Doctoral Thesis in Chemical Engineering

The dynamic behavior of the NiMH battery – Creating a versatile NiMH battery model

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Stockholm, Sweden 2023
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Academic Dissertation which, with due permission of the KTH Royal Institute of Technology, is submitted for public defence for the Degree of Doctor of Philosophy on Wednesday the 22nd of November 2023, at 2:00 p.m. in Kollegiesalen, Brinellvägen 8, Stockholm.

Doctoral Thesis in Chemical Engineering
KTH Royal Institute of Technology
Stockholm, Sweden 2023
Abstract

To facilitate the shift from fossil to renewable energy sources, energy storage is needed to cope with the intermittent nature of technologies such as solar, wind, and wave power. One storage alternative is battery-based stationary energy storage. There are many battery types to choose from, but Nickel Metal Hydride (NiMH) is a type that is especially well suited. These batteries have a high energy density, a large temperature operating window and are a safe alternative for large scale energy storage.

In this thesis, the behavior of the NiMH battery is studied with the aim to develop a dynamic battery model, a model that is capable of reproducing the battery voltage and pressure, also for dynamic usage. Such a model can be used to facilitate development of NiMH batteries, improvement of the algorithms used in the Battery Management System (BMS), quality control, and dimensioning of energy storage systems. These improvements can lead to stationary energy storage with a higher efficiency and longer usable lifetime.

To increase the understanding of the battery function, deeper study was carried out of two behaviors that are typical for the NiMH battery and are deemed to have a large impact on the battery: Open circuit voltage (OCV) hysteresis and the battery gas phase behavior. The OCV hysteresis complicates modelling because it causes the battery rest voltage at a certain degree of charge to depend on the charge/discharge path taken to get there. OCV hysteresis is not noticeable for all batteries, and it is especially prominent for the NiMH battery. The gas phase in the NiMH battery is active since the electrolyte is water based and the voltage window during operation causes oxygen evolution at the positive electrode. The oxygen is then recombined into water at the negative electrode. The amount of hydrogen in the gas phase varies over a cycle due to the the dependence on temperature and state of charge of the hydrogen equilibrium pressure over the negative metal hydride electrode.

Two models were developed separately to study these behaviors. The models showed good qualitative reproduction capabilities. The hysteresis phenomenon was also studied using structural analysis methods. Differences were identified in the material structure between two samples of the positive electrode material at the same state of charge but different hysteresis states. These differences were
found in both the bulk and the surface region of the particles. The differences in bulk were related to degree of disorder and the differences in the surface region to inhomogeneity in Li distribution in the cobalt oxyhydroxide layer. The gas composition was studied using mass spectrometry. The gas phase was mostly composed of nitrogen, but hydrogen was responsible for the majority of the pressure changes of the battery during a charge/discharge cycle. Oxygen could be detected at the end of charge, where it is produced due to high voltage on the positive electrode.

Finally, the two models were added to a P2D-model. This model type is commonly used to simulate battery behavior, and is based on electrochemical theory with approximations used for the porous electrode behavior. The spacial distribution is modeled in one dimension with an additional dimension added locally to simulate intra particle diffusion. The combined model showed that the behavior seen from a NiMH during dynamic usage could be recreated qualitatively through adding OCV hysteresis and the gas phase behavior to this standard model type.

**Keywords**

NiMH batteries, Battery Modeling, OCV hysteresis, NiMH gas phase, P2D model
Sammanfattning


I den här avhandlingen studeras NiMH batteriets beteende med målet att ta fram en dynamisk batterimodell, en modell som är kapabel att reproduera batteriets spänning och tryckbeteende även för dynamiska körcykler. En sådan modell kan användas till att underlätta utveckling av NiMH batterier, förbättra algoritmerna i batteriernas styrsystem, kvalitetskontroll och dimensionering av system. I fölajngningen innebär det stationära energilager med högre verkningsgrad och längre livslängd.


I arbetet så utvecklades två modeller separat för att beskriva dessa två beteenden. Modellerna visade upp en god kvalitativ överensstämmelse. Hystersfenomenet studerades med hjälp av strukturchemiska metoder, och skillnader identifierades i materialstrukturen mellan positivt elektrodmaterial vid samma laddningsrad men olika hysteresställstand. Dessa skillnader återfanns både i bulken och ytre regionen i de aktiva partiklarna. Skillnaderna i bulken hängrörde från graden av oordning, och skillnaderna i ytre regionen i ojämnhet i
Li distributionen i koboltoyhydroxidlagret. Gassammansättningen studerades med hjälp av masspektrometri. Gasfasen utgjordes till största delen av kväve, men vätskagas var ansvarig för majoriteten av tryckförändringen hos batteriet under en laddcykel. Syrgas kunde mätas vid slutet av laddning, där det produceras till följd av höga spänningar på den positiva elektroden.

Slutligen så adderades de två utvecklade modellerna till en så kallad P2D modell. Denna modelltyp är vanlig för att simulera batterier och bygger på elektrokemisk teori med uttryck för att approximera beteendet hos de porösa elektroderna. Modellen är byggd i en rumsdimension, med en ytterligare dimension för att simulera diffusionen i de aktiva partiklarna som räknas ut lokalt. Den sammanslagna modellen visade att de beteenden som ses hos ett NiMH batteri vid blandad drift kunde återskapas kvalitativt genom att ta öppetkretsspänningshysteresen och gasfasbeteendena i beaktan.

**Nyckelord**
NiMH batterier, Batterimodellering, OCV hysteres, NiMH gasfas, P2D modell
Preface

Research is the final frontier, a foray beyond the collective knowledge of humanity. Standing on the shoulders of those who came before and peering out into the fog can be daunting, but the feeling of removing part of it and starting to see clearly is unlike anything else. With this thesis I hope to share the realizations that I’ve come to over the last few years and perhaps inspire others to take the step into the unknown. As long as there is curiosity, there is hope.
List of appended papers

Paper I

Paper II
Jenny Börjesson Axén, Gustav Ek, Alice Gratrex, Göran Lindbergh, Dag Noréus, Ingmar Persson, Helen Y Playford, Kajsa Sigfridsson Clauss, Jakob Thyr, Erika Widenkvist Zetterström, “A Structural Investigation into the OCV Hysteresis of the Ni(OH)2 Electrode”. Manuscript. 2023

Paper III

Paper IV
Aleksandra Lindberg, Björn Eriksson, Amrita Pushkaran Sandra, Jenny Börjesson Axén, Göran Lindbergh, “Gas Phase Composition of a NiMH Battery during a Work Cycle”. Manuscript. 2023

Paper V

Paper VI
Jenny Börjesson Axén, Henrik Ekström, Erika Widenkvist Zetterström, Göran Lindbergh, “Creating a Dynamic P2D Model for the Nickel Metal Hydride Battery”. Manuscript. 2023
Author contributions

Paper I
Model design and verification. Design of experiments and selection of application data. Data analysis. Writing and illustration.

Paper II
Conceptualization. Experimental design of electrochemical experiments. Sample extraction. Project coordination. Experimental measurements, neutron diffraction. Writing and discussion. Main editor.

Paper III
Experimental design of electrochemical measurements. Experimental work. Data analysis. Writing and illustration.

Paper IV
Conceptualization. Design of electrochemical experiments. Writing and editing.

Paper V
Model design and verification. Selection of experimental data. Data analysis. Writing and illustration.

Paper VI
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# Nomenclature

## Abbreviations

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<tr>
<td>$-\Delta V$</td>
<td>Negative Delta Voltage</td>
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<tr>
<td>0D</td>
<td>Zero dimensional model</td>
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<tr>
<td>BEV</td>
<td>Battery Electric Vehicle</td>
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<tr>
<td>BMS</td>
<td>Battery Management System</td>
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<tr>
<td>EEC</td>
<td>Equivalent Electric Circuit</td>
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<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
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<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
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<tr>
<td>GITT</td>
<td>Galvanostatic Intermittent Titration Technique</td>
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<tr>
<td>HSA</td>
<td>Hydrogen Storage Alloy</td>
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<tr>
<td>MH</td>
<td>Metal Hydride</td>
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<tr>
<td>NiCd</td>
<td>Nickel Cadmium battery</td>
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<tr>
<td>NiH$_2$</td>
<td>Nickel Hydrogen battery</td>
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<tr>
<td>NiMH</td>
<td>Nickel Metal Hydride battery</td>
</tr>
<tr>
<td>NMC</td>
<td>Nickel Manganese Cobalt oxide Li-ion battery</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>P2D</td>
<td>Pseudo Two Dimensional model</td>
</tr>
<tr>
<td>PCT</td>
<td>Pressure Composition Isotherm</td>
</tr>
<tr>
<td>SOC</td>
<td>State of Charge</td>
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<td>SOH</td>
<td>State of Health</td>
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</table>
NOMENCLATURE

SP Single Particle
TEM Transmission Electron Microscopy
VSC Voltage Source Converter
XANES X-ray Absorption Near Edge Structure
XAS X-ray Absorption Spectroscopy
XRPD X-ray Powder Diffraction

Parameters

$\chi$ Hysteresis parameter
$\Delta H^0$ Standard enthalpy of reaction
$\Delta H_{H/M}^0$ Standard enthalpy of hydrogen absorption
$\Delta S^0$ Standard entropy of reaction
$a_{H_2O}$ Water activity
$D_s^{neg}$ Diffusion constant, negative
$D_s^{pos}$ Diffusion constant, positive
$E_{MH}^0$ Standard Potential MH
$E_{factor}^{neg}$ Negative OCV adjustment factor
$E_{eq}^{O_2}$ Equilibrium potential, oxygen evolution
$E_{eq}$ Equilibrium Potential
$E_{MH}$ Equilibrium Potential MH
$E_{OC, ch}$ Open circuit potential, charge
$E_{OC, dch}$ Open circuit potential, discharge
$E_{OC}$ Open circuit potential
$F$ Faraday constant
$i_0^{neg}$ Exchange current density, negative
$i_0^{pos}$ Exchange current density, positive
$I_{cell}$ Cell current
$k_{\chi_{ch}}$ Hysteresis kinetic constant, charge

$k_{\chi_{dch}}$, Continuous discharge Hysteresis kinetic constant, continuous discharge

$k_{\chi_{dch}}$, Pulsed data Hysteresis kinetic constant, discharge, pulsed data

$k_{\chi}$ Hysteresis kinetic constant

$K_{O_2}$ Oxygen recombination kinetic constant

$k_{OER}$ Oxygen evolution kinetic constant

$K_T$ Heat transfer parameter

$p_{H_2}^0$ Hydrogen reference pressure at standard conditions

$p_{H_2}^{\text{ref}}$ Reference hydrogen pressure PCT

$p_{H_2}$ Hydrogen pressure

$Q$ Cell capacity

$R$ Universal gas constant

$R_{\text{contact}}$ Contact resistance

$T$ Temperature

$T_{\text{ref}}$ Reference temperature PCT
Chapter 1

Introduction

The world is on the cusp of a major technological shift when it comes to energy supply. For one and a half centuries, humanity has utilized fossil fuels to sustain our energy needs [1]. However, due to rising concerns over climate change and the effect on human living conditions, there is a movement towards using renewable energy sources to achieve a green energy transition. One important part of such a transition is stationary battery energy storage. The United Nations have defined 17 goals for sustainable development [2], and the use of stationary energy storage can help fulfill a number of these goals. Goal 7 concerns affordable and clean energy and that it should be available to everyone. Here the use of batteries for stationary energy storage makes it possible to use clean electric energy sources that are not continuous, such as solar, wind and wave power. It also makes electricity available around the clock in remote or underdeveloped regions through the use of these energy sources. Goal 9 concerns sustainable development in industry, innovation, and infrastructure. Battery energy storage makes grid equalization possible. It also enables the realization of an electricity infrastructure that supports the use of renewable energy sources of a periodic nature. In addition, use of batteries for phase-shifting and time-shifting can help regulate power spikes in both production and consumption, increasing the stability of the grid. Using energy storage to supplement power can also change how we use the grid, such as fast charging stations for electric vehicles, aiding implementation of electromobility. Goal 10 is to support the marginalized and disadvantaged. By supplying, and reducing the cost for stationary energy storage, it’s possible to create local electricity infrastructure for communities and societies who cannot afford to invest in large scale infrastructure. Goal 11 is to make cities and human settlements inclusive, safe, resilient, and sustainable. Using stationary energy storage makes it possible to have local production of electricity in the city itself, for example through the use of solar cells or small-scale wind power that are built into the architecture of homes and businesses. This makes the cities more sustainable and reduces
the need to burn fossil fuels for cooking and heating, reducing pollution levels. Lastly, goal 12 is to ensure sustainable consumption and production patterns. Here, stationary energy storage facilitates localized production of clean energy, as well as clean energy supply to industry through enabling the use of clean periodic power sources such as solar and wind.

