Analysis of the Novel LiFePO$_4$ (LFP) Electrical Traction Batteries: Functional and Constructive Characteristics

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Resumo

As baterias de lítio ferro fosfato (LiFePO₄) representam uma nova gama de baterias de iões de lítio no mercado dos sistemas de tracção eléctrica. Assim, o seu envelhecimento é uma das questões prioritárias a estudar uma vez que o seu desempenho será afetado a longo prazo, havendo por isso uma necessidade de estimação dos parâmetros internos da bateria.

Inicialmente, foi feita uma revisão do mecanismos electroquímicos principais que decorrem numa bateria de iões de lítio, com especial relevância para a elevada estabilidade térmica no caso das baterias de LiFePO₄.

O estudo do envelhecimento foi feito através da análise da resposta em frequência (curva de Nyquist) obtida por espectroscopia de impedância electroquímica. A partir da curva foi estabelecido um circuito eléctrico equivalente de parâmetros concentrados, cujos elementos estão relacionados com um determinado fenómeno físico, por forma a modelar a curva em toda a gama de frequências consideradas. Esse circuito representa, então, a impedância interna da bateria em estudo.

A partir de dados experimentais fornecidos por um instituto belga para a pesquisa tecnológica (VITO), foi analisada a evolução temporal de cada elemento desse circuito, bem como a sua dependência com a temperatura ou estado de carga. No entanto, devido à pouca qualidade dos dados fornecidos, não foi possível observar sinais de envelhecimento significativos.

Para além disso, estabeleceu-se um modelo térmico de parâmetros concentrados para uma bateria de LiFePO₄, cujos resultados obtidos em simulação foram validados por comparação com um artigo científico e por análise experimental.

O capítulo final deste trabalho é dedicado ao desenvolvimento dos algoritmos de estimação de estados, com ajuste automático dos parâmetros internos da bateria, sendo que o passo seguinte seria a validação experimental dos mesmos.

Palavras-Chave

Tracção eléctrica; Bateria de LiFePO₄; Envelhecimento; Impedância interna; Modelo térmico; Algoritmo de estimação de estados
Abstract

Lithium iron phosphate batteries (LiFePO₄) represent a new type of lithium ion batteries in the electrical traction systems’ market. It’s, therefore, essential to study the degradation mechanisms since they affect a battery’s performance in the long term, and consequently evaluate its internal parameters.

Initially, the main electrochemical mechanisms that occur in a lithium ion battery were revised, with special relevance for the high thermal stability of the LiFePO₄ battery, which is one of its most important characteristics.

The frequency response of a LiFePO₄ battery cell, acquired from an impedance electrochemical spectroscopy (EIS), was used to analyze its aging processes and an electrical lumped parameter circuit developed to model the Nyquist curve in its range of frequencies. It represents the internal impedance of the cell, being each element from the circuit related to a particular physical phenomenon.

The data from the EIS mentioned above was provided by VITO, the Flemish institute for technological research, which allowed to analyze the temporal trend of each element as well as its dependence with temperature or the battery’s state of charge. However, the data was insufficient and in some cases incomplete, which prevented any significant conclusion about the aging mechanisms.

Furthermore, a lumped parameter thermal model for a LiFePO₄ battery cell was also established, whose simulation results were validated through comparison with a scientific paper and experimental analysis.

The final chapter is related with the estimation algorithms with automatic adjustment of the internal parameters. The implementation process would be the next step, followed by its experimental authentication.

Keywords

Electric traction; LiFePO₄ battery; Degradation mechanisms; Electrical model; Internal impedance, Thermal model; Estimation algorithms
Index

ACKNOWLEDGMENTS ........................................................................................................... II

RESUMO ................................................................................................................................ III

ABSTRACT ........................................................................................................................... IV

LIST OF TABLES .................................................................................................................... XIII

LIST OF SYMBOLS .............................................................................................................. XV

1 INTRODUCTION .................................................................................................................. 1
  1.1 MOTIVATION AND GOALS ......................................................................................... 2
  1.2 THESIS’ STRUCTURE ................................................................................................. 3

2 BASIC CONCEPTS ............................................................................................................. 5
  2.1 ELECTROCHEMICAL PRINCIPLES AND REACTIONS .................................................. 5
    2.1.1 Operation of a battery cell – Charge and Discharge .................................................. 5
    2.1.2 Thermodynamic Background .................................................................................. 6
    2.1.3 Internal resistance .................................................................................................. 7
    2.1.4 Charge transfer – electrodes ................................................................................. 8
    2.1.5 Ionic mass transfer ................................................................................................. 8
    2.1.6 Electrical double-layer ......................................................................................... 9
    2.1.7 Electrolyte ............................................................................................................ 9
  2.2 LIFEP04 BATTERIES VS. LICO2 BATTERIES .............................................................. 10
    2.2.1 Thermal Stability .................................................................................................. 11
  2.3 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) ........................................... 12

3 LIFEP04 BATTERY ............................................................................................................. 15
  3.1 INTERNAL IMPEDANCE: AN ELECTRICAL LUMPED PARAMETER CIRCUIT REPRESENTATION .................. 15
    3.1.1 First approach: the Randles’ Electric Circuit ......................................................... 15
    3.1.2 Second approach ................................................................................................. 18
    3.1.3 Third approach ................................................................................................... 19
  3.2 DEGRADATION MECHANISMS ................................................................................... 20
    3.2.1 Degradation due to cycling – cycling aging ......................................................... 21
    3.2.2 Degradation due to storage – calendar aging ...................................................... 21
  3.3 RESULTS AND DISCUSSION ..................................................................................... 22
    3.3.1 Preliminary conclusions ....................................................................................... 24

4 THERMAL STUDY ............................................................................................................. 27
4.1 THEORETICAL PRINCIPLES................................................................................................................. 27
4.1.1 The Plane Wall geometry - without internal heat generation......................................................... 27
4.1.2 The Plane Wall geometry - with internal heat generation............................................................... 29
4.2 LifePO4 CELL......................................................................................................................................... 30
4.2.1 Lumped parameter thermal model ................................................................................................. 31
4.2.2 Simulation – Results and discussion ............................................................................................. 34
4.2.3 Experimental analysis..................................................................................................................... 35

5 ESTIMATION ALGORITHMS .................................................................................................................. 37

5.1 INTRODUCTION .................................................................................................................................. 37
5.1.1 First methodology .......................................................................................................................... 37
5.1.2 Second methodology ...................................................................................................................... 40

5.2 Randles Circuit – Estimation Algorithm ............................................................................................. 40
5.2.1 R estimation .................................................................................................................................... 42
5.2.2 R and C estimation ......................................................................................................................... 42
5.2.3 R and C estimation ......................................................................................................................... 43
5.2.4 Additional adjustment .................................................................................................................... 44
5.2.5 Simulation ....................................................................................................................................... 47

5.3 Randles Circuit with Inductive Part – Estimation Algorithm ................................................................. 48
5.3.1 R estimation .................................................................................................................................... 49
5.3.2 R and L estimation ......................................................................................................................... 49
5.3.3 R and C estimation ......................................................................................................................... 50
5.3.4 R and C estimation ......................................................................................................................... 51
5.3.5 Additional adjustment .................................................................................................................... 52
5.3.6 Simulation ....................................................................................................................................... 52

5.4 Modified Randles Circuit – Estimation Algorithm ............................................................................... 54
5.4.1 R estimation .................................................................................................................................... 54
5.4.2 R and C estimation ......................................................................................................................... 55
5.4.3 R, R, C and C estimation ............................................................................................................... 55
5.4.4 Additional adjustment .................................................................................................................... 57
5.4.5 Simulation ....................................................................................................................................... 58

5.5 Modified Randles Circuit with Inductive Part – Estimation Algorithm .............................................. 59
5.5.1 R estimation .................................................................................................................................... 60
5.5.2 R and L estimation ......................................................................................................................... 60
5.5.3 R and C estimation ......................................................................................................................... 61
5.5.4 R, R, C and C estimation ............................................................................................................... 62
5.5.5 Additional adjustment .................................................................................................................... 63
5.5.6 Simulation ....................................................................................................................................... 63
List of figures

Figure 1.1 - Theoretical and actual specific energy of battery systems (taken from [25]) .......................... 1
Figure 1.2 - Thermal evolution of different types of batteries (taken from [3]) ................................. 2
Figure 2.1 - Discharge a) and Charge b) mechanisms of lithium ion rechargeable batteries (taken from [15]) .......................................................................................................................... 5
Figure 2.2 - Double-layer capacitance illustration (taken from [16]) ..................................................... 9
Figure 2.3 - Exothermic reaction evolution with temperature obtained through differential scanning calorimetry (DSC) (taken from [3]) .......................................................................................................................... 11
Figure 2.4 - Decay of the positive electrode’s mass due to oxygen release with increasing temperature obtained through thermal gravimetry (TG) (taken from [3]) ................................................................. 12
Figure 2.5 - Example of impedance evolution with time (Nyquist diagram). (Data obtained by VITO and curves drawn with EC-lab V10.23 with 7 points per decade and frequencies ranging from 0.05 Hz to 10 kHz) .......................................................................................................................... 13
Figure 2.6 - Example of impedance evolution with temperature (Nyquist diagram). (Data obtained by VITO and curves drawn with EC-lab V10.23 with 7 points per decade and frequencies ranging from 0.05 Hz to 10 kHz) .......................................................................................................................... 13
Figure 2.7 - Example of a Nyquist curve for the LiFePO4 cell (Data obtained by VITO and curve drawn with EC-lab V10.23) .......................................................................................................................... 14
Figure 3.1 - Randles’ circuit ....................................................................................................................... 15
Figure 3.2 - Randles’s circuit spectrum for Re = 20 Ω, Cdl = 25 μF, Rct = 100 Ω and Ax = 300 Ω.s^-0.5 (taken from [17]) .......................................................................................................................... 16
Figure 3.3 - First approach with one RC circuit ......................................................................................... 17
Figure 3.4 - Difference between the Nyquist diagram of the first approach circuit (red dots) and the experimental data (blue line). (Experimental data obtained by VITO and curve drawn with EC-lab V10.23) .......................................................................................................................... 18
Figure 3.5 - Second approach – lumped parameter impedance circuit ....................................................... 18
Figure 3.6 - Misrepresentation between the second approach (red dots) and the experimental data (blue line). (Experimental data obtained by VITO and curve drawn with EC-lab V10.23) .......................................................................................................................... 19
Figure 3.7 - Final impedance lumped parameter model ............................................................................ 19
Figure 3.8 - Difference between the Nyquist diagram of the final approach circuit (red dots) and the experimental data (blue line). (Experimental data obtained by VITO and curve drawn with EC-lab V10.23) .......................................................................................................................... 20
Figure 3.9 - Representative illustration of SEI - charging process (taken from [18]) ............................... 21
Figure 3.10 - Display of the data .............................................................................................................. 22
Figure 3.11 - Select option Z fit to open the fitting menu .......................................................................... 23
Figure 3.12 - Z fit menu .......................................................................................................................... 23
Figure 3.13 - Final result .......................................................................................................................... 24
Figure 4.1 - Plane wall geometry with heat transfer through it ................................................................. 28
Figure 4.2 - Lumped parameter circuit according to equations (4.15) and (4.18) ................................................. 30
Figure 4.3 - Simplified cross section of the LiFePO4 cell ................................................................................................. 30
Figure 4.4 - Lumped parameter circuit representation of a material with internal heat generation .................. 32
Figure 4.5 - Lumped circuit representation of a material that does not produce heat ............................................ 33
Figure 4.6 - Final 2D model of the battery cell ..................................................................................................................... 33
Figure 4.7 - Block diagram of the thermal model .................................................................................................................. 34
Figure 4.8 - System used to test the thermal behaviour of the cell pack ................................................................. 35
Figure 5.1 - First approach circuit ........................................................................................................................................ 37
Figure 5.2 - Shortened circuit, neglecting the $R3C2$ time constant .................................................................................. 40
Figure 5.3 - Randles circuit and corresponding Nyquist curve (98 points) for a particular case \(R1 = 1.967 \, m\Omega, R2 = 1.066 \, m\Omega, R3 = 14.793 \, m\Omega, C1 = 36 \, F \text{ and } C2 = 739.1 \, F\) .................................................. 40
Figure 5.4 - Simplified Randles’ circuit and corresponding Nyquist curve (98 points) for a particular case \(R1 = 1.967 \, m\Omega, R2 = 1.066 \, m\Omega \text{ and } C1 = 36 \, F\) ........................................................................................................ 41
Figure 5.5 - Complete Randles’ circuit, its simplifications according to each time constant and corresponding Nyquist curves (98 points) \(R1 = 1.967 \, m\Omega, R2 = 1.066 \, m\Omega, R3 = 2.793 \, m\Omega, C1 = 36 \, F \text{ and } C2 = 739.1 \, F\) .................................................. 41
Figure 5.6 - Measurement of $RDC$ through a load resistor $RL$ exemplification ............................................................ 43
Figure 5.7 - Error function dependind on a variable (this case, $C1$), when all other estimated parameters do not present a deviation \(R1 = R1 = 1.967 \, m\Omega, R2 = R2 = 1.066 \, m\Omega, R3 = R3 = 2.793 \, m\Omega, C1 = C1 = 36 \, F \text{ and } C2 = C2 = 739.1 \, F\) ........................................................................................................ 45
Figure 5.8 - Error function depending on a variable (this case, $C1$), when all other estimated parameters present a deviation \(R1 \equiv R1 = 1.967 \, m\Omega, R2 \equiv R2 = 1.066 \, m\Omega, R3 \equiv R3 = 2.793 \, m\Omega, C1 = 36 \, F \text{ and } C2 \equiv C2 = 739.1 \, F\) ........................................................................................................ 46
Figure 5.9 - Simulation results for 98 points: estimated (red crosses) and to be estimated (blue line) curves ................................................................................................................................................................. 47
Figure 5.10 - Randles circuit with inductive component and corresponding Nyquis curve (for 35 points) for a particular case \(R1 = 1.967 \, m\Omega, R2 = 1.066 \, m\Omega, R3 = 14.793 \, m\Omega, C1 = 36 \, F, C2 = 739.1 \, F, R5 = 0.02023 \, \Omega \text{ and } L1 = 53.59 \, nH\) ........................................................................................................ 48
Figure 5.11 - Simplified circuit for the higher frequencies and corresponding Nyquist curve (335 points) for a particular case \(R1 = 1.967 \, m\Omega, R5 = 0.02023 \, \Omega \text{ and } L1 = 53.59 \, nH\) ........................................................................................................ 49
Figure 5.12 - Simulation results for 35 points: estimated (red crosses) and to be estimated (blue line) curves ................................................................................................................................................................. 49
Figure 5.13 - Modified Randles circuit and corresponding Nyquist curve (38 points) for a particular case \(R1 = 1.741 \, m\Omega, R2 = 0.5697 \, m\Omega, R3 = 1.007 \, m\Omega, R4 = 22.11 \, m\Omega, C1 = 5.206 \, F, C2 = 71.39 \, F, C3 = 1172 \, F\) ........................................................................................................ 53
Figure 5.14 - Shortened circuit, neglecting $R3C2$ and $R4C3$ time constants ........................................................................ 55
Figure 5.15 - Complete Randles’ circuit, its simplifications according to each time constant and corresponding Nyquist curves (38 points) \(R1 = 1.741 \, m\Omega, R2 = 0.5697 \, m\Omega, R3 = 1.007 \, m\Omega, R4 = 22.11 \, m\Omega, C1 = 5.206 \, F, C2 = 71.39 \, F, C3 = 1172 \, F\) ........................................................................................................ 56
List of tables

