunz, B.
Deutschlands Stromversorgung im Jahr 2050
Ein szenarioorientiertes Verfahren zur vergleichenden Bewertung von Systemvarianten und Flexibilitätsoptionen

ABISEA Band 83
Hofmann, A.
Direct Instantaneous Force Control Key to Low-Noise Switched Reluctance Traction Drives
1. Auflage 2016, 244 Seiten ISBN 978-3-8440-4715-8

ABISEA Band 84
Budde-Meiwes, H.
Dynamic Charge Acceptance of Lead-Acid Batteries for Micro-Hybrid Automotive Applications

ABISEA Band 85
Engel, S. P.
Thyristor-Based High-Power On-Load Tap Changers Control under Harsh Load Conditions

ABISEA Band 86
VanHoek, H.
Design and Operation Considerations of Three-Phase Dual Active Bridge Converters for Low-Power Applications with Wide Voltage Ranges

ABISEA Band 87
Diekhans, T.
Wireless Charging of Electric Vehicles - a Pareto-Based Comparison of Power Electronic Topologies

ABISEA Band 88
Lehner, S.
Reliability Assessment of Lithium-Ion Battery Systems with Special Emphasis on Cell Performance Distribution

ABISEA Band 89
Käblitz, S.
Untersuchung der Alterung von Lithium-Ionen-Batterien mittels Elektroanalytik und elektrochemischer Impedanzspektroskopie
1. Auflage 2016, 257 Seiten urn:nbn:de:hbz:82-rwth-2016-120944

ABISEA Band 90
Witzenhausen, H.
Elektrische Batteriespeichersysteme: Modellbildung, Parameteridentifikation und Model reduktion

ABISEA Band 91
Münlix, J.
Einfluss von Stromstärke und Zyklentiefe auf graphitierte Anoden

ABISEA Band 92
Pliatowicz, G.
Failure Detection and Battery Management Systems of Lead-Acid Batteries for Micro-Hybrid Vehicles

ABISEA Band 93
Drillkens, J.
Aging in Electrochemical Double Layer Capacitors: An Experimental and Modelling Approach

ABISEA Band 94
Magnor, D.
Globale Optimierung netzgekoppelter PV-Batteriesysteme unter besonderer Berücksichtigung der Batteriealterung

ABISEA Band 95
Iliksu, M.
Elucidation and Comparison of the Effects of Lithium Salts on Discharge Chemistry of Nonaqueous Li-O2 Batteries
ABISEA Band 96
Schmalstieg, J.
Physikalisch-elektrochemische Simulation von Lithium-Ionen-Batterien: Implementierung, Parametrierung und Anwendung
1. Auflage 2017, 176 Seiten
DOI: 10.18154/RWTH-2017-04693

ABISEA Band 97
Soltau, N.
High-Power Medium-Voltage DC-DC Converters: Design, Control and Demonstration
1. Auflage 2017, 176 Seiten
ISBN 978-3-942789-42-4

ABISEA Band 98
Stieneker, M.
Analysis of Medium-Voltage Direct-Current Collector Grids in Offshore Wind Parks
1. Auflage 2017, 144 Seiten
ISBN 978-3-942789-43-1

ABISEA Band 99
Masomtob, M.
A New Conceptual Design of Battery Cell with an Internal Cooling Channel