As can be read from the title, this thesis focuses on NiMH batteries. One might question why one should continue to develop an older battery technology when Li-ion technologies are commercially available, with a widespread implementation. The short answer to that is that all battery technologies have strengths and weaknesses that make them better suited for different applications, but beyond that it is a question of volume. This can be illustrated using a short calculation. According to IEA, the global sales of cars for personal transportation in 2020 amounted to 73 million vehicles [3]. This was a decrease from 2019 due to the impact of Covid 19 on the global economy. Let us assume that all of these cars were battery electric vehicles (BEV). If these BEVs were Nissan Leafs, with a nominal battery capacity of 40kWh [4], the total needed battery capacity would have been 2.92 TWh. If they instead were Tesla Model 3 cars, with a nominal battery capacity of 60kWh [5], the required battery capacity would be even higher at 4.38 TWh. To make these numbers relatable, one can compare with the production capacity of Northvolt Ett, a production facility currently starting up production in Skellefteå, Sweden. It is a sizeable facility, the Swedish company secured 1 billion dollars from investors to finance the construction [6], with a production capacity of 60 GWh/year when ramped up to full capacity [7]. At full production capacity, 48.7 factories of this size would be required to produce enough cars if they were Nissan Leafs, and 73 factories if they were Tesla Model 3s. This is the amount

![Ragone plot of different battery technologies](image-url)
1.1. AIM AND SCOPE

of battery factories needed just for humanity to sustain current standard of living with a fully electrified personal vehicle fleet. On top of this there will be a demand for high-capacity batteries to cover electrification of other modes of transportation, off-grid energy storage, and for stationary energy storage to support the grid as a part of the green energy shift in electricity production. The demand will be vast, and diversifying into other battery types than Li-ion will help supply that demand. This helps to free up Li-ion large cell production to supply electromobility, where its unique properties of high energy and power density, as illustrated in Figure 1.1, are needed the most. The aim of this thesis is to increase the understanding of the NiMH battery behavior through modeling to better make use of it in energy storage applications, increasing energy efficiency and longevity of battery systems.

1.1 Aim and scope

The NiMH battery is a complex electrochemical cell, and it is not fully understood how the different processes in the battery interact and influence each other. While modeling of Li-based batteries has progressed significantly over the last twenty years, the research interest in NiMH batteries waned just as the methods and tools for battery modelling developed to be truly useful. As a consequence, models that sufficiently recreate and explain the behavior of the NiMH battery during use in application were never developed. Such a model would be a vital tool, not only to further develop the battery but also to improve battery usage through development of better battery management systems and digital twins.

This thesis aims to study the dynamic behavior in NiMH batteries, mainly through physics-based modeling, but also using experimental methods. To gain further understanding of the system, this thesis focuses on factors that have significant influence on the behavior of the battery. Two main factors in need of further study have been identified: Open Circuit Voltage (OCV) hysteresis and gas reactions stemming from the use of an aqueous electrolyte. These factors were studied more thoroughly during the course of the work. On the matter of OCV hysteresis, the main questions are how it affects the electrochemical performance of the battery and why it occurs. For the gas reactions connected to the use of an aqueous electrolyte, the questions are how these reactions affect the battery behavior and through what mechanisms.

Finally, a unified model was constructed with the aim to incorporate these two factors. This is to test the hypothesis that including them in our understanding of the NiMH battery is sufficient to predict the battery behavior under normal operating conditions.
Chapter 2

Background

2.1 The NiMH battery

The nickel metal hydride battery (NiMH) is a secondary battery technology, i.e. it is rechargeable. The positive electrode consists of a nickel hydroxide and the negative electrode of a hydrogen storage alloy, also called metal hydride (MH). The electrolyte is alkaline, primarily using potassium hydroxide but also using different additives. For example LiOH is mixed in to suppress oxygen evolution on the positive electrode. The NiMH battery was developed from the nickel cadmium (NiCd) and nickel hydrogen (NiH$_2$) batteries, which share the same positive electrode, after the discovery of hydrogen storage alloys. The MH materials offered a negative electrode that was more lightweight, less toxic, and had better oxygen recombination properties than the cadmium electrode in the NiCd batteries. At first, NiMH batteries had poor high-power capabilities, leading to NiCd retaining applications with high power demands such as power tools. As the NiMH batteries improved, NiCd was eventually phased out in these applications. The high power and energy density of NiMH compared to the other technologies on the market at the time, as shown in Figure 2.1 lead to its use in the early hybrid electric vehicles such as the Toyota Prius. The specific energy of NiMH is lower compared to the different Li-ion battery types, but the technology has advantages in terms of safety and producibility. The use of an aqueous electrolyte in lieu of the organic electrolyte used in Li-ion batteries makes the battery safer in case of a fire.

The NiMH battery stores energy through the transfer of hydrogen between the electrodes: At the positive electrode, protons are deintercalated during charge with nickel changing oxidation state from +II to +III to maintain electroneutrality. At the negative electrode, hydrogen is reduced to $\text{H}^0$ and intercalated into the structure of the alloy, forming the metal hydride compound MH. The reactions are noted below, where reaction 2.1 occurs at the positive
CHAPTER 2. BACKGROUND

Figure 2.1: Reactions in a NiMH battery [9]

The equilibrium potential ($E_{eq}$) for the two reactions depends on state of charge (SOC) of the electrodes, as well as charge/discharge history for the positive electrode. The SOC of an electrode is the current concentration of the charged species in the electrode normalized to the maximum theoretical concentration. In this case the charged species are NiOOH for the nickel electrode and MH for the metal hydride electrode. The $E_{eq}$ of the two electrodes specific for this system will be discussed in detail in the corresponding section, but the plateau voltage for the positive electrode, equation 2.1, is $\sim$0.57 V vs. SHE during charge and $\sim$0.44 V vs. SHE during discharge. For the hydrogen alloy, the plateau voltage is $\sim$0.73 V vs. SHE. To avoid excessive hydrogen production, the NiMH battery is designed to be positive electrode capacity limited, meaning that the battery capacity is determined by the capacity of the positive electrode, and that the negative electrode has excess capacity. Due to processes occurring during the formation process, there is also an over-discharge capacity in the negative electrode. This means, that when the positive electrode is
fully discharged the negative electrode is not fully deintercalated, as illustrated in Figure 2.1. Consequently, the shape of the open circuit voltage (OCV) of the battery is determined by the OCV behavior of the positive electrode, as the negative electrode rarely moves out of the plateau region. An OCV curve recorded for the battery used in this work is shown in Figure 2.2.

Figure 2.2: Open circuit voltage of a NiMH battery. Recorded on module using GITT and EEC modelling.

In addition to the charge/discharge reactions there are also side reactions due to the aqueous electrolyte. When approaching the fully charged state on the positive electrode, oxygen evolution starts to compete with the charge (deintercalation) reaction. The oxygen evolution increases in intensity in the upper part of the voltage window as the SOC increases, until it eventually takes over completely during overcharging. The oxygen produced at the positive electrode is recombined on the negative electrode, releasing the energy as heat. These reactions are shown in equation 2.3.

$$2 \text{H}_2\text{O} + \text{O}_2 + 4 e^- \xrightarrow{\text{MH/ Ni}} 4 \text{OH}^-$$  \hspace{1cm} (2.3)

During continuous overcharging, these two reactions reach an equilibrium and the battery eventually reaches a steady state. The oxygen evolution/recombination cycle makes it possible to build sealed NiMH batteries with no safety issues re-
lated to prolonged overcharging, provided that the battery is sufficiently cooled, creating a battery that does not require refilling of water like flooded lead-acid or NiCd batteries.

Should overdischarge occur, hydrogen will be evolved on the positive electrode and then recombined on the negative electrode according to equation 2.4

\[
2H_2O + 2e^- \xrightarrow{\text{Ni}} 2OH^- + H_2
\]  

Unlike oxygen evolution, overdischarge is not a part of the working voltage window and will cause irreversible damage to the conductive network of the positive electrode. The cycling limits are therefore set to avoid overdischarge. A summary of the battery reactions can be found in Figure 2.1

2.1.1 The Nilar module

The battery studied in this work is the Nilar Energy module, shown in Figure 2.3, a 10-cell battery module with a capacity of 10Ah. The module differs from the conventional NiMH battery due to a different production technology and design. The module is bipolar, which means that instead of having a localized contact point, such as a current collector tab, the current collector is in contact with the entire surface of the electrode. The cells are stacked
on-top of each other, resembling a battery lasagna, with bi-plates between each cell and individual gaskets to retain the electrolyte, see Figure 2.3. The electrodes are separated by a polymer felt that is wetted with a limited amount of KOH electrolyte, creating a starved electrolyte configuration. This allows for both ionic conductivity in the liquid phase and empty space for gas to pass through. The electrolyte is highly concentrated 6:1 KOH/LiOH, with LiOH added to suppress oxygen evolution. The bipolar configuration ensures an even current distribution across the cell, which allows the cells to age uniformly. The electrodes are not sintered or formed from a slurry, instead they are produced through calendaring a dry powder mixture onto a polymer scrim [10]. This process eliminates the need for solvents and drying during production, and instead of having a nickel structure coated with slurry, the conductive structure is achieved by adding nickel powder to the active material during powder mixing.

2.1.2 Positive electrode

The positive electrode stores energy using the Ni(OH)$_2$/NiOOH redox pair. As the electrode is charged, Ni(II) is transformed to Ni(III) and H$^+$ is deintercalated, as seen in equation 2.1. Bode et al. [11] studied the phase transformation of the Ni(OH)$_2$/NiOOH redox pair, and summarized it graphically, as shown in Figure 2.4. In the uncharged state Ni is present as $\beta$-Ni(OH)$_2$, a hexagonal, brucite type structure, which is then transformed into $\beta$-NiOOH as the electrode is charged. This structure is hexagonal with a lower $a$-distance (Ni distance within the crystal layer) and a higher $c$-distance (distance between crystal layers) than the $\beta$-Ni(OH)$_2$ [16]. Overall, the cell unit volume is lower for $\beta$-NiOOH than for $\beta$-Ni(OH)$_2$. During overcharge, the crystal layers of the $\beta$-NiOOH are parted and water and supporting ions intrude into the increased intra layer spacing, creating a phase where the oxidation state of Ni increases further, to an average oxidation state that ranges between $+3$ and $+3.75$ [16]. In addition, the alignment of the crystal layers is skewed, resulting in an expanded, more disordered state. This phase is named the $\gamma$-NiOOH phase. This phase can be discharged either to the $\beta$-Ni(OH)$_2$ phase, or a Ni(OH)$_2$ phase that retains the disorder from the $\gamma$-NiOOH. This is called the $\alpha$-Ni(OH)$_2$ phase. The alpha phase will convert to the more stable beta phase over time [16]. When used in a battery the fully discharged electrode will not be pure $\beta$-Ni(OH)$_2$. Instead, part of the nickel will stay as Ni$^{3+}$ in the $\beta$-NiOOH phase. This is due to the poor conductivity of $\beta$-Ni(OH)$_2$. Deabate et al. [17] estimates that the average oxidation state of nickel when discharge is terminated ranges from $+2.2$ to $+2.35$. In the Nilar batteries, the positive electrode consists of a mixture of active Ni(OH)$_2$ material and metallic nickel. The nickel is added to enhance the conductivity of the electrode and works as an adhesive when the powder is pressed together into the finished electrode. The active
material is not pure Ni(OH)$_2$, instead it consists of spherical Ni(OH)$_2$ particles that are doped with cobalt and zinc to improve performance. The particles are covered by a coating that consists of different cobalt oxides and hydroxides, added to form a conductive network in the electrode. The particle size ranges from 5 to 20 µm in diameter, and the cobalt oxide layer thickness varies but is
2.1. THE NIMH BATTERY

Figure 2.5: SEM image of positive \( \text{Ni(OH)}_2 \) electrode. Round spheres: cobalt oxide coated \( \text{Ni(OH)}_2 \) active particles. Smaller particulates: \( \text{Ni}_\text{(s)} \). Inset: Magnification of a broken particle, with inner structure visible.

approximately 60 nm. An SEM image of the positive electrode can be found in Figure 2.5 where the spherical particles is the active material and the smaller particulates is the added metallic nickel.

The equilibrium voltage of the positive electrode varies with both state of charge and charge/discharge history, commonly known as hysteresis, see Figure 2.6. The curve shape is flatter in the middle, a feature that is common for all solid solution phase change materials.

2.1.3 Negative electrode

The active material of the negative electrode in a NiMH battery is a hydrogen storage alloy (HAS). HSA materials, or metal hydrides (MH), are intermetallic compounds capable of intercalating hydrogen in the lattice structure. They are made from a mixture of metals that form thermodynamically stable hydrides, denoted by A, and metals that forms thermodynamically unstable hydrides, denoted by B. In the first category, A, metals such a La, Ti, Zr, and Mg can be found. In the second category, B, we find Ni, Co, Fe, Mn among others[18].

These compounds exist in different configurations divided into different cat-
CHAPTER 2. BACKGROUND

Figure 2.6: OCV of positive electrode, measured in flooded half-cell set-up using GITT with 5% SOC intervals.

egories: AB, A2B, AB2, AB5, and A2B7. The AB5 type alloys are the most commonly used in NiMH battery applications. An early example of the AB5 type alloys is LaNi$_5$ which was the first intermetallic alloy to be tested as a negative electrode material for NiMH batteries [9]. Like all AB5 type alloys it has a hexagonal, CaCu$_5$ type structure [19]. The intermetallic alloys have two phases: an $\alpha$-phase with a low hydrogen content and a $\beta$-phase with a high hydrogen content. These phases have a significant difference in lattice volume [19].

In a non-electrochemical setting, hydrogen storage alloys are controlled through changing the surrounding hydrogen pressure and temperature. Increasing the pressure and decreasing the temperature will drive the equilibrium towards storing the hydrogen in the metal lattice, while decreasing the pressure and increasing the temperature will force the hydrogen stored in the lattice to go back to a gaseous state. In a NiMH battery, energy is stored through reduction of H$^+$ to H$^0$. The reduced hydrogen is then intercalated into the metal lattice that expands to make room for the hydrogen, as shown in Figure 2.7. As hydrogen goes from a gaseous state to a solid state, the reaction is exothermal, causing the material to warm up as hydrogen is absorbed. Reversely, when releasing hydrogen back into the gas phase during discharge, the material is cooled.