Table I - Comparison between LiCoO$_2$ and LiFePO$_4$ cathodes (theoretical values)................................. 10
Table II - Thermal and physical properties of each material of the cell (taken from [19]).............................. 31
Table III - Information about the geometry of the battery cell (taken from [19])............................................. 31
Table IV - Analogy between electrical and thermal properties ............................................................................ 32
Table V - Temperature achieved in each element by the model with a current of 14 A and a room temperature of 30.2 ºC and corresponding error compared with [9]......................................................... 34
Table VI - Temperature achieved in each element by the model with a current of 70 A and a room temperature of 30.2 ºC and corresponding error compared with [9]......................................................... 35
Table VII - Temperatures achieved by each element through the model, for a room temperature of 23.1 ºC and a discharging current of 8.043 A compared with the experimental analysis ...................... 36
Table VIII - Temperatures achieved by each element through the model, for a room temperature of 22.4 ºC and a discharging current of 16.10 A compared with the experimental analysis......................... 36
List of symbols

A – Electrochemical species
B – Electrochemical species
C – Electrochemical species
D – Electrochemical species
a – Number of molecules of species A
b – Number of molecules of species B
c – Number of molecules of species C
d – Number of molecules of species D
n – Number of electrons
$\Delta G^0$ – Standard free energy [J/mol]
F – Faraday’s constant [C.mol$^{-1}$]
$E^0$ – Standard electromotive force [V]
E – Electromotive force [V]
R – Universal gas constant [JK$^{-1}$mol$^{-1}$]
T – Absolute temperature [K]
X – Electrochemical species’ concentration [kg/m$^3$]
LiFePO$_4$ – Lithium Iron Phosphate
LiCoO$_2$ – Lithium Cobalt Oxide
R – Electrical resistance [Ohm]
i – Electrical current [A]
A – Area [m$^2$]
k – Rate constant
$c_a$ – Concentrations of oxidized elements [kg/m$^3$]
$c_r$ – Concentrations of reduced elements [kg/m$^3$]
a – transfer coefficient
$i_{ac}$ – Current that flows from the anode to the cathode [A]
i$_{ca}$ – Current that flows from the cathode to the anode [A]
J – Diffusion flux [mol.m$^2$.s$^{-1}$]
D – Diffusion coefficient [m$^2$.s$^{-1}$]
C – Substance’s concentration [mol.m$^{-3}$]
LiPF$_6$ – Lithium hexafluorophosphate
PF$_6$ – Hexafluorophosphate
LiC$_6$ – Lithiated graphite
Co$_3$O$_4$ – Cobalt oxide
$R_e$ – Ionic and electronic resistance of the electrolyte and electrodes/current collectors [Ohm]
$R_{ch}$ – charge transfer resistance [Ohm]

$C_{dl}$ – double layer capacitance [F]

$Z_w$ – Warburg impedance [Ohm.s$^{1.5}$/rad]

$A_x$ – Warburg coefficient [Ohm.s$^{0.5}$]

$\sigma$ – Parameter which depends on the electrochemical phenomenon [Ohm.s.rad$^{-0.5}$]

$\tau$ – time constant [s]

$R_n$ – constant value

$C_n$ – constant value

$R_w$ – resistance related to the Warburg impedance [F]

$C_w$ – capacitance related to the Warburg impedance [F]

$C$ – capacitance [F]

$L$ – inductance [H]
1 Introduction

Lithium-ion (Li-ion) batteries belong to a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge and backwards when charging. They were first used in the 1970s in military applications.

Currently, such batteries are used in many sectors such as electronics, military purposes, electrical traction vehicles or aerospace applications. These batteries have high specific energy [Wh/kg] (Fig. 1.1) and a low self-discharge rate when not in use, when compared to other types of batteries.

Nowadays, the majority of Li-ion batteries’ cathodes are based on lithium cobalt oxide (LiCoO$_2$), which offers high specific energy, but presents safety risks, especially when exposed to high temperatures. Cathodes based on lithium iron phosphate (LiFePO$_4$) offer lower specific energy, but since it’s safer (thermally more stable) it results in a longer cycle life (less damaging with high temperatures). For temperatures above 200°C, LiCoO$_2$ starts to present an exothermal reaction. On the other hand, LiFePO$_4$ does not show that trend, at least for temperatures up to 350°C. This is expressed in figure 1.2 [3].
1.1 Motivation and goals

In electric traction, hybridization of combustion engines currently provides an interim solution prior to the establishment of a fully electric traction solution. The challenge today in the development of vehicles with electric traction is not just optimizing their traction chain from the point of view of cost, consumption and autonomy, but also the adjustment of the energy management system according to its driver's routines and the type of vehicle.

It is, thus, necessary to estimate the internal parameters of the cell. In order to do so, an online parameter estimator will be developed.

This work addresses a lumped-parameter modeling approach for the LiFePO$_4$ battery electrochemical phenomena taking into account aging and temperature effects on battery components. The electrical model developed will be identified from experimental data (acquired by VITO, the Flemish institute for technological research, located in Belgium of its frequency response determined with the software EC-lab V10.23, a free version by Bio-Logic Science Instruments SAS).

The model previously identified will serve as a basis for the design of an on-line methodology to determine its internal parameters.

In that context, this thesis takes into account two different points: focus on the promising LiFePO$_4$ batteries and embedded automatic battery diagnosis.
1.2 Thesis’ structure

This work is divided in six major chapters. The first one introduces the basic concepts of a lithium battery and a brief comparison between the LiFePO$_4$ and LiCoO$_2$ batteries, with special reference to their thermal stability. The second chapter analyzes the degradation mechanisms of a LiFePO$_4$ cell and presents its internal impedance modeled by an electrical lumped parameter circuit. Chapter 4 describes the thermal study of a particular LiFePO$_4$ cell when operating. It starts with its theoretical principles, followed by a simulation in Matlab environment and corresponding experimental validation. Chapter 5 describes four different algorithms to estimate the parameters of the chosen electrical circuit to model the internal impedance of the cell and this work’s conclusions are presented in the final chapter.
2 Basic concepts

A battery is a device that converts the chemical energy contained in its active materials directly into electric energy through an electrochemical oxidation-reduction (redox) reaction. In case of a rechargeable system, the battery is recharged by the reverse process. This type of reaction involves the transfer of electrons from one material to another through an electric circuit.

Three major components constitute a cell: the anode (negative electrode) which is usually made of graphite or hard carbon with intercalated lithium; the cathode (positive electrode), which in this case is made of LiFePO₄ or LiCoO₂; and the electrolyte, which is an ionic conductor providing the medium for transfer of charge (lithium ion only) inside the cell, between the anode and cathode. Note that, to prevent short-circuits, there is also a porous membrane called separator in the electrolyte, obviously permeable to lithium ionic flow to keep the electric circuit closed.

2.1 Electrochemical Principles and Reactions

2.1.1 Operation of a battery cell – Charge and Discharge

During discharge, electrons flow from the anode (oxidized) through the external load towards the cathode, where they are “accepted” and lithium ions are reduced. The electric circuit is closed by the electrolyte where lithium ions flow.

During charge, the electronic current flow is reversed and oxidation occurs at the positive electrode (cathode) and reduction at the negative electrode (anode).

Both processes are exemplified in figure 2.1 [15]:

![Discharge and Charge Mechanisms](image)

**Figure 2.1** - Discharge a) and Charge b) mechanisms of lithium ion rechargeable batteries (taken from [15])
2.1.2 Thermodynamic Background

Considering a standard cell, the reaction at one electrode can be [5] (eq. 2.1)

\[ aA + ne \rightleftharpoons cC \]  

where \( a \) is the number of molecules of specie \( A \), \( n \) is the number of electrons and \( c \) is the number of molecules of specie \( C \). At the other electrode, the reaction can be represented as [5] (eq. 2.2)

\[ bB - ne \rightleftharpoons dD \]  

where \( b, B, n, D \) and \( d \) have analogous meaning. Hence, the overall reaction in the cell is [5] (eq. 2.3)

\[ aA + bB \rightleftharpoons cC + dD \]  

The change in the standard free energy \( \Delta G^0 \) of a cell reaction is the leading force which enables a battery to deliver electrical energy to an external load [5], and is expressed as (eq. 2.4)

\[ \Delta G^0 = -nFE^0 \]  

where, \( F \) is Faraday’s constant (96,487 coulombs) and \( E^0 \) is the standard electromotive force. The voltage \( E \) of a cell is given by the Nernst equation [5] (eq. 2.5),

\[ E = E^0 - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b} \]  

where \( R \) is the universal gas constant (8,314.472 JK\(^{-1}\)mol\(^{-1}\)), \( T \) is the absolute temperature, \([X]\) is the specie’s concentration.

Redox reactions for both LiCoO\(_2\) and LiFePO\(_4\)’s cells are listed in the next sections.