Depending on the composition of the hydrogen storage alloy, the hydrogen
storage properties are different, both in regard to temperature dependence and pressure dependence of the hydrogen storage. These properties are commonly recorded using a pressure composition isotherm, or PCT curve, which gives the equilibrium pressure of hydrogen over the metal hydride as a function of degree of hydrogen intercalation. These curves are often recorded during both adsorption and desorption of hydrogen, as well as at different temperatures. An example of a PCT curve can be found in Figure 2.8 a). Here the \( \alpha \)-phase dominates at low hydrogen contents, once the plateau is reached the material transforms into a solid solution which is a mix of the \( \alpha \)- & \( \beta \)-phases. Finally, at high hydrogen contents the \( \beta \)-phase dominates.

Figure 2.7: Hydrogen absorption/desorption in a hydrogen storage alloy.
CHAPTER 2. BACKGROUND

Figure 2.8: a) Adsorption PCT curve of AB5 material at 60°C. b) Corresponding calculated OCV curve at 20°C.

Figure 2.9: SEM image of negative MH electrode. Large angular blocks: MH active particles. Smaller particulates: Ni_{(s)}. Inset: Magnification of a cluster of Ni_{(s)} particles.

The equilibrium potential of the alloy is connected to the PCT curve of the material. Iwakura et al. [20] showed that the OCV could be calculated from
2.2. HYSTERESIS – AN INFLUENTIAL BATTERY PROPERTY

PCT data using Nernst equation:

\[
E_{\text{MH}} = E_{\text{MH}}^0 - \frac{RT}{2F} \ln \left( \frac{p_{\text{H}_2}}{a_{H_2}^0 p_{\text{H}_2}^0} \right) \tag{2.5}
\]

Where \( p_{\text{H}_2} \) is the hydrogen equilibrium pressure as a function of degree of hydrogen intercalation. This results in an OCV curve as shown in Figure 2.8 b). Similar to the positive electrode, the OCV curve has a plateau derived from the solid solution phase change.

Like the positive electrode, the negative electrode of the Nilar Energy module is dry pressed, and nickel is added to the powder mixture to make the finished electrode hold together. An SEM picture of the electrode is found in Figure 2.9, where the large angular blocks are the active material particles, and the small particulates are the nickel.

2.2 Hysteresis – An influential battery property

Hysteresis is a term for when the properties of a material at the same state are different depending on its history, so called path dependence. It is observed in several different physical phenomena, for example in magnetism and absorption. In batteries, hysteresis can affect electrochemical properties such as the open circuit voltage (OCV) or the exchange current density of the charge/discharge reactions. For the NiMH battery the OCV hysteresis is the most severe and the most influential of these properties. OCV hysteresis is the term for how the OCV as a function of state of charge (SOC) of a battery changes depending on its charge and discharge history. In the case of the NiMH system it is pronounced. Tests done on Ni(OH)\(_2\) film (positive electrode only) shows that a substantial part of the effect arises from the positive Ni(OH)\(_2\)-electrode [21].

The OCV is bounded by an upper limit at charge-only rest states and a lower limit at discharge-only rest states. Mixed charge and discharge history fall between these two boundaries. Mixed charge and discharge states are reset upon full charge or full discharge. An example of how this can look for charging can be seen in Figure 2.10. A mid-range OCV value can hence correspond to an SOC that varies as much as 70% depending on the charge-discharge history. The magnitude of the OCV hysteresis makes it necessary to take it into account when modelling dynamic behavior, as well as when predicting the SOC of the battery. The OCV hysteresis also results in an energy loss when cycling, affecting the energy efficiency negatively.

Not all batteries exhibit this behavior notably enough to have a significant impact on battery function and battery management system (BMS) algorithms. It is believed to affect intercalation electrodes with phase expansion, such as the
Ni(OH)$_2$ electrode in our studied battery. Along with the NiCd/NiMH (nickel-cadmium/nickel-metal hydride) batteries, in lithium-ion batteries LiFePO$_4$ is an example with significant OCV hysteresis. The flatter charge/discharge curves in these chemistries are an advantage in many applications, but also makes the impact of OCV hysteresis larger on BMS algorithms [21], [23], [24]. In addition to these examples, hysteresis may play an important role in future battery types with intercalation electrodes that have a large phase expansion, such as LiS batteries [25]–[27].

So why does this behavior occur in intercalation materials? The proposed theoretical explanations found in literature vary but are often centered around the existence of a phase transition with more than one metastable state. A metastable state is a thermodynamically unstable phase that is moving so slowly towards a thermodynamically stable phase that it is for all intents and purposes

Figure 2.10: State of charge as a function of OCV, with impact of hysteresis, for a NiMH cell. Recorded using the Galvanostatic Intermittent Titration Technique (GITT) on a Nilar 10-cell battery module. SOC for five different hysteresis paths at 1.34V marked for clarity. [22].
2.2. HYSTERESIS – AN INFLUENTIAL BATTERY PROPERTY

kinetically stable. No generally accepted physical explanation for the existence of metastable states in intercalation materials has been presented, but there are a number of theoretical models that have been proposed [21], [28]–[32]. One of these models assumes that the existence of metastable states is due to phase transitions, and that the resulting state is dependent on the direction of the phase transition [21]. Srinivasan et al. [21] uses a combination of domain theory and metastable states with different potentials to explain hysteresis. In this theory the system is made up of many small domains that can each exist in one of the metastable states. Since the intercalation/deintercalation energy would differ in the different states, the distribution of the metastable states would explain the observed hysteresis.

Figure 2.11: Illustration of metastable state hysteresis mechanism as proposed by Dreyer et al. [28]

Dreyer et al. [28] instead combines the metastable state assumption with a multiple particle theoretical model for porous electrodes. They investigated whether the particles in a fully communicating system can be assumed to be charged/discharged simultaneously or if they are charged/discharged sequentially until reaching a metastable state. If the former hypothesis is true, mathematical models show that hysteresis effects would disappear below a certain size of the particles. However, when assuming that the latter hypothesis is true, hysteresis effects persist beyond this size limit. Experimental studies carried out by Delmas [33] and Wagemaker [34] suggest that the latter hypothesis is true, with existence of mono-phase particles in both LiFePO\textsubscript{4} and LiTiO\textsubscript{2} particle electrodes. Dreyer et al. [28] use these results to justify the use of a many-particle model. In this model, hysteresis depends on the distribution of particles in different metastable states. The influence of their proposed model on the voltage behavior of a porous electrode is illustrated in Figure 2.11.

Schwarz and Khachaturyan [29] created a model looking at the adsorption/desorption of a metal hydride. In this model the thermodynamic hysteresis present is caused by coherency strain generated by the transforming phase, cre-
CHAPTER 2. BACKGROUND

ating a macroscopic barrier. The strength of the barrier is proportional to the size of the transforming phase. During absorption and desorption this barrier locks the system into a metastable state. They note that the model is only valid for isometric systems, where the two phases have similar structure (In the example case, the structure is cubic.) [29].

Several materials have been studied experimentally to map hysteresis phenomena in batteries, and different origins of the behavior have been proposed. Some fit with the domain theory: Lim et al. [30] used operando X-ray microscopy to study the hysteresis behavior in LiFePO$_4$ and reported that the presence of domains depends on the charge/discharge rates, where higher rates lead to a more uniform solid solution phase change and lower rates resulted in the formation of domains. Li et al. [31] used X-ray absorption spectroscopy (XAS) and transmission electron microscopy (TEM) and similarly reported that hysteresis in FeF$_3$ conversion electrodes was due to differences in spatial distribution of the electronically active phases, but assumed this was due to differences in layering rather than the existence of domains. Meanwhile, Khatib et al. [32] studied the LiCoP conversion electrode using X-ray powder diffraction (XRPD), and found evidence that the presence of hysteresis was due to different reaction mechanisms during charge and discharge, with three different processes making up the discharge and only two processes for the full charge.

All of the above-mentioned research was carried out on other battery types than the one investigated in this thesis, but there are studies of the OCV hysteresis effect in the Ni(OH)$_2$/NiOOH redox-pair, some studies published over 30 years ago. Despite this long history, the physical explanation of the hysteresis phenomenon for this material is still unclear. Tests on thin film electrodes, both pure nickel hydroxide and co-precipitated with cobalt, has been carried out by Ta and Newman [35] who performed both CV and galvanostatic tests. They claim to be the first to quantify the hysteresis when charging and discharging the nickel hydroxide electrode. The hysteresis gap was smaller with co-precipitated cobalt hydroxide and the charge and discharge reactions were lowered in potential, separating the intercalation reaction from the oxygen evolution reaction. The CV also showed that the hysteresis effect was not kinetic as the positions of the oxidation and reduction potential ranges were unaffected by the sweep rate, although the reduction peak position was shifted due to kinetic effects. Their explanation for the observed behavior is that there are changes in lattice expansion during the intercalation/deintercalation processes. To back up this claim they refer to a study where charging of the Ni(OH)$_2$ electrode has been observed using extended X-ray absorption fine structure (EXAFS) measurements [36]. The results indicate that the nickel-oxygen atom distance decreases from 2.07 to 1.88 Å during charging (deintercalation). These bond distances are typical for nickel(II) and nickel(III) in octahedral oxygen environments, respectively [37], [38]. Where the Ta and Newman study was
only concerned with the hysteresis boundaries, Srinivasan et al. [21] looked closer at the effect of reversing current in the middle of the SOC window and the resulting internal paths (scanning curves). Like the study by Ta and Newman, the experiments were performed on thin film electrodes, both of the pure Ni(OH)$_2$ and a Co doped Ni(OH)$_2$ variant.

2.3 The NiMH gas phase

There are mainly four gases present in the NiMH gas phase: hydrogen, oxygen, nitrogen, and water. As mentioned in previous sections, the NiMH battery uses a water-based electrolyte. As a consequence of this, water splitting and gas recombination are active parts of the battery function. In addition, the shift of hydrogen equilibrium pressure over the negative electrode with state of charge impacts the gas phase in the cell. The result is a gas phase that changes both pressure and composition over a charge/discharge cycle, Figure 2.12. As the battery is charged, the increase in the state of charge of the negative electrode, as well as the temperature increase caused by the charging reactions, makes the gas pressure in the cell increase. As the oxygen evolution region is reached, the oxygen produced causes a sharp increase in pressure, soon to be followed by an equally sharp increase in temperature as the oxygen is recombined and the energy released as heat. During rest and discharge the pressure and temperature rapidly decrease as the oxygen is consumed through recombination on the negative electrode, and the corresponding discharge of the negative electrode is endothermic. The two other gases, nitrogen – a remnant from the electrolyte filling process - and water vapor, do not contribute as dramatically to the pressure changes in the cell. This leaves hydrogen and oxygen to dominate the dynamic pressure behavior in the cell. Therefore, two topics are identified to further explore to understand this behavior: PCT temperature dependence and the oxygen evolution/recombination cycle.

2.3.1 Temperature dependence of PCT curves

As discussed previously, the PCT curve is a way to characterize the properties of any given hydrogen storage alloy. However, while the PCT curves are recorded isothermally, in a battery the temperature conditions vary significantly, as made evident in Figure 2.12. Therefore, to properly estimate the hydrogen pressure inside a battery, and by extension the OCV of the negative electrode, see section 2.1.3, a temperature dependent PCT curve is needed.

If several PCT isotherms are recorded and plotted together, the type of behavior seen in Figure 2.13 is observed. At low hydrogen contents there is a sharp increase in pressure with increasing intercalation as the $\alpha$-phase (where hydrogen occupies interstitial places in the lattice) is populated and the energy
required to occupy additional spaces is increased. The pressure then reaches a plateau as a solid solution is created, which is a mixture of the $\alpha$- and $\beta$- phases. During this plateau the pressure remains constant since no additional driving force is required to intercalate hydrogen into the material. The constant driving force in this phase is caused by the structure and bond distances of the material not changing with the degree of charging. Finally, the slope of the curve increases again as the pure metal hydride $\beta$- phase is reached, and additional intercalation requires structural changes. The length of the plateau decreases with temperature until a critical temperature, $T_c$, is reached. Above this temperature the mixed phase does not occur, and the alloy remains in the $\alpha$-phase \[39\]. If the logarithm of the plateau pressure is plotted against the inverse of the temperature you get a linear relationship that is called a Van’t Hoff plot.

In an ideal system, the Van’t Hoff plot corresponds to the following equation \[41\]:

---

Figure 2.12: Charge/discharge cycle. Charge to 120% DoC on Nilar Energy Module. Pressure measured in the common gas channel, and temperature measured on the outside of the module casing.
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\[ \ln p_{H_2} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \] (2.6)

Here the slope of the curve, the temperature dependence, is determined by the intercalation enthalpy and the intercept by the entropy of the intercalation. If we assume that the enthalpy and entropy are temperature independent, we can calculate the enthalpy at any temperature if we know the entropy:

\[ \Delta H^o_{H/M} = RT \left( \frac{\Delta S^o}{T} - \ln p_{H_2} \right) \] (2.7)

Taking this one step further, by equating the enthalpy calculated at two different temperatures an expression for the pressure at a new temperature is obtained, given a recorded PCT curve and an entropy value for the alloy:

\[ \ln p_{H_2} = \frac{\Delta S^o}{R} \left( 1 - \frac{T_{\text{ref}}}{T} \right) + \frac{T_{\text{ref}}}{T} \ln p_{H_2}^{\text{ref}} \] (2.8)

The entropy values vary depending on the alloy composition but is in the region of 100-140 Jmol\(^{-1}\)K\(^{-1}\). To show the viability of these expressions, calculations using equation 2.8 were carried out on data from literature which was recorded at three different temperatures: 40°C, 60°C and 80°C. A \(\Delta S\) value of 115 Jmol\(^{-1}\)K\(^{-1}\) was chosen and the PCT curve from 40°C was transformed to the two other temperatures, Figure 2.14. The results show that the method...
works well in this temperature range when the material is in the mixed \(\alpha+\beta\) phase region or in the pure \(\beta\)-phase region. In the \(\alpha\)-phase region the method overestimates the pressure. An interpretation is that the entropy value, which is measured in the plateau-region, is higher in the \(\alpha\)-phase region due to the phase expansion needed to accommodate the intercalating hydrogen atoms. However, since there is an over-discharge reserve in NiMH batteries, the active cycles will take place mostly in the mixed region and the \(\beta\)-phase region. Therefore, the equation can be used to introduce temperature dependence in a battery model.