2.1.2.1 Redox equations - Lithium Cobalt Oxide Battery

- Cathode reaction (eq. 2.6)

\[ \text{LiCoO}_2 \xrightarrow{\text{Charge}} 2x\text{Li}^+ + xe^- + \text{Li}_{1-x}\text{CoO}_2 \]  

- Anode reaction (eq. 2.7)

\[ C_6 + x\text{Li}^+ + xe^- \xrightarrow{\text{Discharge}} \text{Li}_xC_6 \]
• Global reaction (eq. 2.8)

\[
\text{LiCoO}_2 + C_6 \xrightarrow{\text{Discharge}} \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x C_6
\] (2.8)

2.1.2.2 Redox equations - Lithium Iron Phosphate Battery

• Cathode reaction (eq. 2.9)

\[
\text{LiFePO}_4 \xrightarrow{\text{Discharge}} x\text{Li}^+ + xe^- + \text{Li}_{1-x}\text{FePO}_4
\] (2.9)

• Anode reaction (eq. 2.10)

\[
C_6 + x\text{Li}^+ + xe^- \xrightarrow{\text{Discharge}} \text{Li}_x C_6
\] (2.10)

• Global reaction (eq. 2.11)

\[
\text{LiFePO}_4 + C_6 \xrightarrow{\text{Discharge}} \text{Li}_{1-x}\text{FePO}_4 + \text{Li}_x C_6
\] (2.11)

Being \(x\) the amount of lithium (in percentage) involved in the reaction, which is obviously equal to the amount of electrons since each electron must be recombined with each lithium ion. This number is limited to the quantity of ions that can be extracted/inserted from/in the electrode without damaging it.

2.1.3 Internal resistance

Although it is common to manufacturers to give a single value for the internal resistance of a battery cell, it is not a constant. It depends on temperature, age and depth of discharge, for example.

Nevertheless, its value comes from the sum of two components [5]: the electric and ionic resistances. The first includes the electric resistance of the battery materials. The latter encompasses factors resulting from the movement of ions within the cell, which include electrolyte conductivity, ionic mobility, electrode porosity, electrode surface area, etc. That is expressed through eq. 2.12,

\[
R_{\text{int}} = R_{\text{ionic}} + R_{\text{electric}}
\] (2.12)
2.1.4 Charge transfer – electrodes

Considering equation (2.1) and a kinetic analysis [5], current flowing through the electrodes comes from the difference between two currents: one originated from the reduction reaction and the other originated from the oxidation reaction (eq. 2.13),

\[
i = i_{ac} - i_{ca} = nF A k C_o \exp\left(-\frac{a n F E^0}{RT}\right) - nF A k C_r \exp\left(\frac{(1-a)F E^0}{RT}\right)
\]

where \( A \) is the area of the electrode, \( k \) the rate constant, \( C_o \) and \( C_r \) are the concentrations of oxidized and reduced elements respectively, at the surface of the electrode, \( E^0 \) the formal standard potential and \( \alpha \) is the transfer coefficient.

Hence, \( i_{ac} \) is the current that flows from the anode to the cathode and \( i_{ca} \) the current that flows from the cathode to the anode.

2.1.5 Ionic mass transfer

Ionic mass transfer can occur by convection, electrical migration and diffusion.

2.1.5.1 Convection

This phenomenon is related to the ion movement under the effect of a temperature gradient or mechanical agitation [6].

2.1.5.2 Electrical migration

The electrical field established between the electrodes has an important part of the ions transfer through electric forces. Therefore, lithium ions acquire acceleration which means they start moving towards the anode or cathode, depending on the process that is occurring (charge or discharge of the cell) [6].

2.1.5.3 Diffusion

It is typically the dominant process in batteries where ions move under the effect of a concentration gradient, whose expression is given by Fick’s first law [6] (eq. 2.14):
\[ J(x) = -D \frac{\partial C(x)}{\partial x} \] (2.14)

where \( J \) is the diffusion flux, \( D \) the diffusion coefficient and \( C \) the substance’s concentration.

### 2.1.6 Electrical double-layer

When an electrode is immersed in an electrolyte, the electric charge on it attracts ions of opposite charge and orients the solvent dipoles, which creates a layer of charge in the metal and a layer of charge in the electrolyte. This charge separation establishes the so called electrical double layer, represented in Fig. 2.2 [16].

![Double-layer capacitance illustration](image)

**Figure 2.2** - Double-layer capacitance illustration (taken from [16])

This phenomenon appears during the battery cell’s first charge and remains until it is operable. It has an important role on the impedance analysis done later in this work.

### 2.1.7 Electrolyte

The electrolyte is a substance that ionizes when dissolved in a solvent. It is, thus, the ionic conductor that allows the transfer of lithium ions between the electrodes. Common solvents are ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), methyl ethyl carbonate (EMC),
or even a combination between them, being LiPF$_6$ (lithium hexafluorophosphate) a much used organic electrolyte in Li-ion batteries [11].

Assuming a battery constituted cell by a compound mentioned before, when mixed with LiPF$_6$ dissolves according to equation (2.15).

$$LiPF_6 \rightarrow Li^+ + PF_6^- \quad (2.15)$$

This means, Li$^+$ and PF$_6^-$ will be the positive and negative ions, respectively, referred previously in sections *Operation of a battery cell – Charge and Discharge and Electrical double-layer*.

### 2.2 LiFePO$_4$ batteries vs. LiCoO$_2$ batteries

The LiCoO$_2$ battery cells are by far much more used in electrical traction vehicles than the LiFePO$_4$ ones, since the latter appeared later. However, that is changing mostly because LiFePO$_4$ batteries offer a major advantage: higher thermal stability and, consequently, lower risk of fire/explosion when compared to LiCoO$_2$ batteries. Another advantage is the cheaper cost of iron, comparing to cobalt, since iron is abundant in the earth crust. In addition, LiFePO$_4$ cells are environmentally friendly, unlike LiCoO$_2$ ones because cobalt is very toxic.

When it comes to characteristics such as voltage [14], cathode’s specific capacity [14] cell’s specific energy and cell’s specific capacity, table below resumes those specifications for both materials. Note that these are often only theoretical values. Practical ones tend to be lower.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>Cell’s Voltage [V]</th>
<th>Cathode’s specific capacity [mAh/g]</th>
<th>Cell’s specific capacity [mAh/g]</th>
<th>Cell’s specific Energy [Wh/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>3.9</td>
<td>274</td>
<td>158</td>
<td>616.2</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>3.5</td>
<td>169</td>
<td>116</td>
<td>406</td>
</tr>
</tbody>
</table>

Considering the negative electrode is the same (LiC$_6$) and has a specific capacity of 2.69 g/(Ah) [5], cell’s specific capacity and specific energy for both electrodes were obtained as listed below. Hence, for LiCoO$_2$ (equations 2.16 to 2.18),

$$Li_xC_6 + Li_{1-x}CoO_2 \rightarrow LiCoO_2 + C_6 \quad (2.16)$$

Specific capacity: $2.69 \text{ g.Ah}^{-1} + (274 \text{ mAh.g}^{-1})^{-1} = 6.34 \text{ g.Ah}^{-1} = 158 \text{ mAh.g}^{-1} \quad (2.17)$

Specific energy: $3.9 \text{ V} \times 0.158 \text{ Ah.g}^{-1} = 616.2 \text{ Wh.kg}^{-1} \quad (2.18)$
and for LiFePO$_4$ (equations 2.19 to 2.21),

$$\text{Li}_x\text{C}_6 + \text{Li}_{1-x}\text{FePO}_4 \rightarrow \text{LiFePO}_4 + \text{C}_6$$  \hspace{1cm} (2.19)

Specific capacity: $2.69 \text{ g. Ah}^{-1} + (169 \text{ mAh. g}^{-1})^{-1} = 8.61 \text{ g. Ah}^{-1} = 116 \text{ mAh. g}^{-1}$  \hspace{1cm} (2.20)

Specific energy: $3.5 \text{ V} \times 0.116 \text{ Ah. g}^{-1} = 406 \text{ Wh. g}^{-1}$  \hspace{1cm} (2.21)

2.2.1 Thermal Stability

LiFePO$_4$ cathode material stability comes from its decomposition reaction when exposed to high temperatures. For temperatures up to 350°C, LiFePO$_4$ produces an endothermic reaction (absorption of heat from its surroundings) (Fig. 2.3) and almost no weight is lost due to release oxygen (Fig. 2.4) [3]. Therefore, there is low risk of fire. On the other hand, in LiCoO$_2$’s decomposition reaction when exposed to high temperatures [2] (shown in equation (2.22)),

$$\text{Li}_x\text{CoO}_2 \rightarrow x\text{LiCoO}_2 + \frac{(1-x)}{3}\text{Co}_3\text{O}_4 + \frac{(1-x)}{3}\text{O}_2$$  \hspace{1cm} (2.22)

there’s oxygen released, which makes this compound unsafe for temperatures above 200°C, since the reaction starts to release heat as well (exothermic reaction) (Fig. 2.3) [3].

![DSC/mW/mg](image)

**Figure 2.3 -** Exothermic reaction evolution with temperature obtained through differential scanning calorimetry (DSC) (taken from [3])
That is so because of the strong P-O bond. The necessary energy to break this link is approximately 62% higher than the energy needed to disrupt the Co-O bond [4]. Therefore, there is less chance of LiFePO$_4$ batteries to release oxygen than LiCoO$_2$ for the same temperature, which make the first ones much safer.

LiFePO$_4$’s batteries are thus extremely stable in overcharge and short circuit conditions, unlike LiCoO$_2$’s batteries.

### 2.3 Electrochemical Impedance Spectroscopy (EIS)

Impedance analysis is a powerful tool to determine the mechanism involved in an electrochemical reaction and the values of the kinetic parameters of this mechanism.

The EIS is a process in which a small amplitude AC signal (~10 mV) on top of the DC polarization potential is imposed to the battery cell’s terminals to determine the system’s response, in this case to define both real and imaginary parts of the cell’s impedance. These measurements are carried out at different frequencies, creating a Nyquist curve.

The Nyquist curve obtained helps to establish an equivalent electric circuit of the battery, representing its main dynamic characteristics. This will have a special importance in the study of degradation mechanisms in the cell that will be analyzed and explained later on, since the impedance varies with both time (Fig. 2.5) and temperature (Fig. 2.6), as exemplified in figures below.
Figure 2.5 - Example of impedance evolution with time (Nyquist diagram). (Data obtained by VITO and curves drawn with EC-lab V10.23 with 7 points per decade and frequencies ranging from 0.05 Hz to 10 kHz)

Figure 2.6 - Example of impedance evolution with temperature (Nyquist diagram). (Data obtained by VITO and curves drawn with EC-lab V10.23 with 7 points per decade and frequencies ranging from 0.05 Hz to 10 kHz)

Figure 2.7 is a Nyquist curve obtained for a LiFePO₄ cell at 25°C, a state of charge (SOC) of 50%, with 7 points per decade and frequencies ranging from 0.05 Hz to 10 kHz. Knowing the frequency increases from right to left through the blue curve, three separate sections can be distinguished: at high frequencies (1 kHz < f < 10 kHz), the battery has an inductive behavior (note that the vertical axis is inverted); for frequencies between 1 kHz and 0.5 Hz, both the charge transfer and the electrical double layer phenomenon are shaped close to two semi-circumferences; for lower frequencies (0.05 Hz < f < 0.5 Hz), the diffusion phenomenon is the most prominent and is expressed as a 45° slope [6].
Figure 2.7 - Example of a Nyquist curve for the LiFePO4 cell (Data obtained by VITO and curve drawn with EC-lab V10.23)

Nyquist curves will have a special importance in the study of their degradation mechanisms, which will be analyzed and explained later on.
3 LiFePO4 battery

3.1 Internal impedance: an electrical lumped parameter circuit representation

3.1.1 First approach: the Randles’ Electric Circuit
The most usual representation of LiFePO4 cell impedance is the Randles’ circuit represented in figure 3.1 [20],

![Figure 3.1 - Randles’ circuit](image)

where \( R_e \) represents the ionic and electronic conductivity of both the electrolyte and electrodes/current collectors, respectively; \( R_{ch} \) the charge transfer resistance of both electrodes, which is related to the electrochemical reaction at the electrode–electrolyte interface; \( C_w \) denotes the double layer capacitance in the electrodes; and \( Z_w \) is the so called Warburg impedance related to the lithium ion diffusion in both electrodes (eq. 3.1):

\[
Z_w(j\omega) = \frac{A_x}{(j\omega)^{1/2}}
\]

(3.1)

with \( A_x \) being the Warburg coefficient. An example of the impedance spectrum of this circuit is represented in next figure [17]. The diameter of the semicircle corresponds to the charge transfer resistance and the sloping line in the very low frequency region is attributed to the Warburg impedance [12].
3.1.1.1 Warburg impedance

The Warburg impedance referred in the previous section is drawn as a box (Fig. 3.1) and is theoretically defined as a 45° slope in the Nyquist plot.

In the framework of a semi-infinite diffusion, this impedance is theoretically expressed as a non-integer function (eq. 3.2) [13]

\[ Z_W(j\omega) = \frac{A}{(j\omega)^{1/2}} = \sigma \omega^{-1/2}(1 - j) \]  

(3.2)

where \( \sigma \) is a parameter that depends on the electrochemical phenomenon. This expression can be mathematically modified to another non-integer transfer function (eq. 3.3) [14],

\[ Z_W(s) = \frac{(1 + \tau_2 s)^{n_2}}{\left(\tau_1 s\right)^{n_1}} \]  

(3.3)

in which \( \tau_1, \tau_2 \) are time constants and \( n_1, n_2 \) are non-integer values to be determined.

Such expression gives good performances for the representation of the battery’s dynamic behavior. However this model has two drawbacks [13]:

- On one hand, the temporal expression of non-integer transfer function requires the knowledge of injected currents from the initial time up to the final one. This feature is due to the recursivity of diffusion phenomena and, forbid as a consequence, the use of this model in real time applications.
- On the other hand, such a pure mathematical model gives a good representation of dynamic behavior but misses energetic aspects. Consequently, it does not make possible the evaluation of energetic losses inside the battery. In order to overcome this lack, a research
[13] was lead to an equivalent electric scheme of Warburg impedance, the resistive component of which could be used for the estimation of energetic losses.

The method consists in developing an analytical model of Warburg impedance in function series, and identifying this development with an equivalent composed of capacities and resistances.

Warburg impedance $Z_w$ can be mathematically represented as a hyperbolic tangent frequency function as in equation (3.4), where $k_1$ and $k_2$ are constants to be estimated. [13],

$$Z_w(s) = \frac{k_2}{\sqrt{s}} \tanh\left(\frac{k_1}{k_2} \sqrt{s}\right)$$

(3.4)

The hyperbolic tangent is developed, thanks to Mittag-Leffler’s theorem into RC parallel circuits in series [13] (eq. 3.5),

$$Z_w(s) = \sum_{n=1}^{\infty} \frac{1}{C_n s + \frac{1}{R_n}}$$

(3.5)

With $R_n$ and $C_n$ expressed as (eq. 3.6):

$$R_n = \frac{8k_1}{(2n - 1)^2 \pi^2} \quad C_n = \frac{k_1}{2k_2^2}$$

(3.6)

Hence, the optimal number of $n$ RC parallel circuits would be infinite. Since that is not possible, a finite number has to be chosen in order to achieve a good approximation of the battery’s diffusion model to the experimental impedance profile provided by EIS experiments. At first, it was assumed an approximation of diffusion phenomenon using only one RC circuit, as shown in figure 3.3.

![Figure 3.3 - First approach with one RC circuit](image)

However, figure 3.4 shows that this electric circuit was not capable to represent all significant dynamics of the electrochemical phenomena for the LiFePO$_4$ battery tested, since the inductive behavior is inexistent, the charge transfer and double layer capacitance phenomena are poorly approximated by one semicircle and the diffusion slope region is misrepresented.
Figure 3.4 - Difference between the Nyquist diagram of the first approach circuit (red dots) and the experimental data (blue line). (Experimental data obtained by VITO and curve drawn with EC-lab V10.23)

3.1.2 Second approach
The next step was to attribute the previous electric circuit to represent each electrode, thus trying to solve the problem of the number of semicircles. Hence, the new cell’s electric circuit is shown next in which, now, \( C_{dl}, R_{ch}, R_w \) and \( C_w \) have the same meaning but only for one electrode. \( R_e \) is the only parameter still representing exactly the same Joule losses phenomena: the ionic plus the electronic resistances of both the electrolyte and electrodes/current collectors.

Figure 3.5 - Second approach – lumped parameter impedance circuit

Although the previously problem was practically solved, there is also the imaginary part running along both positive and negative portions of its axis. The negative imaginary part means the circuit must also have an inductive part. Additionally, it was visible that only one RC circuit in each electrode could not fully represent the diffusion phenomenon. Figure 3.6 shows the misrepresentation of the second approach.
3.1.3 Third approach

Considering the problems mentioned before, it was required to add an inductive component and to increase the number of RC circuits in each electrode, in which it was seen that three of them showed good fitting results. The final electric circuit is represented in figure 3.7.

In the circuit, \( L_1 \) and \( L_2 \) represent the inductive component of the cables connected to the cell, the current collectors and electrodes as well. Terms \( R_9 \) and \( R_{10} \) represent the electrical resistance in the cables and the connection between electrodes and current collectors. Doing a similar reasoning with the electrical line’s lumped circuit, \( C_5, \ C_6, \ R_{11}, \) and \( R_{12} \) were added. Element \( R_3 \) represents the electrolyte ionic resistance, \( R_5 \) and \( R_4 \) the charge transfer resistance, and \( C_1 \) and \( C_2 \) the double layer capacitance that is formed between each electrode and the electrolyte. Both RC blocks, constituted by \( R_{6-7}, \ R_{13-16}, \ C_{3-4} \) and \( C_{7-10} \), are associated with the lithium ions diffusion phenomena in the electrodes.
In figure 3.8, it is visible that both the experimental data and the final circuit curves are almost coincident, therefore the model proposed correctly represents the battery's impedance (values of each parameter for this case in attachment 1).

![Difference between the Nyquist diagram of the final approach circuit (red dots) and the experimental data (blue line). (Experimental data obtained by VITO and curve drawn with EC-lab V10.23)](image)

**3.2 Degradation mechanisms**

The degradation of a cell is a very important aspect to study. With increasing cycling or storage time, the maximum capacity and power fades to the point at which they are not acceptable anymore. The degradation during cycling occurs, however, much faster than storage under the same conditions (state of charge and temperature).

The degradation of a cell is, thus, related to its impedance. Nor only it varies with the number of charge/discharge cycles, but as well with the storage time. Therefore, the analysis made in this thesis will focus on the changes in the impedance.

Various studies were conducted about the aging of a cell, especially about cycling aging. It is so, because of the application of these batteries in systems like an electrical vehicle, in which it has multiple charge/discharge cycles in a small period of time. However, there are several other applications in which the cell, or battery pack, is only needed to operate during a short period of time, such as a battery backup system for a network failure.

The degradation of a battery cell depends on its type of use. That's why it is necessary to differentiate both types of aging mechanisms.
3.2.1 Degradation due to cycling – cycling aging

The main mechanisms of cycle degradation are the loss of lithium ions and electrode material. According to [7], in this type of ageing, the impedance increase is mainly due to deposit of electrolyte decomposition products in the pores of the electrode and loss of electrode material. The loss is seemed to be linked to electronic isolation of electrode material due to particle cracking. Another study [8], states that the increase of ohmic resistance with cycling comes mainly from the increase in electrolyte resistance, resulting from the lithium loss within the electrolyte due to lithium consuming in the Solid Electrolyte Interphase (SEI) layer, represented in the next figure [18].

![Figure 3.9 - Representative illustration of SEI - charging process (taken from [18])](image)

The reaction of the anode with the electrolyte solution in the formation stage results in the creation of species such as ROCO₂Li and CO₂OLi, on the anode surface. The layer formed by these species is the SEI. At higher battery potentials, during intercalation of lithium ions into the anode lattice structure, the graphite anode oxidizes. At this potential, electrolyte co-solvents, such as EC, which is highly reactive, react with the lithium ions and the reaction products quickly precipitate and grow on the anode surface. As the layer grows, lithium is consumed in the reaction and the increased thickness inhibits Li⁺ transfer [9].

3.2.2 Degradation due to storage – calendar aging

Li-ion cells do not only degrade as a result of usage, but also when the cells are barely used and stored. In this case, the loss of cyclable lithium is the main source of aging [10]. The active anode material is still exposed to the electrolyte through the porous SEI layer, and side reactions will enhance this SEI layer. However, the damage is much less than the previous case.
3.3 Results and discussion

First, a special note here is required, since all the experimental data was acquired by VITO, the Flemish institute for technological research, located in Belgium.

The data provided contained the impedance characteristic curve in Nyquist representation, obtained for a time-lapse of 10 months. In each month, a different curve was acquired for 6 temperatures (-10°C, 0°C, 10°C, 25°C, 40°C, 60°C) and 3 different states of charge (SOC). Some tests were incomplete and, therefore, its corresponding data was useless. Every month, each cell (or pack, this information was not provided, so it was assumed it was a cell) was made 4 charge/discharge cycles, which means that the only possible study was the degradation due to storage.

EC-lab V10.23 software was used to process the data acquired by VITO. The impedance lumped parameter model was fitted to the curve given by the experimental data and each element was attributed a value. The process is explained next.

- First thing to do is to display the data that is supposed to be fitted to the model, as shown in the figure below;

![Figure 3.10 - Display of the data](image)

- Then, right click on the mouse’s button in order to choose the Z fit menu, as shown in the figure bellow;
Figure 3.11 - Select option Z fit to open the fitting menu

- After the Z fit window appear, select the equivalent circuit desired and select the minimize button to start the fitting process, as shown in the figure bellow:

Figure 3.12 - Z fit menu

- Stop the fitting process when the result achieves a satisfactory error, as shown in the figure bellow.
Figure 3.13 - Final result

3.3.1 Preliminary conclusions

Although the circuit’s elements were described individually, i.e. had a physical phenomenon related to each one of them, the results obtained weren’t conclusive about some individual parameters. However, some combinations of elements showed a trend. That’s because the software fits the model to the curve blindly, not knowing any physical phenomenon related to the parameters. For example, with two resistances in series, the software could attribute any value for both of them, as long as the sum would fit the curve. It cannot distinguish both phenomena and attribute a correct value to each resistance.

Other important thing to mention is that, for a given month and temperature, although the impedance was measured for 3 different SOC’s it did not show much difference in most cases. Therefore, the conclusions taken were only about temperature and time storage.

The majority of the results covered a large range of values. Thus, it was chosen a logarithmic scale in the y-axis and the data displayed are the order of magnitude and not the value itself (figures presented in attachment 2).

Taking that into consideration, the conclusions taken were:

- $L_1 + L_2$ – the magnitude of this values appeared to be an approximately constant value of order slightly below $10^{-7}$ H, independently of time and temperature;
- $R_9 + R_{10}$ – the magnitude of this values appeared to be an approximately constant value of order $10^{-2.5}$ Ω, independently of time and temperature;
- $C_6 + C_5$ – the magnitude of this values was found approximately between the orders of $10^0$ F and $10^3$ F, independently of time and temperature;
- $R_{11} + R_{12}$ – the magnitude of this values was found approximately between the orders of $10^{-2}$ and $10^4 \, \Omega$, independently of time and temperature;
- $R_2, R_3$ and $R_4$ – the magnitude of this values appeared to be between the orders of $10^{-8} \, \Omega$ and $10^{-3} \, \Omega$, independently of time and temperature;
- $R_6 + R_{13} + R_{15}$ – the magnitude of this values was found approximately between the orders of $10^{-3.5} \, \Omega$ and $10^{-2} \, \Omega$, independently of time and temperature;
- $R_7 + R_{14} + R_{16}$ – the magnitude of this values was found approximately between the orders of $10^{-3} \, \Omega$ and $10^{-2} \, \Omega$, independently of time and temperature;
- $C_3 + C_7 + C_9$ – the magnitude of this values was found approximately between the orders of $10^0 \, F$ and $10^3 \, F$, independently of time and temperature;
- $C_4 + C_8 + C_{10}$ – the magnitude of this values was found approximately between the orders of $10^1 \, F$ and $10^3 \, F$, independently of time and temperature;
- $C_1$ – the magnitude of this values appeared to be between the orders of $10^{-2} \, F$ and $10^{-3} \, F$, independently of time and temperature;
- $C_2$ – the magnitude of this values appeared to be between the orders of $10^{-2} \, F$ and $10^{3} \, F$, independently of time and temperature;

Taking into account the conclusions mention before, it is only possible to conclude something meaningful about $L_1 + L_2$ and $R_9 + R_{10}$. The magnitude of both combinations remained approximately unchanged, independently of both time and temperature.