Figure 2.14: Transformation of PCT curve using equation 2.8. Data from study by Bjurström et al. [43]

2.3.2 Oxygen evolution and recombination

In the oxygen evolution/recombination cycle, oxygen is produced on the positive electrode when the electrode potential increases towards the end of charge. As the charging goes on, more of the current is diverted to oxygen production until all of the current is used for oxygen evolution, see Figure 2.15. The produced oxygen moves to the negative electrode where it is recombined to water and the diverted energy is released as heat. These processes take place through
Ayeb & Notten [44] studied the oxygen evolution taking place on the positive electrode in a NiMH battery, and concluded that it occurs through the following mechanism:

\[ M + OH^- \rightarrow MOH + e^- \] (2.9)

\[ MOH + OH^- \rightarrow MO + H_2O + e^- \] (2.10)

\[ 2MO \rightarrow O_2 + 2M \] (2.11)

They found that there are two kinetic regions with different Tafel slopes depending on the charging conditions: one during partial charging and a different one during overcharge. They attribute the changes in the kinetics to the phase change of NiOOH, from β- to γ-NiOOH. As the reaction changes from partial charging to overcharging, there is also a change of the rate limiting step. During partial charging the mechanism is limited by oxygen absorption, according to equation 2.10, while during overcharge the reaction is limited by molecular oxygen formation, as shown in equation 2.11.
The kinetics of the oxygen recombination reaction on the negative electrode are proportional to the oxygen pressure in the cell and have a temperature dependence. Notten et al. \cite{45} studied the oxygen evolution and recombination in NiCd batteries during overcharge conditions. They concluded that the rate limiting step of the oxygen recombination was the diffusion of oxygen to the reaction surface. Ye & Noréus \cite{46} studied the oxygen recombination during rest in a NiMH battery, and got similar results to what Notten et al. found during overcharging. They hypothesized that a surface related reaction step is rate limiting for the oxygen recombination. In both studies, batteries with a starved electrolyte configuration were used, making it plausible that the reaction mechanism is similar in nature even though the reaction surface is different.

\subsection{2.3.3 The gas phase and aging}

The gas reactions in the cell are intimately connected with aging, both as a cause and a symptom. The primary aging mechanism of the NiMH battery is corrosion of the negative electrode, following the general formula:

\begin{equation}
2.15 \text{M} + 1.15 \text{H}_2\text{O} \rightarrow 1.15 \text{MH} + \text{M(OH)}_{1.15}
\end{equation}

\[(2.12)\]

Where M represents the alloy in the metal hydride \cite{47}. The alloy is oxidized, deactivating the affected storage sites. In addition, the hydrogen produced by the corrosion reaction occupies additional storage sites. In practice, that means that for each corroded storage site, a bit more than twice that of the hydrogen storage capacity is lost. The corrosion of the metal hydride is aggravated by the presence of oxygen and high temperature. Therefore, avoiding unnecessary oxygen production helps prolong the life of the battery. When the negative electrode is corroded, the gas behavior of the cell changes. Since the capacity is reduced at the same time as more hydrogen is intercalated into the material during the corrosion process, the active window is shifted to higher values in the PCT diagram, see Figure \ref{fig:2.6}. This results in the pressure rising earlier during charging. Eventually, when the capacity has been reduced enough, the cell is no longer positive electrode limited and charging will be terminated early due to the pressure reaching the safety limits.

\subsection{2.4 Electrochemical modeling}

Electrochemical modeling aims to reproduce the behavior of electrochemical cells using mathematical expressions. The resulting models have a multitude of different uses: Investigating the simulated cell, system control, cell design, and sensitivity analysis among others. There are a number of different methods for constructing these types of models with a varying degree of realism and
complexity. These two go hand in hand, as the model becomes more realistic the mathematical complexity usually increases. Below, the most common types are listed in order of ascending complexity/realism, as illustrated in Figure 2.16.

**Black-box model** – A black-box model is a computational model that is based on experimental data. The model is trained on experimental data and will be able to reproduce the behavior that it has learned. There is no possibility to draw any conclusions on the electrochemical workings of the cell, and the model cannot extrapolate beyond the scope of the training data. An example of this is a machine learning type model.

**Equivalent Electrical Circuit model (EEC)** – An EEC model uses electrical circuits to approximate electrochemical behavior. The behavior of the studied cell is reproduced through constructing a circuit containing resistances and capacitances connected in series or parallel. The model is parametrized through fitting it to experimental data, and the properties of the components in the circuit vary with the state of the cell, such as state of charge or state of health of a battery. EEC models are often used in system simulation as they are easy to implement and integrate with a system wide circuit model.

**Zero-dimensional model (0D)** – A 0D model is a model based on electrochemical theory, but without any spatial dimensions included. They make it possible to study the average behavior in an electrochemical cell except for behavior attributed to differences over a spatial distribution, such as diffusion.

**Single particle model (SP)** – A single particle model, like the 0D model, is based on electrochemical theory. Here, however, a particle diffusion model is added. This means that the average behavior of the cell can be modeled, including intra particle diffusion.

**Pseudo two-dimensional model (P2D)** – The P2D model, or the Newman model after its creator, is the most commonly used model to study electrochemical cells with porous electrodes [48]. It has a one-dimensional spatial distribution, x, complimented with a single particle model that is evaluated for each individual x-value. It is a homogenized model for the porous electrodes...
and uses Bruggeman expressions to approximate the transport path lengths, both in the electrolyte and in the solid phase. This allows for potential and concentration distributions to be modeled in both phases. For the electrolyte phase, concentrated electrolyte theory is used. If one adds an additional spatial dimension to a P2D model one would get a P3D model. This allows study of the parameter distribution over the chosen length parameter of the cell, as well as the thickness. Coupled with a thermal model, the P3D model can be used to evaluate mass and temperature transport distributions over the thickness and length of a cell. This is useful if the thermal distribution varies greatly due to differences in the environment of the cell (such as localized cooling) or thermal conduction properties of the cell casing. Adding yet another spatial dimension to the P3D model, one would get a P4D model, which models all of the spatial dimensions of the cell.

**Heterogeneous model** – In the heterogeneous model, the aim is to model the cell as realistically as possible. This means that instead of approximations of the porous electrodes, the structure is measured and recreated in a 3D environment. This can be done using tomographic methods. One method of measuring the structure is focused-ion beam/scanning electrode microscopy [49]. All of the relevant expressions are then modeled for each point in the structure. This method is very computationally expensive.

When choosing what type of model to use for a certain application or study, it is important to consider what results are desired. For example, if the model is to be used in-situ in a system it is important to choose a model that can achieve the required reproducibility with as little computational cost as possible. For this reason, black-box models and EEC models are commonly used in battery management systems (BMS). If one, on the other hand, is interested in how a specific battery parameter behaves, the chosen model needs to resolve that behavior. For example, if the topic of study is the intra particle diffusion, a SP model at least is required. If one wants to study the impact of porosity or SOC distribution in an electrode, a P2D model is necessary. It would be easy to assume that one would always want to use the most complex type of model when studying the electrochemical processes in a battery. However, the increased degree of complexity can draw the attention from the process one wishes to study, and the required parametrization introduces more potential sources of error. In addition, the computational resources needed increase, which is a nuisance at best and a potential hurdle should time on a computing-cluster be required. Therefore, it is a good idea to choose the model that has enough complexity to study the phenomenon of interest but is as simple as possible otherwise. This is the root of the popularity of the P2D model, as it is complex enough to study most electrochemical phenomena in cells with porous electrodes while still being manageable in terms of parametrization and computation.
Due to the ebb in interest for the NiMH chemistry in the last twenty years, published works on modelling of the NiMH battery are sparse. The models are roughly divided into two categories, battery study/design and SOC/SOH determination. Of these, studies of SOC/SOH determination are the most numerous. The first category is of greater interest for this thesis, as they are centered around a wish to understand the inner workings of the battery rather than focusing on state prediction. In the first category, Notten and Danilov [50] propose the use of an EEC model derived from the physical principles of the battery. Ledovskikh et al. [51] presented a model of higher complexity, a 0D model, that is capable of simulating voltage, pressure, and temperature. Neither of these studies present simulation of discharge data. Albertus et al. [52] took it one step further and modelled the side reactions and nonisothermal effects in the battery for both charge and discharge. However, the hysteresis properties of the positive electrode were not included in the model.

The second category can be divided in EEC based models and black-box models. Examples of the first type were presented by Windarko et al. [53] and Lu et al. [54]. In these studies, an EEC model is used to calculate an OCV that is used for SOC estimation. The black-box models are more varied. Bundy et al. [55] uses the partial least square method to relate electrochemical impedance spectroscopy (EIS) data to SOC values. This is then used for SOC estimation during discharge and OCV conditions by taking an EIS spectrum of the cell and comparing to the collected data. To determine SOH, Galeotti et al. [56], [57] used EIS to construct diagnostic diagrams through a mathematical model based on Dempster-Schafer Theory of Evidence in order to determine SOH in NiMH batteries. In all, the SOC/SOH determination category are dominated by models with low complexity. This facilitates their use in battery managements systems with limited computational resources.

When it comes to modeling hysteresis phenomena, there are three types of models used: discrete zero state, discrete, and continuous. The discrete zero state model is an empirical model where the voltage flips between the charge and discharge OCV boundary depending on the current direction. A model of this type was developed by Plett et al. [58]. While this model type is easy to implement, it does not give good accuracy for a cell with a large OCV hysteresis, such as the NiMH battery. The second type, the discrete model, is a very common solution to the hysteresis problem in any system. The Preisach model is most commonly used to describe systems with magnetic hysteresis. It has also been used to model the hysteresis in LiFePO₄, NiCd and NiMH batteries [53], [59–61]. This type of model is easy to combine with discrete battery models, such as EEC, but does not mix well with a continuous model. This is where the last hysteresis model type comes in, the continuous model. Here a differential equation is used to describe the OCV movement between the upper and lower hysteresis limit [62], [63]. This model is empirical, but can
still be used with a physically based model (from 0D models and upwards in complexity) as they are both continuous.

While there are models of the different aspects of the NiMH battery, there are currently no models published that address NiMH batteries that are run in dynamic conditions with mixed charge and discharge current profiles. To further the usability of the NiMH models for battery management, models that are equipped to handle these types of conditions need to be developed.
Chapter 3

Method

3.1 Hysteresis studies

Setting out to understand the hysteresis behavior in the NiMH system there are two main questions to be addressed: How does it behave, and why does it behave like that? To answer these questions two different studies were made, with vastly different methods of approaching the topic.

The first study, *Evaluation of hysteresis expressions in a lumped voltage prediction model of a NiMH battery system in stationary storage applications – Paper I*, investigated the OCV hysteresis behavior of the battery empirically [64]. Varieties on a lumped single particle voltage prediction model were then used to attempt to recreate the found behavior. The methodology used in the study is briefly described here. For a more detailed explanation the reader is referred to *Paper I*. This study was concerned with the how rather than the why. Since the thermodynamical origins of OCV hysteresis is poorly understood, the study aimed to model the hysteresis through using a purely mathematical expression. Using a continuous mathematical expression rather than the traditional Preisach model for hysteresis makes it usable in a physics-based model. The tested expressions were based on a dimensionless variable, $\chi$, that varies between 0 and 1 depending on charge/discharge history of the battery. By keeping track of this dimensionless variable, the position in between the two hysteresis boundaries can be predicted, which gives the following expression for the OCV of the battery:

$$E_{OC} = E_{OC,dch} + \chi (E_{OC,ch} - E_{OC,dch}) \quad (3.1)$$

In this expression, $E_{OC,ch}$ and $E_{OC,dch}$ are the open circuit voltages at a given state of charge for the upper and lower hysteresis boundaries respectively. These variables were experimentally determined. An example of the hysteresis behavior
between the boundaries is given in Figure 3.1, where a discharge from the upper boundary followed by an equal charge creates a hysteresis loop.

![Figure 3.1: NiMH cell open circuit voltage as a function of SOC, with the upper line representing $E_{OC, ch}$ and the lower line representing $E_{OC, dch}$. The three loops are the OCV when starting discharge at different SOCs, discharging 25% of the full capacity before starting charge again to the initial loop SOC value [64].](image)

To find the best mathematical expression to use, the hysteresis behavior in the battery was mapped using GITT measurements (Galvanostatic Intermittent Titration Technique) following different charge and discharge paths [65]. These paths consisted of either charging or discharging from 0% or 100% SOC respectively. During both the charge and the discharge, the direction was switched at different SOCs. The GITT technique was carried out by dividing the charging or discharging in short pulses, in the case of this study the length of the pulses was chosen to be 5% SOC. The pulse was followed by a rest period before the current was applied again. The voltage relaxation during each rest pulse was fitted to a model. In this case an equivalent electrical circuit (EEC) model with double Thenevin elements was used. The characteristic parameters were then extracted for each tested SOC, including OCV [64].