All other parameters showed too many variations in their magnitudes, disabling any satisfactory conclusion about them.

Nevertheless, some details might still be interesting to analyze. For instance, the fact that $R_2, R_3$ and $R_4$ values range between the same magnitude orders, which means the charge transfer and electrolyte resistances in the model can be approximately equal. Once this values, in particular the ones referred to $R_3$, remained approximately constant, the degradation phenomenon referred in section (3.2) was not visible.

Both diffusion parameters of both electrodes ($R_6 + R_{13} + R_{15}$ and $R_7 + R_{14} + R_{16}$; $C_3 + C_7 + C_9$ and $C_4 + C_8 + C_{10}$) range approximately between the same magnitude order, which might indicate the diffusion phenomenon might be almost equal in both electrodes.

Since $C_1$ and $C_2$ values range between the same orders of magnitude, the double-capacitance layer might be equal in both electrodes.
4 Thermal Study

It’s important to understand how the temperature of a battery cell changes, especially when it is operating, since it can give extra clues about its ageing processes. Thus, a lumped parameter thermal model was developed in this work, in order to evaluate the cell behavior when charging or discharging.

There are three types of heat transfer processes:

- conduction, which refers to the heat transfer across a stationary medium (a solid or fluid) when in presence of a temperature gradient;
- convection, which refers to the heat transfer that occurs between a surface and a moving fluid when they are at different temperatures;
- radiation, which refers to the energy emitted through a surface of finite temperature, in the form of electromagnetic waves.

The next section mentions the theoretical principles for one-dimensional, steady-state conduction only. Convection and radiation phenomena were neglected and will be later justified.

4.1 Theoretical principles

Fourier’s law states that the heat flux \( q'' \) [W/m²] transferred through a material in the \( x \) direction is described by the following equation [21]:

\[
q'' = -k \nabla T = -k \frac{dT}{dx}
\]  

where \( k \) is the thermal conductivity [W/(m.K)] and \( T \) is the temperature [K]. The negative sign refers the fact that heat transfer occurs from the higher to the lower temperatures.

The conservation of energy formulation is given by equation (4.2) [21]:

\[
-\nabla q'' + q' = \rho c \frac{dT}{dt}
\]  

where \( q' \) is the rate at which energy is generated per unit of volume in the medium [W/m³], \( \rho \) is the material’s density [kg/m³] and \( c \) the material’s specific heat [J/(kg.K)].

Using Fourier’s law in the previous equation, the heat equation is obtained (eq. 4.3) [21]:

\[
\rho c \frac{dT}{dt} = k \frac{d^2T}{dx^2} + q'
\]  

4.1.1 The Plane Wall geometry - without internal heat generation

The geometry referred in this section is represented in the next figure, with heat transfer through it.
Figure 4.1 - Plane wall geometry with heat transfer through it

\( T_{\omega,1} \) and \( T_{s,1} \) refer to the temperature in the exterior and on the surface of the wall, both on the left side, respectively. \( T_{\omega,2} \) and \( T_{s,2} \) have the same meaning, but they both refer to the right side.

In this case, the appropriate form of the heat equation is (eq. 4.4) [21]:

\[
k \frac{d^2T}{dx^2} = 0
\] (4.4)

If the wall's thermal conductivity is assumed to be constant, the general solution is (eq. 4.5) [21]

\[
T(x) = Ax + B
\] (4.5)

To obtain both constants of integration, \( A \) and \( B \), boundary conditions must be considered. Therefore, the following were chosen (eq. 4.6) [21]:

\[
T(0) = T_{s,1} \quad \text{and} \quad T(L) = T_{s,2}
\] (4.6)

Hence (eq. 4.7),

\[
T(x) = (T_{s,2} - T_{s,1}) \frac{x}{L} + T_{s,1}
\] (4.7)

Using Fourier's law, it's possible to determine the heat flux (eq. 4.8) [21],

\[
q''_o = -k \frac{dT}{dx} = \frac{k}{L} (T_{s,1} - T_{s,2})
\] (4.8)
Finally, the conduction heat transfer rate [W] is (eq. 4.9) [21]:

\[ q = Aq''_x = -kA \frac{dT}{dx} = \frac{kA}{L} (T_{s,1} - T_{s,2}) \]  

(4.9)

It is important to refer at this point the analogy between the heat diffusion and electrical charge. Likewise the electrical resistance, which is associated with the conduction of electrons, there is a thermal resistance related to the conduction of heat. Without internal heat generation, it is defined as (eq. 4.10) [21]:

\[ R^{th} = \frac{(T_{s,1} - T_{s,2})}{q} = \frac{L}{kA} \]  

(4.10)

### 4.1.2 The Plane Wall geometry - with internal heat generation

In the case where the material itself produces heat, the heat equation is written as (eq. 4.11) [21]

\[ k \frac{d^2T}{dx^2} + q'_i = 0 \]  

(4.11)

The general solution is (eq. 4.12) [21]:

\[ T(x) = -\frac{q'_i}{2k} x^2 + Ax + B \]  

(4.12)

where \( A \) and \( B \) are constants of integration. Applying the following boundary conditions (eq. 4.13) [21],

\[ T(-L) = T_{s,1} \quad \text{and} \quad T(L) = T_{s,2} \]  

(4.13)

It follows that (eq. 4.14),

\[ T(x) = \frac{q_i L^2}{2k} \left( 1 - \frac{x^2}{L^2} \right) + \frac{T_{s,2} - T_{s,1}}{2} + \frac{T_{s,1} + T_{s,2}}{2} \]  

(4.14)

Knowing that (eq. 4.15),

\[ T_{med} = \frac{1}{2L} \int_{-L}^{L} T(x) \, dx = \frac{T_{s,2} + T_{s,1}}{2} + \frac{q_i}{6} R^{th} \]  

(4.15)

Being \( q_i \) the heat produced by a material such as an electrode (Joule losses). Applying Fourier’s law to equation (4.14), comes equation (4.16):

\[ q''_x(x) = -k \left[ -2 \frac{q_i}{4ALk} x + \frac{T_{s,2} - T_{s,1}}{2L} \right] \]  

(4.16)

Hence (eq. 4.17),
The heat transfer rate in both ends of the wall is (eq. 4.18):

\[
\begin{align*}
q(-L) &= -\frac{q_i}{2} - \frac{T_{s,2} - T_{s,3}}{2R_{th}} \\
q(L) &= \frac{q_i}{2} - \frac{T_{s,2} - T_{s,1}}{2R_{th}}
\end{align*}
\] (4.18)

Equations (4.15) and (4.18) suggest the following lumped parameter’s circuit in the next figure:

4.2 LiFePO\textsubscript{4} cell

Firstly, it’s important to describe the materials which constitute the cell. That information was taken from [19]. Thus, it is shown in the next figure a simplified representation of a cell’s cross section.

![Figure 4.3 - Simplified cross section of the LiFePO4 cell](image)
The plastic considered was the high density polyethylene [HDPE], the anode and cathode are made of graphite and LiFePO$_4$, respectively, the separator is polypropylene (PP) and the electrolyte constitutes are mentioned in section (2.1.7). Their thermal and physical properties are expressed in Table II and the information about the geometry of the cell is in Table III.

Note that, since the thermal losses in the electrolyte are very low, when compared with the other components in the cell, its thermal and physical properties were neglected [19].

### Table II - Thermal and physical properties of each material of the cell (taken from [19])

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>950</td>
<td>1886</td>
<td>0.42</td>
</tr>
<tr>
<td>Graphite</td>
<td>1347.33</td>
<td>1437.4</td>
<td>1.04</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>2328.5</td>
<td>1269.21</td>
<td>1.58</td>
</tr>
<tr>
<td>PP</td>
<td>1008.98</td>
<td>1978.16</td>
<td>0.3344</td>
</tr>
</tbody>
</table>

### Table III - Information about the geometry of the battery cell (taken from [19])

<table>
<thead>
<tr>
<th></th>
<th>Size of the cell (L x W x H)</th>
<th>Size of the cell without the plastic shell (L x W x H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of the HPDE case</td>
<td>4 mm</td>
<td>115 mm x 61 mm x 203 mm</td>
</tr>
<tr>
<td>Thickness of the PP separator</td>
<td>0.036 mm</td>
<td>100 mm x 49 mm x 165 mm</td>
</tr>
<tr>
<td>Thickness of the anode</td>
<td>0.067 mm</td>
<td></td>
</tr>
<tr>
<td>Thickness of the cathode</td>
<td>0.079 mm</td>
<td></td>
</tr>
</tbody>
</table>

As mentioned before, the convection phenomenon was neglected due to the lack of mobility of fluids inside the cell. The air inside the cell is, therefore, considered as a perfect insulator. Furthermore, the heat dissipation through the air surrounding the cell was also neglected since, that way, the worst case scenario was considered.

Radiation was ignored as well due to the opaque structure of the battery cell.

### 4.2.1 Lumped parameter thermal model

In a lumped parameter thermal circuit, the procedure is the same as an electrical circuit. The following table presents the analogy between electrical and thermal properties.
### Table IV - Analogy between electrical and thermal properties

<table>
<thead>
<tr>
<th>Thermal Property</th>
<th>Unity</th>
<th>Electrical Property</th>
<th>Unity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Kelvin</td>
<td>Voltage</td>
<td>Volt</td>
</tr>
<tr>
<td>Heat transfer rate</td>
<td>Watt</td>
<td>Current</td>
<td>Ampère</td>
</tr>
<tr>
<td>Thermal Resistance</td>
<td>Kelvin/Watt</td>
<td>Electrical Resistance</td>
<td>Volt/Ampère</td>
</tr>
<tr>
<td>Thermal Capacitance</td>
<td>Joule/Kelvin</td>
<td>Electrical Capacitance</td>
<td>Coulomb/Volt</td>
</tr>
</tbody>
</table>

As it was discussed in section 4.1.2, there are materials that produce heat. It’s the case of both electrodes and the separator. The losses in the electrolyte are insignificant, thus not important to consider [19]. Hence, the lumped circuit of those elements is remembered again.

![Lumped parameter circuit representation of a material with internal heat generation](image)

**Figure 4.4** - Lumped parameter circuit representation of a material with internal heat generation

Being the grey area the material in question (an electrode or the separator), the current source $q_i$ symbolizes the heat generated by the substance, in this case Joule losses due to battery’s electrical current ($q_i = R_e I^2$) and $R_e$ is the electrical resistance of the material.

The rest of the elements of the cell do not produce heat. Hence, the circuit is simply the thermal resistance, represented below.
Connecting every material and considering the cell is not settled on the floor, the final 2D circuit can be seen below.

Each DC voltage source represents the temperature imposed from the environment to the battery cell. $R1$ represents the thermal resistance, of the left side of the cell plus half of the top. $R2$ has the same meaning but for the right side. Although the air was considered a perfect insulator, the top part still is important to consider since it affects the heat transfer rate.
4.2.2 Simulation – Results and discussion

With the help of the Matlab software, the thermal model was tested. It was considered a LiFePO₄ battery cell inside a climate chamber with constant temperature and discharging at a constant current as well. In the next figure is the thermal network designed in the block diagram environment Simulink, which is equal to the one in figure 4.6.

![Block diagram of the thermal model](image)

Figure 4.7 - Block diagram of the thermal model

According to [19], when the cell is discharging at a constant current of 14 A with a climate chamber temperature of 30.2°C, the maximum surface temperature measured during the experiment was 32.1°C. The results obtained for the temperatures of the anode, cathode and separator in the same conditions are shown in the next table, as well as the error committed when compared with [19].

| Table V - Temperature achieved in each element by the model with a current of 14 A and a room temperature of 30.2 °C and corresponding error compared with [9] |
|---|---|---|
| Temperature [°C] | Anode | Cathode | Separator |
| Error | 30.44 | 30.42 | 30.58 |
| Error | 5.17 % | 5.23 % | 4.74 % |

Once again, according to [19], when the cell is discharging at a constant current of 70 A with a climate chamber temperature of 30.2°C, the maximum surface temperature measured during the experiment was 39.8°C. The results obtained for the temperatures of the anode, cathode and in the same conditions are shown in the next table, as well as the error committed when compared with [19].
Table VI - Temperature achieved in each element by the model with a current of 70 A and a room temperature of 30.2 ºC and corresponding error compared with [9]

<table>
<thead>
<tr>
<th>Temperature [ºC]</th>
<th>Anode</th>
<th>Cathode</th>
<th>Separator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Error</td>
<td>9.02 %</td>
<td>10.30 %</td>
<td>0.53 %</td>
</tr>
</tbody>
</table>

Since the temperature of an element inside the cell is not too different from its surface’s temperature and considering both conclusions taken previously for discharging currents of 14 A and 70 A with a room temperature of 30.2ºC, it is possible to conclude that the model developed in this work is accurate.

4.2.3 Experimental analysis

Besides the simulation, an experimental analysis was conducted on a pack of 8 LiFePO₄ cells connected in series, but different from the ones in [19] that were considered to create the model. Although these batteries had a different size structure (length (L) of 182 mm, width (W) of 56 mm and height (H) of 275 mm), it would still be interesting to test the model developed with these different cells since they too have a prismatic geometry and it was assumed that its interior does not vary much from cell to cell. Figure 4.8 displays the system used to do the experimental analysis.

The pack of cells was connected to a load resistor in order to obtain a constant discharging current. The battery management system (BMS) was used as a protection device to avoid that each cell would reach a deep level of voltage during a test. Two different tests were conducted: the first one with a current of 8.043 A and room temperature of 23.1 ºC. The temperature measured at one terminal of the
cell pack was 24.7 °C. The temperatures obtained through the model and their respective errors are resumed in the next table.

Table VII - Temperatures achieved by each element through the model, for a room temperature of 23.1 °C and a discharging current of 8.043 A compared with the experimental analysis

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>Cathode</th>
<th>Separator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [°C]</td>
<td>23.15</td>
<td>23.15</td>
<td>23.2</td>
</tr>
<tr>
<td>Error</td>
<td>6.19 %</td>
<td>6.19 %</td>
<td>6.07 %</td>
</tr>
</tbody>
</table>

The second test was conducted with a room temperature of 22.4 °C and a discharging current of 16.10 A. The temperature measured at one terminal of the cell pack was 26.2 °C. The temperatures obtained through the model and their respective errors are resumed in the next table.

Table VIII - Temperatures achieved by each element through the model, for a room temperature of 22.4 °C and a discharging current of 16.10 A compared with the experimental analysis

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>Cathode</th>
<th>Separator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature [°C]</td>
<td>23.31</td>
<td>23.28</td>
<td>23.49</td>
</tr>
<tr>
<td>Error</td>
<td>11.03 %</td>
<td>11.15 %</td>
<td>10.34 %</td>
</tr>
</tbody>
</table>

Since the model itself has several limitations (for example, 2D design and neglecting the heat transfer through convection) it is possible to validate the model developed in this work.
5 Estimation algorithms

5.1 Introduction

The following chapter refers to the algorithms developed in order to online estimate the internal parameters of a LiFePO$_4$ cell, to possibly be integrated into a microcontroller. The estimation methods are based on the Nyquist curves, since the information contained in each one is related to a certain aging time and temperature. As so, both electrical and thermal parameters can be evaluated, after every parameter from the internal impedance equivalent circuit is determined.

Previously in this work, three different circuits were established with the purpose of accurately describe the cell’s internal impedance. Although the first two approaches did not provide a good fit, that was due to the data used which is associated to a specific cell. It does not mean that every LiFePO$_4$ cell has as a similar behavior. The first two approaches can, indeed, truthfully represent the internal parameters of other cells and actually are the most frequent scenarios (for example, [6],[22],[23]), since the majority of the Nyquist curves in literature exhibit a much smoother shape. That determined the fact that the two estimation algorithms developed in this work were based on the first two approaches.

5.1.1 First methodology

The first idea was to set a system of equations from the transfer function $Z(s)$ (eq. 5.1) of each circuit. For the first approach with only one RC circuit (figure 5.1),

\[
Z(s) = \frac{V(s)}{I(s)} = R_1 + \frac{R_2 + R_3 + sR_2R_3C_2}{s^2R_2R_3C_1C_2 + s(R_2C_2 + R_3C_1) + 1}, \quad s = j\omega \tag{5.1}
\]

Since this circuit has five elements, with the Nyquist curve obtained experimentally, it is possible to write the following set of equations:
Being $\omega_a$, $\omega_b$, $\omega_c$ the angular frequency related to a certain point on the Nyquist curve, $Zr_a$ and $Zi_b$, $b = 1,2$ the real and imaginary parts of the referred point, respectively. The fact that a complex equation provides two real ones means that only three points in the curve are enough to set a system of five real equations, being the unknowns the parameters which constitute the circuit. That's why there are three $Zr_a$ but only two $Zi_b$.

The next question is how to solve this set of equations. There are several numerical methods available in the literature. Nonetheless, it is required a good initialization of every unknown in order to get a good convergence of the method, which goes against the main purpose of this chapter. All parameters must be accurately and automatically estimated without previous knowledge of their values or even order of magnitude.

It is also possible to solve this system of equations by continuously substituting one equation into another in order to isolate each unknown variable and, thus, obtaining at the end one parameter depending only on known variables. The following example demonstrates the process, based on the system of equations (5.2):

Step 1: Substituting $R_1$ in $R_2, R_3, C_1, C_2$ (eq. 5.3)

$$\Rightarrow \begin{cases} R_2(R_2, R_3, C_1, C_2, \omega_1, Zi_1) \\ R_3(R_2, R_3, C_1, C_2, \omega_2, Zi_2) \\ C_1(R_2, R_3, C_1, C_2, \omega_3, Zi_3) \\ C_2(R_2, R_3, C_1, C_2, \omega_4, Zi_4) \end{cases}$$

Step 2: Substituting $R_2$ in $R_3$ (eq. 5.4)

$$\Rightarrow R_3(Zr_2, R_3, C_1, C_2, \omega_1, Zi_2)$$

Step 3: Substituting $R_3$ in $C_1$ (eq. 5.5)

$$\Rightarrow C_1(Zr_3, R_3, C_1, C_2, \omega_1)$$

Step 4: Substituting $C_1$ in $C_2$ (eq. 5.6)

$$\Rightarrow C_2(Zr_4, R_3, C_1, C_2, \omega_1)$$
Step 5: Substituting $R_3$ in $C_2$ (eq. 5.7)

$$ \Rightarrow C_2(Zr_3, \omega_3, R_2, \omega_2, Zr_2, Zi_1, Zr_1, \omega_1, C_1, Zi_2) $$ \hfill (5.7)

Step 6: Substituting $R_2$ in $C_2$ (eq. 5.8)

$$ \Rightarrow C_2(Zr_3, \omega_3, R_3, \omega_2, Zr_2, Zi_1, Zr_1, \omega_1, C_1, Zi_2) $$ \hfill (5.8)

Step 7: Substituting $R_3$ in $C_2$ (eq. 5.9)

$$ \Rightarrow C_2(Zr_3, \omega_3, \omega_2, Zr_2, Zi_1, Zr_1, \omega_1, C_1, Zi_2) $$ \hfill (5.9)

Step 8: Substituting $R_2$ in $C_1$ (eq. 5.10)

$$ \Rightarrow C_1(Zi_2, \omega_2, R_3, Zr_2, Zr_1, Zi_1, \omega_1, C_2) $$ \hfill (5.10)

Step 9: Substituting $R_3$ in $C_1$ (eq. 5.11)

$$ \Rightarrow C_1(Zi_2, \omega_2, Zr_2, Zr_1, Zi_1, \omega_1, C_2) $$ \hfill (5.11)

Step 10: Substituting $C_1$ in $C_2$ (eq. 5.12)

$$ \Rightarrow C_2(Zr_3, \omega_3, \omega_2, Zr_2, Zi_1, Zr_1, \omega_1, Zi_2) $$ \hfill (5.12)

From here, it is possible to determine $C_2$ since it only depends on known variables, which follows the evaluation of $C_1$, $R_3$, $R_2$ and $R_1$ by that order.

However, estimating every resistance and capacitance is not that simple. That are several parameters from the set of equations (5.2) whose solutions are a second order polynomial (in this case, every parameter except $R_1$) and it is not simply a negative/positive one. The correct solution depends on the other parameters' values as well as the points chosen from the Nyquist curve ($\omega_a, Zr_{a}, Zi_{b}$). Hence, when substituting a variable into another (starting in step 2), the next step becomes a pair of equations, the following becomes four and so on. At the final step, there will be multiple solutions for $C_2$ and consequently several solutions for the remaining parameters, which means that it is necessary to assess every single one of them and select the correct solution.

That is a very demanding process since, for a simple circuit with five elements, the number of possible solutions goes up to 1024 and the size of each equation is significantly big. A microcontroller has a limited processing capacity, which makes this methodology not the appropriate one.
5.1.2 Second methodology

The second idea was to think about the whole circuit has a combination of elementary ones, because every RC time constant is related to a different portion of the Nyquist curve and, hence, the circuit could be simplified depending on the range of frequencies it is being excited. For instance, in the circuit exhibited in figure 5.1, assuming that the pair $R_3C_2$ is associated with the low frequencies (from the lowest frequency displayed on the curve up to 0.5 Hz), the overall circuit can be shortened into the one shown in figure 5.2 for the highest frequencies interval (the $R_3C_2$ time constant can be neglected).

![Figure 5.2 - Shortened circuit, neglecting the $R_3C_2$ time constant](image)

The purpose of the reasoning made above is to simplify the approach and, consequently, estimate each parameter in an easier way than the one described in the previous section. For the case of the circuit in figure 5.2, for example, it lacks two elements being its transfer function simplified when comparing to the one in equation (5.1). Therefore, its solution is easily obtained when isolating each variable, which can improve the performance of a microcontroller when running the algorithm.

This is the methodology applied in this work, being each algorithm analyzed in next sections.

5.2 Randles circuit – estimation algorithm

This chapter explains into detailed the method developed to estimate the parameters in the circuit of figure 5.3.

![Figure 5.3 - Randles circuit and corresponding Nyquist curve (98 points) for a particular case ($R_1 = 1.967 \, m\Omega$, $R_2 = 1.066 \, m\Omega$, $R_3 = 14.793 \, m\Omega$, $C_1 = 36 \, F$ and $C_2 = 739.1 \, F$)](image)
With the corresponding transfer function $Z_1(s)$ (eq. 5.13),

$$Z_1(s) = R_1 + \frac{R_2 + R_3 + sR_2R_3C_2}{s^2R_2R_3C_1C_2 + s(R_3C_2 + R_2C_1) + 1} \quad (5.13)$$

First, it is important to understand the Nyquist curve created by a simple RC parallel in series with a resistor circuit (figure 5.4).

![Simplified Randles' circuit and corresponding Nyquist curve](image)

**Figure 5.4** - Simplified Randles’ circuit and corresponding Nyquist curve (98 points) for a particular case ($R_1 = 1.967 \text{ m}\Omega$, $R_2 = 1.066 \text{ m}\Omega$ and $C_1 = 36 \text{ F}$)

Being its transfer function (eq. 5.14):

$$Z_{R1R2C1}(s) = R_1 + \frac{R_2}{1 + sR_2C_1} \quad (5.14)$$

Each curvature in the Nyquist curve for the circuit in figure 5.3 is shaped by each RC circuit’s own semicircle, although there is an evident overlap of time constants along the overall curve (figure 5.5). That’s the reason why the global curve is not exactly coincident with the one created by the RC circuit related to the lower frequencies (it would be at even lower frequencies, if the overall curve was drawn from the null frequency).

![Complete Randles' circuit, its simplifications according to each time constant and corresponding Nyquist curves](image)

**Figure 5.5** - Complete Randles’ circuit, its simplifications according to each time constant and corresponding Nyquist curves (98 points) ($R_1 = 1.967 \text{ m}\Omega$, $R_2 = 1.066 \text{ m}\Omega$, $R_3 = 2.793 \text{ m}\Omega$, $C_1 = 36 \text{ F}$ and $C_2 = 739.1 \text{ F}$)
The strategy adapted was, as mentioned before, to separate the parameters in the global circuit and estimate them individually or in pairs.

### 5.2.1 $R_1$ estimation

Figure 5.3 shows that the global Nyquist curve tends to $R_1$ with increasing frequency. That is (eq. 5.15),

$$\lim_{s \to \infty} Z(s) = \lim_{s \to \infty} R_1 + \frac{R_2 + R_3 + sR_2R_3C_2}{s^2R_2R_3C_1C_2 + s(R_3C_2 + R_2C_1) + 1} = R_1$$

Hence, $R_1$ can be directly determined from the overall curve, being its approximated value obtained through the real part or absolute value of the highest frequency point.