Once the hysteresis approximation expression was chosen, it was evaluated for use in a continuous model. Here the model chosen was the simplest physical model possible: A single particle lumped model. This model describes the physical processes in the battery by lumping together all overpotentials of the...
same type, so that the activation overpotential of both the positive and the negative electrodes are lumped together as well as the overpotential from the diffusion processes in both electrodes. The diffusion processes are modeled through using Fick’s law applied on a single particle, where the particle size and concentration gradient behavior are assumed to be the same for both electrodes. This assumption has been shown to be valid for nickel manganese cobalt oxide (NMC) lithium-ion batteries with porous electrodes [66]. The model was then fitted to four types of data. Two from test-modules in the lab with constructed run cycles, one with random charge pulses followed by random discharge pulses. The other two sets were taken from systems in the field, with user data from different applications: time-shifting and phase-shifting. To verify the predictive properties of the model in these four cases, different data from each set was used.

The second study, *A structural investigation into the OCV hysteresis of the nickel hydroxide electrode in a NiHM battery – Paper II*, tried to answer the
CHAPTER 3. METHOD

Figure 3.3: Sensitivity of the three different techniques in Paper II: XRPD, EXAFS/XANES and Raman.

question of why [22]. By analyzing samples from the positive electrode at different hysteresis states, the differences in structure causing the hysteresis were studied. Four samples at different hysteresis states were analyzed in the study: 0% charged, 100% charged and two samples at 50% SOC. These two samples were brought to 50% SOC from either 0% or 100% respectively. The positions of the samples on the OCV hysteresis curve are shown in Figure 3.2. The composition of the positive electrode material is complex, with both metallic nickel and active Ni(OH)$_2$ particles with a mixed cobalt oxide surface layer. Therefore, no single technique could be used to gain understanding of the structural changes in the material. The complexity of the material introduces too many uncertainties in the techniques on their own. To circumvent this problem, the study used several different techniques to gain a more complete picture of the material. Two different bulk techniques were used: x-ray powder diffraction (XRPD) and x-ray absorption spectroscopy (XAS). For the latter, both extended x-ray absorption fine structure (EXAFS) and x-ray absorption near edge structure (XANES) were applied. The XAS measurements were carried out on three different elements present in the samples: nickel, cobalt and zinc. The techniques have different mechanisms which allow them to collect different types of information about the structure, as illustrated in Figure 3.3. XRPD
3.1. HYSTERESIS STUDIES

uses x-rays of a wavelength that allows for diffraction to occur due to intra-layer spacing in the structure. As the sample is in powder form, the sample will have crystal structure in all possible orientations relative to the incoming x-ray source, and so the resulting reflections will have information on all different layer spacings in the structure. Since the penetration depth of x-rays is high, the collected signal will be an average of all crystalline phases in the sample. The XAS techniques are also based on x-rays, but of a much higher energy and of a specific wavelength distribution depending on the atom studied. These x-rays are able to excite the electrons of the inner orbitals of the studied atom, and by observing the absorbed wavelengths it is possible to gather information on oxidation states of the atom and the bond distances to other atoms in the structure. Like XRPD, the information is averaged over the sample.

To compliment the bulk techniques, the surface sensitive Raman spectroscopy technique was used to study specific areas of a sample. In Raman spectroscopy, an optical microscope is used to find an area to study, whereafter a monochromatic laser is targeted at that area. The wavelength of the laser can vary but is chosen to stimulate the vibrational states of the target molecule. The interaction with the studied material will cause the scattered light to vary slightly in energy, and this resulting spectrum gives information about the vibrational modes of the system. Unlike the x-ray based techniques, the relatively low energy of the light used for Raman spectroscopy makes it unable to penetrate all the way through the sample, limiting the penetration depth. This depth varies with the studied material and the energy of the light source chosen.

By combining the strengths of the different techniques with our knowledge of the electrode material composition as detailed in section 2.1.2, we gain a method to better understand the underlying structural causes of hysteresis. XRPD gives the average structure of the electrode material. EXAFS on the Ni-edge gives information on the average oxidation state of Ni for the different samples. However, due to the presence of 30% metallic nickel in the electrode material it is unable to give reliable information on the bond distances of Ni in the bulk of the active particle. EXAFS and XANES on the Zn-edge on the other hand will give such information since Zn is only present as a dopant in the bulk of the active material, granted that zinc is integrated into the nickel hydroxide structure. Finally, EXAFS/XANES on the Co-edge will give information about the average state of the cobalt in the active material. Raman on the other hand provides information on the cobalt oxide surface layer on the active particles. By comparing the results from these two methods, an understanding of the location dependence of the cobalt behavior in the sample can be reached.
3.2 Gas reaction studies

To study the pressure behavior of the NiMH battery a particular feature of the Nilar module was utilized, namely the common gas chamber with the embedded pressure sensor. Two experimental studies and a modelling study were conducted. The first experimental study, *Short-Term Impact of AC Harmonics on Aging of NiMH Batteries for Grid Storage Applications – Paper III*, aimed to investigate the impact of a frequency overlay on the charge/discharge current on the battery voltage, pressure, and temperature behavior [67]. The second experimental study, *Gas phase composition of a NiMH battery during a work cycle – Paper IV*, uses the existence of the common gas chamber to connect a battery module to a mass spectrometer to study the gas composition over a cycle [68]. The modelling study, *A dynamic gas pressure model for management of nickel metal hydride batteries – Paper V*, also investigates the gas composition, but here the pressure sensor itself is used to provide an experimental base line for the total pressure [69]. Both studies used the same basic charge/discharge cycle as presented in Figure 2.12. The cycle started with a 0.25C charge to 120% DoC. After an hour of rest, the battery was discharged with 0.2C to 1V/cell.

In *Paper III*, the battery was subjected to an AC frequency overlay with a 70% amplitude of the tested C-rate. Two different C-rates overlaid by three different frequencies were tested. The frequencies were chosen to represent frequencies that occur in a battery system connected to the grid or single-phase AC loads. To simulate these situations, an experimental setup that could produce these mixed currents was created, as shown in Figure 3.4. The frequency overlay was supplied using a voltage source converter (VSC). The
3.2. GAS REACTION STUDIES

experimental control and signal recording was made through a CAN interface, with the sensors connected to a cDAQ data acquisition system.

The primary aging mechanism of the NiMH battery is corrosion of the negative electrode material, as discussed in section 2.3.3. As this process is exuberated by high temperatures and the presence of oxygen, an increase in pressure or temperature would indicate that the battery has a risk of aging prematurely when subjected to frequency overlay.

To study the gas composition in the battery during a cycle using mass spectrometry, *Paper IV*, two different sampling methods were used. In the first method the battery was connected to a sample volume that could be disconnected from the battery and fed into the mass spectrometer, Figure 3.5 a). The battery was cycled several times, and one sample was taken at different points for each cycle. In this method, the volumetric flow fed to the mass spectrometer was large enough that there were worries about the gas volume in the battery being depleted, and so the battery pressure was brought back to the initial pressure after each cycle using nitrogen. The second method used a much lower volumetric flow, and the battery was connected to the mass spectrometer throughout the cycle, measuring continuously, Figure 3.5 b). The mass spectrometer data was then analyzed to arrive at the measured gas composition, which was also converted to partial pressures using the measured pressure in the battery.

![Figure 3.5: Schematic of experimental setup for mass spectrometer measurements. a) Sample volume. b) Continuous measurement](#)

In *Paper V*, a partially empirical approach is used to isolate the gas behavior from the other battery processes. The model itself is a 0D type model, which means that it consists of theoretical relationships without a spatial dimension as is described in section 2.4. These relationships concern the gas reactions and heat generation/consumption and transfer processes. However, as has been described in section 2.2, the voltage behavior of the cell is difficult to predict. As such, implementing a voltage estimation algorithm in the model focused
on the gas behavior would introduce unnecessary error. The same is true for
the temperature in the cell, as there is no way of measuring the temperature
inside the module casing. Therefore, experimental data for temperature and
voltage is used in the model. This allows us to bypass the complexity of the
voltage behavior and focusing on the gas related processes. It also introduces
limitations on the battery internal temperature. As the measured temperature
is on the outside of the module casing, a uniform modeled inner temperature
is used for all reactions. The unknown parameters in the model, such as the
heat transport properties inside the module and reaction enthalpies, are fitted
through comparing the modeled total pressure with the experimental pressure.

In the fitting process there were two stages. In the first stage, charge cycles
with different charge lengths were fitted to a model without oxygen evolu-
tion/recombination. This allowed us to study the hydrogen related processes
separately. Here, charge lengths between 50%-95% DoC were used, as oxygen
evolution occurs at higher states of charge. The parameters that did not vary
significantly were set to a mean of the fitted value from the different pulses.
In the second stage, the oxygen evolution/recombination related part of the
model was introduced, and the remaining unknown parameters were estimated
through fitting the calculated pressure to the experimental pressure.

The model is verified through data recorded with different C-rates, from 0.1C
to 0.9C with 0.1C increments, on 10 module packs. Here two of the parameters
are refitted to reflect the change in temperature dispersion properties due to
the different form factor, as well as a different age of the pack compared to the
module.

3.3 Creating a dynamic full-cell NiMH model

To investigate whether the knowledge gained in the studies about the hysteresis
and gas behavior of the NiMH battery is enough to accurately reproduce the
qualitative voltage and gas behavior, a final study was made.

In this study, Creating a dynamic P2D model for the nickel metal hydride
battery – Paper VI, a Fuller-Newman P2D model was used as a base for the
predictive model [70]. Chosen parts of the two models presented in Paper I
and Paper V were then added to create the combined dynamic model. Some
adjustments had to be made to the models to account for the increased model
complexity when moving from a 0D & single particle model to a P2D model.
By using a P2D model as a base, there are better possibilities to study how the
battery behavior changes with changes in battery structure and composition.

The hysteresis expressions from the first study, Paper I, was added without
alterations [64]. To add the hysteresis expressions to the P2D model, the
$\chi$ variable was introduced as a dependent variable, computed locally for each
position of the positive electrode, as this is where the hysteresis effect originates.
3.3. **CREATING A DYNAMIC FULL-CELL NIMH MODEL**

The gas composition model, as presented in *Paper V*, involved more detail and complexity than the hysteresis model. To reduce the computational burden, some simplifications were made before it was incorporated into the P2D model. Three factors were found that had little impact on the pressure simulation: The change in gas volume, the heat of the hydrogen sublimation and the heat of the water evaporation. The gas volume was therefore set to constant, using the initial gas volume from the gas composition model, and the hydrogen sublimation heat and the heat of water evaporation were removed. To translate the 0D gas model into a P2D environment the gas space was treated as a homogenous entity, with a uniform temperature and pressure. Since oxygen evolution depends on the positive electrode potential, the oxygen evolution and recombination were located to the positive and negative electrode respectively, contributing to the nonuniform current distribution over the thickness of the electrodes. In the gas composition model, the hydrogen pressure is given as a function of the state of charge of the negative electrode and the temperature. Since the negative electrode state of charge in the P2D model varies over the thickness of the negative electrode the average state of charge of the electrode was used to calculate the hydrogen pressure.

The geometrical parameters of the cell were taken from product data references. The model was then parametrized using half-cell test data with 0.3C GITT measurements for both charge and discharge. While these parameter values were the start of the model parametrization, they had to be adapted to ensure a good model performance. In the end, the OCV curves for the positive electrode and some of the parameters had to be adjusted and an adjustment factor for the negative OCV was added. The values for these assumed parameters are shown in Table 3.1.

Table 3.1: Assumed parameters for the dynamic P2D model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{factor neg}}$</td>
<td>35</td>
<td>mV</td>
</tr>
<tr>
<td>$i_{\text{pos}}^0$</td>
<td>1.5384</td>
<td>A/m²</td>
</tr>
<tr>
<td>$i_{\text{neg}}^0$</td>
<td>0.3</td>
<td>A/m²</td>
</tr>
<tr>
<td>$D_{\text{pos}}^s$</td>
<td>$10^{-13}$</td>
<td>m²/s</td>
</tr>
<tr>
<td>$D_{\text{neg}}^s$</td>
<td>$10^{-13}$</td>
<td>m²/s</td>
</tr>
<tr>
<td>$R_{\text{contact}}$</td>
<td>$10^{-4}$</td>
<td>Ω/m²</td>
</tr>
<tr>
<td>$k_{\chi_{\text{ch}}}$</td>
<td>17.2</td>
<td>-</td>
</tr>
<tr>
<td>$k_{\chi_{\text{dch}}}$, Continuous discharge</td>
<td>15</td>
<td>-</td>
</tr>
<tr>
<td>$k_{\chi_{\text{dch}}}$, Pulsed data</td>
<td>6.1</td>
<td>-</td>
</tr>
<tr>
<td>$K_T$</td>
<td>0.065</td>
<td>W/K</td>
</tr>
<tr>
<td>$k_{\text{OER}}$</td>
<td>$1.2 \times 10^{-5}$</td>
<td>-</td>
</tr>
</tbody>
</table>
CHAPTER 3. METHOD

The model was then evaluated using three data sets. The first set was a continuous charge/discharge curve with a 0.25C charge to 120% DOC, 1h rest, and finally a discharge with 0.2C to 1V/cell. The second set consisted of mixed charge and discharge pulses at different C-rates taken from the hysteresis model study and was chosen to represent the dynamic behavior of the NiMH cell [64]. The final data set was a series of continuous discharges, which was used to evaluate the model’s capability of reproducing different discharge rates.
Chapter 4

Results & Discussion

4.1 Hysteresis studies

The two studies carried out within the scope of this thesis concerning hysteresis aimed to answer two questions: How does the OCV hysteresis of the Ni(OH)$_2$ electrode behave, and why? Below are the results from these studies.

In the first study, Paper I, the focus was on mapping the behavior and trying to replicate it using a model. The results of mapping the OCV behaviors are shown in Figure 4.1 a) for charge and Figure 4.1 b) for discharge. Here, the OCV during charge and OCV during discharge forms the outer limits, and when the current direction is changed the resulting paths are within the outer limits.