### 5.2.2 $R_2$ and $C_1$ estimation

Next step is to determine $R_2$ and $C_1$. Since the Nyquist curves from the overall and $R_2C_1$ circuits are approximately equal for the highest frequencies (can be seen in figure 5.5), two equations can be established using a point in that region and solved in order to $R_2$ and $C_1$. Hence, for the $R_2C_1$ circuit (eqs. 5.16 and 5.17),

$$Z_{R_1R_2C_1}(s) = R_1 + \frac{R_2}{1 + sR_2C_1} = R_1 + \frac{R_2}{1 + \omega R_2^2C_1} - j\frac{\omega R_2^2C_1}{1 + \omega^2 R_2^2C_1} = Z_r + jZ_i$$

$$\begin{align*}
R_1 + \frac{R_2}{1 + \omega^2 R_2^2C_1} & = Z_r \\
-\frac{\omega R_2^2C_1}{1 + \omega^2 R_2^2C_1} & = Z_i
\end{align*}$$

$$\begin{align*}
R_2 & = -\frac{(R_1^2 - 2R_1Z_r + Z_i^2 + Z_r^2)}{R_1 - Z_r} \\
C_1 & = -\frac{R_1^2 - 2R_1Z_r + Z_i^2 + Z_r^2}{\omega(R_1^2 - 2R_1Z_r + Z_i^2 + Z_r^2)}
\end{align*}$$

Being $Z_r$ and $Z_i$ the real and imaginary parts of the chosen point, respectively, and $\omega$ its angular frequency. Ideally, this point would be the highest frequency one since the red curve tends to have the same shape as the blue one with increasing frequency (figure 5.5). However, that choice would make the computation of $R_2$ and $C_1$ impossible since $Z_r = R_1$ (remember eq. 5.15) and $Z_i = 0$ in that case. The second highest frequency point would be, therefore, the required point.

Nevertheless, upon acquirement of the Nyquist curve from the cell, it can display significant error. Thus, every point should be tested and the one that originates the smaller error between the real and estimated curves selected afterwards. Naturally, that error can only be determined once all parameters are estimated.
5.2.3 $R_3$ and $C_2$ estimation

At this point, the remaining parameters to be determined are $R_3$ and $C_2$. The final resistance is estimated with the help of a measurement that is not available in a Nyquist curve, but can be easily measured: the internal resistance $R_{DC}$. Taking into consideration the circuit in figure 5.3 (eq. 5.18),

$$\lim_{s \to 0} Z(s) = R_{DC} = R_1 + R_2 + R_3$$  \hspace{1cm} (5.18)

There are several techniques to do this measurement. An easy way this can be done is by connecting a load resistor $R_L$ to the cell, represented in the next figure.

![Diagram of battery cell with $R_{DC}$, $V_{OC}$, $R_L$, and $V_L$](image)

**Figure 5.6** - Measurement of $R_{DC}$ through a load resistor $R_L$ exemplification

Hence, the internal resistance is (eq. 5.19),

$$R_{DC} = \left(\frac{V_{OC}}{V_L} - 1\right) R_L$$ \hspace{1cm} (5.19)

Being $V_{OC}$ the open-circuit voltage, measured with a simple voltmeter, and $V_L$ the voltage across the load resistor.

Knowing at this point $R_{DC}$, $R_1$ and $R_2$ (eq. 5.20),

$$R_3 = R_{DC} - R_1 - R_2$$ \hspace{1cm} (5.20)

The last parameter, $C_2$, is easily obtained through the transfer function in equation (5.13) and any point in the global Nyquist curve, because all other parameters are now estimated. Therefore (eq. 5.21),

$$C_2 \approx \text{Re} \left\{ \frac{-R_2 + R_3 + (R_1 - Z)(sC_1R_2 + 1)}{R_2(sR_2 + (R_1 - Z)(s^2C_1R_2 + s))} \right\}, s = j\omega$$ \hspace{1cm} (5.21)

Being $Z$ the selected complex point and $\omega$ its associated angular frequency. Once again, there can be an error when doing this operation since the curve has an error itself and all other parameters may be incorrect or contain an error as well. Thus, it is recommended to evaluate the previous equation with
every point in the curve and select the one that minimizes the error between the real and estimated
curves (it is evaluated the real part because there will always be a residual error, resulting in a small
imaginary component).

5.2.4 Additional adjustment

Although every parameter has a particular process into its estimation, it’s convenient to adjust each
one at the end because there are still errors that cannot be avoided. For example, $R_i$ being
determined through the highest frequency point from the Nyquist curve will always be miscalculated
since it is very difficult to obtain a point with null imaginary part.

Each parameter is, therefore, individually fine-tuned in order to get a better estimated curve. The cost
function, i.e, the function to be minimized is the mean square error between both Nyquist curves (eq.
5.22):

$$\varepsilon = \frac{1}{n} \sum_{i=1}^{n} d_i^2$$  \hspace{1cm} (5.22)

Being $n$ the number of points in a curve and $d_i$ the distance between the $i$th estimated point ($\hat{Z}_i$) and
the corresponding one on the curve to be estimated ($Z_i$). Hence (eq. 5.23),

$$\varepsilon = \frac{1}{n} \sum_{i=1}^{n} |Z_i - \hat{Z}_i|^2$$  \hspace{1cm} (5.23)

Once that (eqs. 5.24 and 5.25),

$$\begin{align*}
Z_i &= a_i + jb_i \\
\hat{Z}_i &= \hat{a}_i + j\hat{b}_i
\end{align*}$$

$$\Rightarrow \varepsilon = \frac{1}{n} \sum_{i=1}^{n} \left[ (a_i - \hat{a}_i)^2 + (b_i - \hat{b}_i)^2 \right]$$  \hspace{1cm} (5.24)

With $a_i, b_i, \hat{a}_i, \hat{b}_i \in \mathbb{R}$. This error is, ideally, zero and that condition can only be satisfied if,

$$\begin{align*}
\sum_{i=1}^{n} (a_i - \hat{a}_i)^2 &= 0 \\
\sum_{i=1}^{n} (b_i - \hat{b}_i)^2 &= 0
\end{align*}$$

$$\Rightarrow \begin{cases} a_i = \hat{a}_i, \forall i \\ b_i = \hat{b}_i, \forall i \end{cases}$$  \hspace{1cm} (5.25)

Remembering the transfer function (eq. 5.26),

$$Z(s) = R_1 + \frac{R_2 + R_3 + sR_2R_3C_2}{s^2R_2R_3C_1C_2 + s(R_3C_2 + R_2C_1) + 1}, \quad s = j\omega$$  \hspace{1cm} (5.26)

Then (eq. 5.27),
\[
\begin{align*}
\text{Re}(Z(s)) &= R_1 + \frac{R_2 + R_3 + \omega^2 R_2 R_3^2 C_2 (C_2 - C_1)}{(1 - \omega^2 R_2 R_3 C_1 C_2)^2 + [\omega (R_3 + R_2 C_1)]^2} \\
\text{Im}(Z(s)) &= -\frac{\omega^3 R_2^2 R_3^2 C_1 C_2^2 - \omega (R_2^2 C_1^2 - R_2 R_3 C_1 - R_3^2 C_2)}{(1 - \omega^2 R_2 R_3 C_1 C_2)^2 + [\omega (R_3 + R_2 C_1)]^2}
\end{align*}
\] (5.27)

According to both equations deduced in equation (5.25), when adjusting only one variable (assuming all other ones are already well determined), there can only be one solution (eq. 5.28):

\[\hat{\text{var}} = \text{var}\] (5.28)

Where \(\text{var}\) is the variable to be estimated \((R_1, R_2, R_3, C_1 \text{ or } C_2)\) and \(\hat{\text{var}}\) the corresponding parameter to be estimated. The mean square error is, thus, a convex function when each parameter is adjusted individually and if the estimation is not corrected, the error won’t be zero. The error function presents, therefore, only one zero at the correct estimated value. The purpose is to find that minimum, which can be made analytically or numerically. Figure 5.7 displays an error function for a particular case.

\[\text{Figure 5.7 - Error function dependind on a variable (this case, } C_1\text{), when all other estimated parameters do not present a deviation (} R_1 = 1.967 \text{ m}\Omega, R_2 = 2.466 \text{ m}\Omega, R_3 = 2.793 \text{ m}\Omega, C_1 = 36 \text{ F and } C_2 = 739.1 \text{ F})\]

However, the error function depends on every parameter’s estimation which will always exhibit an error. Thus, the function’s minimum will never be null and now presents a deviation from the correct value to be determined (figure 5.8).
Figure 5.8 - Error function depending on a variable (this case, $c_1$), when all other estimated parameters present a deviation ($R_1 \equiv R_1 = 1.967$ m$\Omega$, $R_2 \equiv R_2 = 1.066$ m$\Omega$, $R_3 \equiv R_3 = 2.793$ m$\Omega$, $C_1 = 36$ F and $C_2 \equiv C_2 = 739.1$ F).

The search for the minimum would be pointless because it provides a wrong estimation. To solve this problem, each parameter is adjusted the same way (seeking for the function’s minimum) and its rectification must be provided to the next parameter correction so that each solution converges towards the correct value. This process occurs until the error (between both curves) reaches an adequate value in a range number of iterations. This reasoning is synthesized in the following pseudocode:

\begin{verbatim}
num_iterations = 0;  % initialization
num_max = 100;       % maximum number of iterations (100, for example)
error = 1;           % initialization
error_max = 1e-10    % error's maximum number (1e-10, for example)

while error > error_max && num_iterations < num_max
    adjustment of $R_1$;
    adjustment of $R_2$ and $R_3$;
    adjustment of $C_1$;
    estimation of $C_2$;
    error = error calculation;
    num_iterations = num_iterations + 1;
end
\end{verbatim}

Note that $R_2$ and $R_3$ are reported to be adjusted together. That is so because, as mentioned above, $R_3$ is determined through $R_{DC}$, $R_1$ and $R_2$, meaning that $R_3$ can be immediately assessed after the
rectification of $\bar{R}_2$. Furthermore, $\bar{C}_2$ is also mention to be estimated instead of adjusted once that $\bar{C}_2$ is calculated through equation (5.20).

The order within the cycle in the pseudocode could be different ($\bar{C}_1$ could be first) and altered at every iteration, but that optimization would require extra processing capacity from the microcontroller. Its benefit would be doubtful since the additional adjustment takes little to no time.

The algorithm is summarized by a flowchart in attachment 3.

### 5.2.5 Simulation

A *Matlab* simulation was conducted in order to validate the proposed algorithm. Hence, each parameter was attributed a value in order to get a Nyquist curve. The goal is to do the contrary: estimate each parameter through the curve.

The values attributed to every parameter were: $R_1 = 1.967 \text{ m}\Omega$, $R_2 = 1.066 \text{ m}\Omega$, $R_3 = 14.793 \text{ m}\Omega$, $C_1 = 36 \text{ F}$ and $C_2 = 739.1 \text{ F}$. Figure 5.9 displays both curves: one obtained through the previously parameters and the estimated one.

![Figure 5.9 - Simulation results for 98 points: estimated (red crosses) and to be estimated (blue line) curves](image)

The error obtained for this simulation was $2.2408 \times 10^{-12}$ and the estimated parameters were (eq. 5.29):

$$
\begin{align*}
\bar{R}_1 &= 1.977 \text{ m}\Omega \\
\bar{R}_2 &= 1.065 \text{ m}\Omega \\
\bar{R}_3 &= 14.794 \text{ m}\Omega \\
\bar{C}_1 &= 35.672 \text{ F} \\
\bar{C}_2 &= 738.873 \text{ F}
\end{align*}$$
Since this simulation is conducted by attributing a value to each parameter beforehand, it is also possible to determine the error for every parameter. Thus (eq. 5.30),

\[
\begin{align*}
\varepsilon_{R_1} &= \left| \frac{R_1 - \hat{R}_1}{R_1} \right| \times 100 = 6.6143 \times 10^{-14} \% \\
\varepsilon_{R_2} &= \left| \frac{R_2 - \hat{R}_2}{R_2} \right| \times 100 = 0.1199 \% \\
\varepsilon_{R_3} &= \left| \frac{R_3 - \hat{R}_3}{R_3} \right| \times 100 = 0.0086 \% \\
\varepsilon_{C_1} &= \left| \frac{C_1 - \hat{C}_1}{C_1} \right| \times 100 = 0.9125 \% \\
\varepsilon_{C_2} &= \left| \frac{C_2 - \hat{C}_2}{C_2} \right| \times 100 = 0.0307 \%
\end{align*}
\]

Based on the error between both curves and each parameter’s individual error, it is concluded that the algorithm is adequate.