When these results were studied the derivative of the hysteresis parameter, $\chi$, with respect to SOC was found to be linear, and independent of the

![Figure 4.1: Hysteresis paths when reversing current direction at different SOC for a) charge and b) discharge](64)
charge/discharge rate. This led to the formulation of the following expressions for the change rate of the hysteresis parameter with respect to time:

\[ \frac{d\chi}{dt} = k\chi \frac{I_{cell}}{Q} (1 - \chi) \]  

(4.1)

\[ \frac{d\chi}{dt} = k\chi \frac{I_{cell}}{Q} \chi \]  

(4.2)

Where equation 4.1 is for charge and equation 4.2 is for discharge. For these expressions, \( Q \) denotes the capacity of the cell, and thus \( \frac{I_{cell}}{Q} \) represents the normalized current, the so-called C-rate. \( k\chi \) is a rate constant that needs to be fitted for the data type. To show that these expressions can accurately reproduce the OCV hysteresis behavior, the data from Figure 4.1 was fitted and showed a good likeness, Figure 4.2.

Figure 4.2: Hysteresis expressions fitted to experimental hysteresis data from different turning points. Each turning point data curve fitted individually. a) Charge b): Discharge.

When comparing the fitted \( k\chi \) parameter for the different turning points for both charge and discharge it was found that the values were similar. This indicates that using the same \( k\chi \) for charge and discharge could be sufficient, but no definite conclusion could be drawn. Therefore, when the model was implemented for dynamic charge/discharge data, both versions were investigated.

When introduced into the single particle model and applied to the test data, there was a clear improvement in voltage predictability for all four data types tested. In the two lab tests the error of the model validation was cut down to 30%, while it was reduced to 50% in the application cases, Table 4.1. In all cases but the time-shifting application, using two \( k\chi \), one for charge and one for discharge, gave a better voltage prediction than using the same for both charge and discharge. There is a significant difference in the value of between the lab datasets and the applied datasets, where \( k\chi \) is a factor of ten.
Table 4.1: Fitting and validation results for the single particle model with a hysteresis expression for all four test cases [64].

<table>
<thead>
<tr>
<th>Test cases</th>
<th>Symbol</th>
<th>Unit</th>
<th>$R_O$</th>
<th>$I_{thorm}$</th>
<th>$\tau$</th>
<th>$k_\times$</th>
<th>$k_{dch}$</th>
<th>$k_{dch}$</th>
<th>$RMS_{fit}$</th>
<th>$RMS_{eval}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hysteresis model</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Randomized pulses</td>
<td>No model ($\chi=0.5$)</td>
<td></td>
<td>5</td>
<td>0.91</td>
<td>36</td>
<td></td>
<td></td>
<td></td>
<td>22</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>$\alpha \chi$</td>
<td>$m \Omega$</td>
<td>5</td>
<td>12</td>
<td>13</td>
<td>9.0</td>
<td>13.0</td>
<td>4.5</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>$\alpha \chi$, split $k_\times$</td>
<td>$10^{-3}$ ks</td>
<td>6</td>
<td>23</td>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Randomized pulses, mixed</td>
<td>No model ($\chi=0.5$)</td>
<td></td>
<td>5</td>
<td>9.67</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td>26</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>$\alpha \chi$</td>
<td>$m \Omega$</td>
<td>5</td>
<td>85</td>
<td>11</td>
<td>8.2</td>
<td>17.2</td>
<td>6.1</td>
<td>12</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>$\alpha \chi$, split $k_\times$</td>
<td>$10^{-3}$ ks</td>
<td>6</td>
<td>229</td>
<td>12</td>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>Time shifting</td>
<td>No model ($\chi=0.5$)</td>
<td></td>
<td>15</td>
<td>940</td>
<td>167</td>
<td></td>
<td></td>
<td></td>
<td>27</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>$\alpha \chi$</td>
<td>$m \Omega$</td>
<td>1</td>
<td>21</td>
<td>160</td>
<td>44.4</td>
<td>4.4</td>
<td>47.1</td>
<td>17</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>$\alpha \chi$, split $k_\times$</td>
<td>$10^{-3}$ ks</td>
<td>2</td>
<td>15</td>
<td>156</td>
<td></td>
<td></td>
<td></td>
<td>16</td>
<td>12</td>
</tr>
<tr>
<td>Phase shifting</td>
<td>No model ($\chi=0.5$)</td>
<td></td>
<td>10</td>
<td>965</td>
<td>507</td>
<td></td>
<td></td>
<td></td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>$\alpha \chi$</td>
<td>$m \Omega$</td>
<td>0</td>
<td>362000</td>
<td>62</td>
<td>76.5</td>
<td>10.5</td>
<td>54.7</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>$\alpha \chi$, split $k_\times$</td>
<td>$10^{-3}$ ks</td>
<td>4</td>
<td>10000</td>
<td>328</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td>11</td>
</tr>
</tbody>
</table>

4.1. HYSTERESIS STUDIES

larger for the two applied datasets, see Table 4.1. When using different $k_\times$, the charge value is of the same magnitude, but there is a factor of ten difference in the discharge value. These differences point to two things; Firstly, that the differences in behavior between the lab datasets and the application datasets is primarily located in the discharge regions. Secondly, that it is important to fit this model to the type of data that one intends to simulate to ensure a good voltage predictability. Finally, while there are differences in error reduction for the different test cases when using a hysteresis model, the reductions are on the same order of magnitude. This indicates that the model is robust enough to be applied in on-line applications where the data is typically less resolved and with more inherent error than in a lab set-up.

In addition to the improvement in error, there are also visual differences between the models with and the model without a hysteresis expression, as shown in Figure 4.3. Here one can see that the areas where there is impact of the added hysteresis expression varies between the data cases. In the two lab experiments the error is seen throughout but is most apparent during rest periods. In the time-shifting case, most of the disparity is seen during discharge. This is reasonable since that is where hysteresis comes into effect for that type of use. In the phase-shifting case there is a very poor fit of the single particle model without a hysteresis expression. This is due to the inability to simulate cycling without hysteresis, resulting in an almost straight voltage line.

In all, this study shows that the open circuit voltage hysteresis can be approximated using a mathematical expression where the change rate of the
hysteresis parameter is proportional to itself. Using this expression, it is possible to simulate the battery hysteresis behavior well enough to create a voltage prediction model for a dynamic charge/discharge pattern.

The second study, Paper II, had the goal of increasing the understanding of the origin of hysteresis in the positive electrode. The hypothesis was that the hysteresis origin is structural in nature, and as such could be studied using structural analysis methods. However, the study concerned an applied system, which is much more complex than systems constructed to work with the experimental characterization techniques. Therefore, it was necessary to use more than one method to understand the changes in structure between the different charge and hysteresis states.

To be able to draw conclusions on the structural behavior of the material we chose three complementary techniques: XRPD, EXAFS/XANES and Raman spectroscopy. Each of these techniques gave clues that can be used to put together a picture of the structural changes in the material. A summary of
4.1. HYSTERESIS STUDIES

Table 4.2: Hysteresis origin clues found studying different hysteresis states with different methods [22].

<table>
<thead>
<tr>
<th>Method</th>
<th>Nickel</th>
<th>Cobalt</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRPD</td>
<td>• Ni(OH)$_2$ dominates, even in 100% charged sample</td>
<td>• Detected phase: LiCoO$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Different amount of undetected mass in samples</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EXAFS/XANES</td>
<td>• Changes in Ni oxidation state between 0% and 100% samples match a full charge</td>
<td>• Detected phase: LiCoO$_2$</td>
<td>• XANES shows bulk hysteresis</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Hysteresis difference in degree of Li-intercalation in Li$_i$CoO$_2$ at 50% SOC</td>
<td>• Zn analysis show hysteresis difference in order, but not average bond length</td>
</tr>
<tr>
<td>Raman spectroscopy</td>
<td></td>
<td>• Detected phase: LiCoO$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Hysteresis difference in degree of Li-intercalation in Li$_i$CoO$_2$ at 50% SOC</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Larger difference than Co EXAFS</td>
<td></td>
</tr>
</tbody>
</table>

these clues are shown in Table 4.2.

First, let’s look at what the different methods have to say about the nickel in the material. In the XRPD data a set of reflections usually ascribed to Ni(OH)$_2$ dominates for all samples, even the sample that is supposed to be fully charged and therefore consisting mostly of NiOOH. When normalizing on the Ni$_{(s)}$ content, that is known to be the same for all samples, there is a difference in the total amount of detected mass in the samples between the two hysteresis states. This indicates a stronger disorder in the 50% discharged sample compared to the 50% charged sample. The fact that no NiOOH was found could be attributed to a self-discharge of the samples. However, those same samples were analyzed using EXAFS on the nickel edge, and while the presence of Ni$_{(s)}$ made it difficult to judge the difference in bond lengths between the samples, the change in mean oxidation state between the fully charged and fully discharged samples corresponded to a full charge. That tells us that the samples analyzed using XRPD had not self-discharged, but that the charged state had instead retained the Ni(OH)$_2$ structure. Looking at the established theory on phase transition in the Ni(OH)$_2$ electrode, which is presented as a Bode-diagram in Figure 5,
during charge the $\beta$-Ni(OH)$_2$ is transformed directly into $\beta$-NiOOH. This does
not correspond to what we see from the experimental data. However, in more
recent literature a different mechanism for phase change is proposed for electro-
chemical oxidation [16], [17], [38], [71]. Here, instead of collapsing directly into
$\beta$-NiOOH, the NiOOH retains the Ni(OH)$_2$ structure when the hydrogen ion is
deintercalated, but with slightly smaller cell dimensions, creating a phase that
is kinetically favored in comparison to $\beta$-NiOOH. Casas-Cabanas et al. [38] call
this phase TP2-NiOOH. This phase can then collapse into the thermodynamically
favored $\beta$-NiOOH. The TP2-NiOOH phase is not found in studies where Ni(OH)$_2$
is oxidized using a redox reaction [72]. This suggests the reaction
paths are different for electrochemical oxidation and redox-oxidation and
I would like to propose an addendum to the Bode-diagram, where these two
paths are defined, Figure 4.4. The existence of the TP2-NiOOH phase would
explain the seemingly contradictory results from the XRPD and the EXAFS
measurements, giving us our first important clue in the hunt for the structural
origin of hysteresis in the Ni(OH)$_2$ electrode. It’s also important to remember
that the degree of disorder in the two hysteresis samples differed, with a higher
degree of disorder in the lower hysteresis boundary sample.

Since the nickel EXAFS was unable to give information on the changes in the
bond lengths of the nickel in the active material, another way had to be found
to investigate this. Since the inability was due to the presence of the metallic
nickel added to the electrode to increase the conductivity, a way to only look at
the material in the active particles was needed. As discussed in the introduction
of the positive electrode there is zinc present in the bulk of the active particles
in the positive electrode, but nowhere else in the electrode. Therefore, we used
zinc edge EXAFS/XANES to study the changes in structure in the bulk of the
active particles. The results indicate that zinc exists distributed in the structure
rather than as islands of Zn or ZnO, as the bond distances correspond to those
expected from Ni(OH)$_2$ rather than Zn or ZnO. This means that we can use the
zinc close range structure to study the Ni(OH)$_2$ structure in the active material.
The XANES analysis shows that there is a hysteresis difference between the two
samples at 50% SOC. The lower hysteresis boundary emanates more from the
fully charged sample and the upper boundary emanates more from the fully
discharged sample. The EXAFS spectra show hysteresis in degree of disorder
for the two 50% SOC samples, but not in average bond length. Here the lower
hysteresis boundary sample is more disordered, which is similar to the XRPD
results. This gives us our second clue on the origin of the hysteresis in the bulk
of the active material.

Finally, studying how cobalt behaves in the sample can tell us how hysteresis
behaves on the surface of the particles, as they are covered by a cobalt oxide
layer. All three methods, XRPD, EXAFS/XANES on the Co-edge, and Raman
4.1. HYSTERESIS STUDIES

Figure 4.4: Extended Bode-diagram, adding different pathways for electrochemical oxidation and redox oxidation of nickel [11]–[15], [38].

Figure 4.4: Extended Bode-diagram, adding different pathways for electrochemical oxidation and redox oxidation of nickel [11]–[15], [38].
spectroscopy, identify the cobalt phase present as LiCoO\(_2\). This is plausible, since there is Li present in the electrolyte that can be substituted into CoOOH. The EXAFS tells us that there is no change in oxidation state of the cobalt, it remains steadily as Co(III) in all samples. There is, however, a difference in the amount of Li present between the fully charged sample and the fully discharged sample. The fully discharged sample has a higher degree of lithiation. In essence, there is a small LCO battery present on the surface of the particle. In the Raman results the same can be seen. The XANES analysis identifies this difference as smaller than the analysis of the Raman data does. Due to a limited penetration depth, Raman only reaches the surface region of the layer. The EXAFS signal, however, comes from the entirety of the sample. Therefore, the difference between the techniques suggests that the fluctuation in Li occupancy originates at the particle surface. Both methods also pick up on a difference between the two hysteresis samples, but only Raman was focused enough to theorize on the origin. Here, the theory is that some of the LiCoO\(_2\) persists as regions of the fully charged state when the battery is discharged to 50% SOC, while the sample charged to 50% SOC has a more homogenous Li\(_x\)CoO\(_2\) mixture.

In all, these clues lead to a combined picture of the phenomenon, where there are two structures that display hysteresis differences. The nickel and zinc analysis show a hysteresis difference in the bulk that is related to the degree of disorder in the material. Here the material is more disordered on the lower hysteresis boundary. If the suggested phase transition through the TP2-NiOOH phase on the way to \(\beta\)-NiOOH during charge is correct, this type of difference could be due to more NiOOH collapsing into \(\beta\)-NiOOH during discharge as the hydrogen ion tries to make its way back through the now slightly smaller structure. This theory corresponds well to the OCV being higher during charge and lower during discharge, which is what was found when the hysteresis behavior was mapped. The thermodynamically unstable but kinetically stable TP2-NiOOH phase represents a higher potential energy than the collapsed \(\beta\)-NiOOH. Therefore, a higher amount of the TP2-NiOOH phase during charge translates to a higher energy state in the system and is thus reflected in the difference in OCV. In the cobalt surface layer of the particle, the hysteresis is again related to an inhomogeneity in the material. This time, however, it is due to retention of delithiated LiCoO\(_2\) from the fully charged state during discharge. The difference in the Raman and XANES analysis indicate that this process originates at the surface of the particle.

This thorough analysis answers the question on the structural behavior of the material at different hysteresis states. Although there is no explicit evidence that this is the origin of the hysteresis and that the bulk and surface behaviors are connected, it is a fair assumption. This considering that the reaction potential of a surface is related to the surface structure and that the behaviors in the
4.2. GAS REACTION STUDIES

surface and the bulk are physically connected through the material structure. As such, both of these behaviors are interesting targets for further study.

4.2 Gas reaction studies

This thesis aims to answer how the gas reactions related to the aqueous electrolyte affect the battery, and through what mechanisms. The first study, Paper III, investigated the effect of AC frequency overlay on battery voltage, temperature, and gas behavior – and thereby aging. The second experimental study, Paper IV, tries to quantify the gas composition in the battery during operation. These results form a basis of comparison, and a sanity check, for the modeling study, Paper V. Here the questions are explored using modeling as a method.

The data from Paper III show no impact on battery behavior when adding

![EIS of NiMH module with tested frequencies indicated](image)

Figure 4.5: EIS of NiMH module with tested frequencies indicated [67].
an AC frequency overlay to the charge/discharge current. This indicates that the frequencies chosen in the study do not affect the gas phase of the battery, of which the oxygen evolution was of the greatest concern as the study was designed. To understand this result, an EIS spectrum was made to identify where the chosen frequencies fit into the kinetics of the different processes in the battery, presented in Figure 4.5. The tested frequencies all fall within the high frequency region, and above the corner frequency below which the electrochemical processes occur [73]. This suggests that none of these frequencies activate the electrochemical reactions or mass transport, which would be required to have any impact on the battery function. Therefore, as long as the overlay frequency does not dip below the corner frequency, an AC frequency overlay has no impact on the battery gas-phase or the battery aging.

![Figure 4.6: Mass Spectroscopy measurements compared to model fitted on the same data during a charge/discharge cycle. Microcapillary method [68.](image)](image)

Looking at the results from the mass spectroscopy study, Paper IV, one can see the general trends for the composition of the gas. Starting with hydrogen, the pressure is at the lowest in the beginning of the cycle, Figure 4.6. The pressure then increases during charge until it peaks at end of charge. Then, as the battery is discharged, the pressure decreases once again. Looking at oxygen, no oxygen is detected until the very end of charge. The pressure level decreases somewhat after the end of charge but remain elevated throughout the discharge
step. Nitrogen makes up the main part of the pressure throughout the cycle. Similar to hydrogen, the nitrogen pressure increases at the end of charge but then dips down. It slowly goes back to the original level as the battery is rested. Water is the smallest component of the gas phase. It is not shown in Figure 4.6 as water was dried from the gas to avoid clogging the microcapillary, but can be found in the sampler measurements in Paper IV. The water pressure is higher during charge than during discharge.

Moving on to the modelling study, Paper V, the partial gas pressures were simulated. The results are shown in Figure 4.7. The modeled total pressure matches well with the experimental pressure, showing that the model is capable of reproducing the overall pressure behavior. Looking at the individual gases, nitrogen makes up the bulk of the gas phase. However, the nitrogen pressure does not change much over the cycle. The water partial pressure is small and does not make much of a difference either. Instead, it is hydrogen and oxygen that make up the bulk of the dynamic pressure behavior. The hydrogen pressure increases steadily during the charge period, only to increase more rapidly toward the end of charge. During the first part of the discharge the total pressure rapidly decreases and then stabilizes. In the model, the hydrogen gas pressure is simulated using a temperature dependent PCT curve of the negative electrode material. As we approach the end of charge, the state of charge surpasses the plateau region of the PCT curve, Figure 2.8. There is also a sharp temperature increase, shifting the system to a higher PCT curve. These two factors contribute to the sharper rise of hydrogen pressure. Conversely, the opposite happens when the battery is discharged, resulting in the sharp pressure decrease at the beginning of discharge. Oxygen only appears towards the end of the charging period and disappears quickly once the charging stops. Oxygen

![Figure 4.7: Partial pressures of modeled gases. a) Absolute, compared with experimental pressure. b) Accumulative illustration of pressure distribution](69)
is evolved on the positive electrode. There is also a temperature increase due to the recombination of the oxygen once it reaches the negative electrode. The model uses a Tafel expression to simulate the oxygen evolution, and a kinetic expression that is linearly dependent on the oxygen pressure for the oxygen recombination.

Comparing the experimental pressure composition with the modeled pressure composition, shown in Figure 4.6, the general trends are the same. Nitrogen makes up the bulk of the gas phase, but the depression of the nitrogen pressure after end of charge seen in the experimental data is not reproduced by the model. The qualitative behavior of hydrogen is also similar, with the peak in pressure at the end of charge followed by a recession. The biggest difference is seen in the oxygen pressure. In the model, the oxygen pressure is reduced to negligible levels as soon as the discharge begins, but in the experimental measurements some oxygen remains throughout discharge. This indicates that there is more to the oxygen evolution/recombination cycle than what has been expressed in the model. In the model, the oxygen recombination rate needs to be matched to the oxygen evolution to avoid a rapid pressure build-up of oxygen, while producing enough oxygen to maintain the mass balance in the cell. Since the model does not make a difference between recombination during charge and during rest/discharge this leads to the rapid recombination after the charge has ended. The experimental data suggest that the recombination rate is slower during rest and discharge. This to account for the rapid oxygen evolution during charge and remaining oxygen pressure during discharge.

Figure 4.8: a) Total heat contribution. b) Model battery temperature [69].

In all, except for the differences in oxygen and nitrogen behavior, the results of the two studies are similar. This means that we can make the assumption that the pressure composition model gives an accurate representation of the gas phase reactions in the battery. It can then be used to explore how these behaviors are connected, and which parts affect the total pressure the most. Looking
in Figure 4.8 we can see the impact of the oxygen evolution/recombination cycle on the temperature behavior of the battery. Figure 4.8 a) shows that the main cause of heating/cooling the battery is the charge/discharge reactions, which are then balanced by convection to/from the outside of the battery. However, when the oxygen evolution region is reached, the heat produced from the recombination causes a spike in heat production, which in turn causes a spike in battery temperature. It is this rapid temperature increase that can be used for charge termination. These graphs also show that the net-cooling contribution of the discharge reactions causes the battery to be colder than the surrounding temperature during a 0.2C discharge, Figure 4.8 b).

Figure 4.9: Comparison of model pressure with different parts removed [69].

Moving on to studying how the different behaviors affect the overall pressure in the battery, the model was modified in four different ways: The temperature dependence was removed, and the temperature was set to the initial temperature for the full cycle; The modification of the free gas volume was removed; The pressure contribution of hydrogen was neglected; And the oxygen evolution/recombination cycle was removed entirely. Looking at the results, Figure 4.9 the greatest impact during beginning of charge was caused by removing the hydrogen contribution and making the model isothermal. This makes sense, as
the pressure increase during the early stages of charging can be contributed to an increase in hydrogen pressure. If the hydrogen pressure was disregarded, this increase could not take place. The fact that making the model isothermal also has a similar result indicates that the hydrogen pressure increase during this period of charging is mainly due to the increase in battery temperature. During the pressure peak, the greatest impact comes from removing the hydrogen contribution and removing the oxygen evolution/recombination reactions. When removing the hydrogen contribution, the modeled pressure retains most of the peak shape, but reduces the height of the peak. When removing the oxygen evolution/recombination reactions, the size of the pressure peak is retained, but the sharp peak shape is lost. Considering this, the conclusion is that hydrogen contributes the most to the dynamic pressure behavior of the battery, but that it is the presence of the oxygen evolution/recombination reaction that causes the sharp pressure spike at the end of charge.

Figure 4.10: Results fitting on 120V pack data with different charge rates. a) 0.1C, b) 0.9C [69].

The comparison of the experimental and modelling results confirmed that the model is able to describe the pressure behaviour and composition of a 12 V module during a 0.25C charge 0.2C discharge cycle. However, it is good to confirm that it is also functional in a different current and battery-size range. Figure 4.10 a) & b) shows the results of fitting the model to two different tests on a 120 V pack. The only fitted parameters are the aging parameter, $k_{corr}$ (to compensate for the age of the modules in the pack being different than the fitting module), and the heat transfer parameter $K_T$ (to compensate for the different form factor of the pack). The results shown are from a 0.1C and a 0.9C cycle. In both cases the model is able to reproduce the pressure behaviour of the pack. This shows that the model is useful also in a system setting, where packs with 10 modules or more are the norm and the currents vary depending on the application.

Looking back at the results, it is possible to answer the research questions on
4.3 Verification of the full-cell model

To verify that the dynamic behavior can be captured by taking the open circuit voltage hysteresis and gas phase of the battery into account, the models produced in the previous papers were implemented in a P2D model in Paper VI. From the results we see that the model is able to qualitatively recreate the features of the behavior of the battery for all three test cases. In the continuous charge/discharge case, Figure 4.11 a), the best adherence to experimental voltage was found during discharge while the deviations are found during rest after discharge, and in the beginning and the end of the charge period. The deviation during the rest after discharge can attributed to the discharge OCV used in the model being too low at low SOCs. During rest, the battery will approach the OCV, and the modeled asymptotic voltage is much lower than what is observed experimentally, indicating a mismatch. The difference between the model and the experimental voltage at the beginning of charge is also likely due to OCV errors. However, the mismatch between the voltages at end of charge is more likely due to errors in the balance between the charge reaction and the oxygen evolution reaction on the positive voltage. This can be seen from how
the state of charge of the positive electrode in the model increases above 100%. Adjustments in the relevant parameters cannot alleviate this without causing over-discharge in the model, suggesting that the oxygen related behaviors are not yet fully captured. The model is able to reproduce the pressure behavior of the battery, with the characteristic peak at end of charge, Figure 4.11(b). Here, similarly to the gas composition model, the bulk of the dynamic pressure behavior is made up of changes in the hydrogen pressure. This can be explained by increasing temperature and state of charge, as the equilibrium pressure of the hydrogen storage alloy increases with both temperature and degree of hydrogen intercalation. The hydrogen pressure increase is supplemented by a sharp oxygen spike at the end of charge.

Applying the model to the second data set, the mixed charge and discharge pulses, Figure 2(a), an ocular inspection yields a better adherence to the experimental voltage behavior than the single particle hysteresis model. The model is able to reproduce the qualitative behavior of changing current direction as well as current size. There is a large variation in the hysteresis parameter $\chi$ during the test, with movement spanning almost the full span, fluctuating between 0.1 and 1. This is an indication of the importance and ability of the hysteresis approximation to accurately depict this behavior in the full P2D model. As for the pressure prediction, Figure 2(b), the model is able to reproduce the qualitative behavior during the full duration of the test. Like for the continuous charge/discharge dataset, most of the pressure changes can be explained by the changes in hydrogen pressure. However, larger temperature fluctuations...
4.3. VERIFICATION OF THE FULL-CELL MODEL

Figure 4.12: Model performance for mixed pulses data set. Pulses ranging from 0.1C to 0.9C. a) Model voltage vs. experimental voltage. b) Model total pressure vs. experimental pressure & model partial pressures [70].

(~20°C) than in the continuous charge/discharge case means that changes in nitrogen pressure also contributes.

Approaching the final data set, the discharges at different C-rates, Figure 4.13 a), the model is able to general shape and mid-point voltages for the different C-rates. At 3C and 5C the adherence to experimental behavior is less successful, with a lower mid-point voltage compared to the data. These

Figure 4.13: a) Experimental and modeled discharge curves: 0.2C, 0.5C, 1C, 2C, 3C & 5C b) Modeled Ragone plot for three different modeled thicknesses, where the $L_{factor}$ is multiplied with the negative and the positive thickness [70].
results were accurate enough to allow us to investigate the effect of a change in electrode thickness on the volumetric energy and power density of the cell. A factor, $L_{\text{factor}}$, is multiplied with both the positive and the negative electrode thickness in the model, and the results are found in Figure 4.13b). The resulting curves have the shape and relative positions that one would expect from a change in electrode thickness. The thickest electrodes, $L_{\text{factor}}=1.1$, have the highest energy density and lowest power density of the three test cases. This is expected, as an increased thickness of the electrode increases the ratio of active material to supporting material in the cell while increasing conduction and diffusion distances in the electrode. As the electrode thickness is decreased the energy density goes down and the power density goes up. However, for the two thinner cases, $L_{\text{factor}}=0.9$ and $L_{\text{factor}}=1$, no difference can be seen in the power density. This suggests that there are resistances at play that do not decrease with the electrode thickness.

Considering that the model is able to reproduce the battery behaviors well it gives an opportunity to study how the processes in the battery interplay to produce the observed behavior. Perhaps the most interesting observation has to do with a voltage feature that occurs at high levels of DOC. The feature is commonly known as negative delta V ($-\Delta V$) and appears as a decrease in voltage at high DOC. It is common to use $-\Delta V$ for charge termination in nickel based batteries, and has long been assumed to occur due to a decrease in resistance caused by the rise in temperature at the end of charge [9]. However, in the model, the IR and ionic resistances have very little impact on battery voltage, but the $-\Delta V$ can still be seen. Instead, looking at the potentials on the positive electrode, Figure 4.14, the reason for $-\Delta V$ can be found in the interplay between the charge reaction and the oxygen evolution reaction. Looking at the equilibrium potential of the oxygen evolution, it can be seen to decrease towards the end of charge. This is due to a temperature dependence of the equilibrium potential. As the temperature goes up due to the oxygen evolution/recombination cycle, the equilibrium voltage goes down further increasing the oxygen evolution current. These two effects feed into one another until eventually $E_{\text{eq}}^{O_2}$ is low enough for the oxygen evolution to start dominating. Eventually the electrode starts to discharge, supplying additional current for oxygen evolution besides the externally supplied current. This is the tipping point at which $-\Delta V$ starts, and if overcharging continues the battery will eventually reach an equilibrium where the voltage & temperature is constant, the heat produced by the oxygen/evolution is lead away in its entirety to the surroundings, and all of the supplied current is used for oxygen evolution without further discharging the positive electrode. Due to the mechanism behind the $-\Delta V$, using it for charge termination has several drawbacks. First and foremost is the fact that due to the self-discharge, the available capacity in the battery will be less than if one terminates charging just before the voltage
4.3. VERIFICATION OF THE FULL-CELL MODEL

Figure 4.14: Potentials on the positive electrode for the continuous charge/discharge dataset. Equilibrium potential and activation overpotential shown for both the charge/discharge reaction and oxygen evolution [70].

derivative turns negative. The second drawback is that the high temperature and oxygen levels in the battery resulting from this method will contribute to battery aging. Finally, the Ah charge efficiency will go down compared to an earlier termination due to the amount of current used for oxygen production.

Although the model is able to reproduce the expected battery behavior, there are a couple of things that can be studied further to improve the performance. Firstly, the expressions for the oxygen evolution/recombination have been simplified in this model. Ayeb et al. [44] showed that the reaction mechanism and kinetics of the oxygen evolution differs depending on if the battery is charging or overcharging. However, it is difficult to elucidate when this switch happens and how to best incorporate this in a mathematical setting. Therefore, only the kinetics for the normal charging has been used in this model. The oxygen recombination may also need to be elaborated on. Experimental studies have shown that oxygen recombination during rest and discharge is slow, and that oxygen remains at the end of discharge in some cases [45], [46], [68]. However, in the model the recombination kinetics are kept high to avoid an extreme pressure build up during charge, and the oxygen is quickly recombined during rest so that no oxygen remains. This suggests that the description of oxygen recombination in the model is not complete, and that the oxygen recombination rates are different during charge and rest/discharge. Finally, different kinetic factors, \( k_{\text{deh}} \), had to be used for the continuous charge/discharge data sets and the mixed pulse data set for the model to reproduce the behavior well. This
is likely due to how OCV and hysteresis is defined in the model. The upper and lower hysteresis boundaries are measured, and it is assumed that $\chi=1$ along the upper measured boundary and $\chi=0$ along the lower boundary. However, in the model $\chi$ moves between the boundaries in the same way even when the current reversal occurs at 0% or 100% SOC, never reaching the measured boundaries. Therefore, using the measured boundaries will causes errors at the SOC extremes. The solution to this would be to find the boundaries where $\chi$ is actually 1 and 0 for all SOC values. However, these boundaries cannot be measured, but instead would have to be derived from how $\chi$ moves between the boundaries in the middle of the SOC window. This through calculating the OCV boundaries at the extremes, assuming that the behavior is the same there as for in the middle of the SOC window.

In addition to the development of the model, the parametrization was also a challenge. Using GITT on battery half cells is a common method to find OCV, diffusion parameters and exchange current density for a battery model. However, the phenomena we have studied in this paper also have an impact on the parametrization using this method. The hysteresis in the positive electrode material causes the OCV to sink at the surface during the evening out of concentration gradients that occurs in the particle during relaxation. As the relaxation voltage is assumed to be the OCV voltage for that state of charge, this means that the measured OCV at the boundaries is different than the actual boundaries, which is above the measured boundary for charge and below for discharge. This also has the consequence of it being difficult to fit a single particle model to the data for parameter determination. The model will be unable to make a difference between the voltage relaxation due to hysteresis and the voltage relaxation due to the relaxation of the concentration gradient. This gives a much higher value of the diffusion time constant, $\tau$, than is reasonable and usable in a more complex model. The oxygen evolution on the positive electrode also makes the method unreliable at high states of charge. Usually, coulomb counting is used to calculate the SOC position of the GITT pulses, but when an unknown part of the current is used for oxygen evolution, this becomes difficult. In conclusion, the behaviors described and discussed in this thesis, the OCV hysteresis and gas reactions, have an impact on parametrization of the standard part of the P2D model as well. Approximations that can be made for a system without these things to isolate certain parameters is made more difficult since these phenomena are so interconnected with each other and the other battery processes.

With all of these considerations taken into account it is possible to address the question whether the two behaviors described in this thesis are enough to predict battery behavior under normal operating conditions. Based on the three test cases, the model is capable of qualitatively reproducing the voltage and pressure behavior of a NiMH cell under different conditions, including mixed
4.3. VERIFICATION OF THE FULL-CELL MODEL

charge/discharge pulses similar to what would be seen in some types of stationary energy storage. The two studied phenomena in this thesis, the gas reactions and the OCV hysteresis, both have a large impact on the voltage behavior of the battery. The biggest impact during a continuous charge to high SOC is made by the oxygen evolution. Performing a sensitivity analysis on the continuous charge/discharge dataset reveals that the parameter with the biggest impact on model voltage performance is $K_T$, which is the heat transfer parameter, followed by $k_{\text{OER}}$ and $K_{O_2}$, the rate constants for oxygen evolution and recombination respectively. These are all factors that affect the oxygen evolution potential. A decreased $K_T$ will increase the temperature inside the cell which in turn decreases $E_{\text{eq}}^{O_2}$, lowering the potential of the positive electrode. $k_{\text{OER}}$ affects the rate of the oxygen evolution, adjusting current distribution between the two reactions occurring on the positive electrode, thereby adjusting the potential, but the amount of oxygen also controls the temperature evolved, which affects the potential as described above. Finally, $K_{O_2}$ regulates the rate of the oxygen recombination reaction, a lower $K_{O_2}$ will lead to a more delayed recombination which delays the temperature response to the oxygen evolution, again with effects on the potential and oxygen evolution rate. It is clear that these effects are interconnected, and that they can be related to the oxygen reactions in the cell. When it comes to the OCV hysteresis, the effect is largest for the dataset with the mixed pulses. Here the hysteresis constant fluctuates between the two boundaries, improving model performance under dynamic conditions. Although the model has some ways to go in order to be fully quantitatively predictive, the results indicate that the described behaviors are enough to create a fully dynamic model for the NiMH battery.
Chapter 5

Conclusions

In the work presented in this thesis, the behavior of the NiMH battery has been investigated with the aim of creating a dynamic battery model capable of recreating this behavior for a battery under normal operating conditions. To do this, the focus has been on two key properties of the battery: OCV hysteresis and the battery gas-phase reactions.

The main questions regarding OCV hysteresis was how it affects the battery and why it occurs. The first study, Paper I, investigated the hysteresis behavior of the battery. The study showed that hysteresis behavior could be added with good results to a single particle model using empirically based mathematical expressions. The second study, Paper II, aimed to deepen the understanding of why OCV hysteresis occurs through studying the structural changes in the positive electrode material at different hysteresis states. It was found that there are structural differences between the material at the two hysteresis boundaries at the same state of charge, both in the bulk of the material and on the surface.

Addressing the gas behavior of the battery, the main questions were how the gas phase reactions affect the battery and through what mechanisms. The third study, Paper III, explored whether the addition of an AC frequency overlay could affect the gas phase reactions, and thereby aggravate aging. No effect was found, suggesting that the battery gas phase is unaffected by addition of the tested frequencies. Paper IV investigated the pressure composition of the battery during a normal charge cycle. It was found that the bulk of the pressure was made up by nitrogen and that the main component of the dynamic pressure came from the hydrogen in the cell. Oxygen also played a part towards the end of charge, making up a significant portion of the pressure spike occurring at the end of charge. The fourth study, Paper V, then presented a model with the aim to simulate the gas-composition of the battery. By using experimental current, voltage and temperature as input, the study was able to isolate and model only the gas behavior of the battery. The results were qualitatively similar to the measured behavior seen in Paper IV.
Finally, to test the hypothesis that including OCV hysteresis and the gas phase reactions is enough to predict NiMH battery behavior, the two models from Paper I and Paper V were implemented in a P2D model in Paper VI. The results show that the model is capable of simulating dynamic NiMH behavior qualitatively, both in terms of voltage and pressure.

This work can contribute to a greater understanding of how the processes in NiMH batteries are connected. In particular, the model presented in Paper VI can be used as a tool to further the understanding and to improve battery handling and design. Examples of possible applications are battery development, sensitivity analysis for production quality control, digital twins for system regulation and system dimensioning. All of these applications can contribute to NiMH based stationary energy storage that is better optimized for the intended application and produced more efficiently, improving the viability of a more renewable and delocalized energy grid.
Chapter 6

Future Outlook

To advance the understanding of the NiMH battery behavior and improve the model presented here, there are some things that can be further explored. Regarding the phenomena studied in this work, there are topics that can be further studied and used to improve the model implementation.

In the case of hysteresis, the current model implementation can be improved at high and low SOCs through empirically adjusting the shape of the hysteresis boundaries to allow the model to better run between the two boundaries when changing current direction at 0% SOC or 100% SOC. It would also be interesting to further study the hysteresis loops described by Srinivasan et al. [21] to devise a method to introduce that part of the hysteresis behavior into a model.

The gas studies have shown a discrepancy between the model and the experimentally recorded behavior in that the oxygen is recombined faster in the model during rest and discharge. While the recombination kinetics have been previously studied for rest and discharge, similar studies do not exist for charge [45], [46]. Additional experimental and modeling studies of this behavior can help improve the predictive properties of the model oxygen pressure. In addition, Ayeb et al. [44] show that the oxygen evolution reaction has different reaction mechanisms and kinetics depending on if the battery is partially charging or overcharging. This is simplified in the model presented in Paper V due to difficulties in how and when the change between the two kinetic expressions occurs. Further study on this topic could help the accuracy of the voltage and pressure model at high states of charge.

Lastly, parametrization of the P2D model using the common GITT method proved to be difficult. The hysteresis behavior and the oxygen evolution made it more difficult to isolate the relevant parameters and so adjustments of the parameters had to be made for the model to function. Further study into a parametrization method that can better handle these behaviors in a battery material would likely result in a more verifiable model with better predictive properties. One suggestion to investigate would be to evaluate open circuit...
CHAPTER 6. FUTURE OUTLOOK

voltage through mathematical methods rather than a relaxation method. For example, Snihir et al. [74] uses a Karhunen-Loeve expression to extract an OCV curve for charging of a NiMH battery, a method that could be further explored for determination of discharge OCV and OCV hysteresis behavior. To better determine the exchange current density for the charge/discharge reactions as well as the diffusion in the particles, shorter current pulses with a low current could be utilized to avoid interference of the hysteresis relaxation observed.

Beyond the topics discussed in this thesis, there are phenomena that if studied and implemented would improve model usability further. Most important of these is battery aging. A model incorporating aging could be used for cycling studies, system dimensioning, and algorithm development for increased system lifespan. An other phenomenon to investigate would be whether changes in battery behavior when using different negative electrode materials can be predicted using PCT curves for the hydrogen storage alloys. Using a model for that purpose would reduce cost and time to implementation for new hydrogen storage materials. Finally, by expanding the model to a P3D or a P4D model, the temperature distribution in the cell could be studied with the goal of ensuring a more even distribution, which in turn would make the aging of the cell more homogenous.
Chapter 7

Acknowledgements

There are many people without whom this work wouldn’t have been possible. When I had finished my masters thesis, I was convinced that I was never going into research and that my personality was not suitable. However, my colleague Stina saw something in me and convinced me to take this opportunity, for which I will forever be thankful. The opportunity to perform this PhD project was created through funding from SSF and support from my employer, Nilar. Later, my supervisor team Gőran, Erika, Henrik, Dag, and Peter continued to support and believe in me during the process, even on the days when everything felt impossible. My colleagues at both Nilar and KTH have provided enthusiastic help over the years, and I’m humbled to be able to present the product of our communal efforts. Two examples are even found in this thesis: Victora Sternhagen took the SEM images used in Figure 2.5 & Figure 2.9. And Alice Gratrex is the mind behind the conceptualization of Figure 2.10, 2.11 & 3.2. I’ve also had the privilege of collaborating with academics outside KTH, who were willing to accompany me on the long and winding road that was the study on hysteresis origins.

My friends have also played a large part, with a special mention of Elias & Annika who have had their PhD journeys alongside mine. Getting support from them and giving them support in return has been invaluable. Also, to my dear friend Emily, who is the artist behind the cover illustration, when we created things together as children I never imagined that it would one day take us to collaborating on my PhD thesis.

Another important part has been music, without which I would not have had the strength to continue on my journey. My choir, and in the last three years my opera, has provided me with friendship and the inimitable feeling of creating art together.

Last but not least, my family who have supported and believed in me throughout my life, without fail. My parents who serve as continuous inspiration to try harder and reach further, still advancing through life without
hesitation. And finally my loving husband Victor, who stands by me in thick
and thin and makes me want to get up to fight another day.
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