### 5.3 Randles circuit with inductive part – estimation algorithm

Although some Nyquist curves do not display any inductive part, it can exist and is thus needed to modify the previous estimation algorithm. Consequently, the circuit needs to incorporate an inductive component (figure 5.10) and the algorithm adapted.

![Randles circuit with inductive component and corresponding Nyquis curve](image)

**Figure 5.10** - Randles circuit with inductive component and corresponding Nyquis curve (for 35 points) for a particular case \( R_1 = 1.967 \, m\Omega, \ R_2 = 1.066 \, m\Omega, \ R_3 = 14.793 \, m\Omega, \ C_1 = 36 \, F, \ C_2 = 739.1 \, F, \ R_s = 0.02023 \, \Omega \) and \( L_1 = 53.59 \, nH \)

Its transfer function \( Z_2(s) \) (eq. 5.31) is

\[
Z_2(s) = \frac{sR_3L_1}{R_5 + sL_1} + R_1 + \frac{R_2 + R_3 + sR_2R_3C_2}{s^2R_2R_3C_1C_2 + s(R_3C_2 + R_2C_1) + 1}
\]
5.3.1 $R_1$ estimation

At a first glance, $R_1$ could not be determined through the point with null imaginary part, because that now corresponds to the circuit’s resonant frequency, i.e., the frequency in which the inductive and capacitive impedances cancel each other, becoming the impedance purely real but its value different from $R_1$. However, it can be approximately estimated the same way and fine-tuned later on. As so (eq. 5.32),

$$R_1 = \frac{\text{Re}(Z_a) + \text{Re}(Z_b)}{2}$$

(5.32)

Being $Z_a$ and $Z_b$ points with the lowest imaginary absolute values, that is, the real axis’ closest points.

5.3.2 $R_5$ and $L_1$ estimation

The addition of two more parameters does not introduce significant modifications when comparing with the previous algorithm. $R_5$ and $L_1$ are associated with the inductive part of the curve, thus, the highest frequency region. A similar reasoning with the estimation of $R_2$ and $C_1$ can be made in order to estimate these new parameters. For the higher frequencies, the circuit in figure 5.10 can be shortened into the one displayed in the figure 5.11.

![Simplified circuit for the higher frequencies and corresponding Nyquist curve](figure.png)

*Figure 5.11* - Simplified circuit for the higher frequencies and corresponding Nyquist curve (335 points) for a particular case ($R_1 = 1.967 \, \text{m} \Omega$, $R_5 = 0.02023 \, \Omega$ and $L_1 = 53.59 \, \text{nH}$)

Its transfer function is (eq. 5.33):

$$Z_{R_1,R_5,L_1}(s) = R_1 + \frac{sR_5L_1}{R_5 + sL_1}$$

(5.33)

Knowing this, $R_5$ and $L_1$ can be determined with two points from the considered region in the curve. Hence (eqs. 5.34 and 5.35),
\[ Z_{R_{1},R_{5},L_{1}}(s) = R_{1} + \frac{s R_{5} L_{1}}{R_{5} + s L_{1}} = R_{1} + \frac{\omega^2 R_{5} L_{1}}{R_{5}^2 + (\omega L_{1})^2} + j \frac{\omega^2 R_{5}^2 L_{1}}{R_{5}^2 + (\omega L_{1})^2} = Z_{r} + j Z_{i}, s = j \omega \] (5.34)

\[
\begin{align*}
R_{1} + \frac{\omega^2 R_{5} L_{1}}{R_{5}^2 + (\omega L_{1})^2} &= Z_{r} \\
\frac{\omega^2 R_{5}^2 L_{1}}{R_{5}^2 + (\omega L_{1})^2} &= Z_{i}
\end{align*}
\]
\[ \Rightarrow \begin{cases} 
R_{5} = \frac{R_{1}^2 - 2 R_{1} Z_{r} + Z_{r}^2 + Z_{r}^2}{R_{1} - Z_{r}} \\
L_{1} = \frac{R_{1}^2 - 2 R_{1} Z_{r} + Z_{r}^2 + Z_{r}^2}{\omega Z_{i}}
\end{cases} \] (5.35)

Where \( Z_{r} \) and \( Z_{i} \) are the real and imaginary parts of the chosen point, respectively, and \( \omega \) its angular frequency. Like \( R_{2} \) and \( C_{1} \), each point of the curve is tested and the one that provides the smallest error is chosen.

Although the individual adjustments part take place at the end of the algorithm, it is a good opportunity to correct \( R_{4} \) after the assessment of \( R_{5} \) and \( L_{1} \). This is possible because, once again, the error function is convex when tuning one variable at a time (this time, the error is computed only considering the points with positive imaginary part). Each time there is a new value for \( R_{1}, R_{5} \) and \( L_{1} \) are calculated again, so that every parameter converges to the correct solution. The pseudocode for this reasoning is described next.

\begin{verbatim}
num_iterations = 0; % initialization
num_max = 100; % maximum number of iterations (100, for example)
error = 1; % initialization
erro_max = 1e-10 % error’s maximum number (1e-10, for example)

while error>erro_max && num_iterations<num_max
    calculation of \( \hat{R}_{5} \) and \( \hat{L}_{1} \);
    adjustment of \( \hat{R}_{1} \);
    error = error calculation;
    num_iterations = num_iterations+1;
end
\end{verbatim}

### 5.3.3 \( R_{2} \) and \( C_{1} \) estimation

These parameters are estimated the same way as in the algorithm with no inductive component, but knowing that now the circuit includes an inductive component. Therefore (eq. 5.36),

\[ Z_{R_{2},C_{1},R_{5},L_{1}}(s) = R_{1} + \frac{R_{2}}{1 + s R_{2} C_{1}} + \frac{s R_{5} L_{1}}{R_{5} + s L_{1}} = Z \] (5.36)
Being \( Z \) the chosen point. Hence (eqs. 5.37 and 5.38),

\[
\begin{align*}
R_1 + \frac{R_2}{1 + \omega^2 R_2 C_1^2} + \frac{\omega^2 R_5 L_1^2}{R_5^2 + (\omega L_1)^2} & = Z_r \\
- \frac{\omega R^2 C_1}{1 + \omega^2 R_2 C_1^2} + \frac{\omega^2 R_5 L_1}{R_5^2 + (\omega L_1)^2} & = Z_i
\end{align*}
\]

\( (5.37) \)  

\[
\Rightarrow \begin{cases}
R_2 = \frac{A + B}{C} \\
C_1 = - \frac{D}{\omega(E + F)}
\end{cases}
\]

\( (5.38) \)

With (eqs. 5.39 to 5.44),

\[
A = \omega^2 L_1^2 R_1^2 + 2 \omega^2 L_1^2 R_1 R_5 - 2 \omega^2 L_1^2 R_5 Z_r + \omega^2 L_1^2 R_5^2 - 2 \omega^2 R_5 L_1^2 Z_r + \omega^2 L_1^2 Z_i^2
\]

\( (5.39) \)

\[
B = \omega^2 L_1^2 Z_r^2 - 2 \omega R_5^2 L_1^2 Z_i + R_1^2 R_5^2 - 2 R_1 R_5 Z_r^2 + R_5^2 Z_i^2 + R_5^2 Z_r^2
\]

\( (5.40) \)

\[
C = R_1 R_5^2 - R_5^2 Z_r + \omega^2 L_1^2 R_1 + \omega^2 L_1^2 R_5 - \omega^2 L_1^2 Z_r
\]

\( (5.41) \)

\[
D = \omega^2 Z_i L_1^2 - \omega R_5^2 L_1 + R_5^2 Z_i
\]

\( (5.42) \)

\[
E = \omega^2 L_1^2 R_1^2 + 2 \omega^2 L_1^2 R_1 R_5 - 2 \omega^2 L_1^2 R_5 Z_r + \omega^2 L_1^2 R_5^2 - 2 \omega^2 L_1^2 R_5 Z_r + \omega^2 L_1^2 Z_i^2
\]

\( (5.43) \)

\[
F = \omega^2 L_1^2 Z_r^2 - 2 \omega L_1 R_5^2 Z_i + R_1^2 R_5^2 - 2 R_1 R_5 Z_r^2 + R_5^2 Z_i^2 + R_5^2 Z_r^2
\]

\( (5.44) \)

Where \( Z_r \) and \( Z_i \) are the real and imaginary components of \( Z \) and \( \omega \) its angular frequency.

### 5.3.4 \( R_3 \) and \( C_2 \) estimation

Again, \( R_3 \) and \( C_2 \) are computed as in the previous algorithm. As so (eq. 5.45),

\[
R_3 = R_{DC} - R_1 - R_2
\]

\( (5.45) \)

With \( R_{DC} \) being the cell’s internal resistance, previously measured (eq. 5.46):
\[ R_{DC} = R_1 + R_2 + R_3 \] \hfill (5.46)

About \( C_2 \), it is determined with the help of the transfer function \( Z_2(s) \) (eq. 5.47):

\[
C_2 \equiv \text{Re}\left\{ \frac{R_2 + R_3 + (sR_2C_1 + 1)(R_1 - Z + \frac{sR_1L_1}{sL_1 + R_3})}{R_4((s^2R_2C_1 + s)(R_1 - Z + \frac{sR_1L_1}{sL_1 + R_3}) + sR_2)} \right\}
\hfill (5.47)

With \( Z \) the selected point that provides the best fit and \( \omega \) its angular frequency. It is evaluated the real part because there will always be a residual error, which will result in a small imaginary component.

### 5.3.5 Additional adjustment

Once again, the final step is to individually adjust every parameter with no significant differences from the equivalent step in the previous algorithm. The describing pseudocode is as follows:

\[
\begin{align*}
\text{num\_iterations} &= 0; \quad \% \text{initialization} \\
\text{num\_max} &= 100; \quad \% \text{maximum number of iterations (100, for example)} \\
\text{error} &= 1; \quad \% \text{initialization} \\
\text{error\_max} &= 1e-10 \quad \% \text{error's maximum number (1e-10, for example)}
\end{align*}
\]

\[
\text{while } \text{error}>\text{error\_max} \text{ } && \text{num\_iterations}<\text{num\_max} \\
\quad \text{adjustment of } R_5; \\
\quad \text{adjustment of } L_1; \\
\quad \text{adjustment of } R_1; \\
\quad \text{adjustment of } R_2 \text{ and } R_3; \\
\quad \text{estimation of } C_2; \\
\quad \text{error } = \text{error calculation}; \\
\quad \text{num\_iterations } = \text{num\_iterations}+1;
\]

\[
\text{end}
\]

The algorithm is summarized by a flowchart in attachment 4.

### 5.3.6 Simulation

Again, a *Matlab* simulation was conducted in order to validate the proposed algorithm, the same way as the previous one. The values attributed to every parameter were: \( R_1 = 1.967 \text{ m\Omega} \), \( R_2 = 1.066 \text{ m\Omega} \), \( R_3 = 14.793 \text{ m\Omega} \), \( C_1 = 36 F \), \( C_2 = 739.1 F \), \( R_5 = 0.02023 \Omega \), \( L_1 = 53.59 \text{ nH} \). Figure 5.12 displays both curves: one obtained through the previously parameters and the estimated one.
The error obtained for this simulation was \(6.6899 \times 10^{-12}\) and the estimated parameters were (eq. 5.48):

\[
\begin{align*}
\hat{R}_1 &= 1.968131586953 \, \text{m}\Omega \\
\hat{R}_2 &= 1.067459936122 \, \text{m}\Omega \\
\hat{R}_3 &= 14.790408476925 \, \text{m}\Omega \\
\hat{C}_1 &= 36.359863052853626 \, \text{F} \\
\hat{C}_2 &= 739.4739601271082 \, \text{F} \\
\hat{R}_5 &= 0.021958475346910 \, \Omega \\
\hat{L}_1 &= 53.27032813718236 \, \text{nH}
\end{align*}
\]

(5.48)

Since this simulation is conducted by attributing a value to each parameter beforehand, it is also possible to determine the error for every parameter. Thus (eq. 5.49),

\[
\begin{align*}
\varepsilon_{R_1} &= \left| \frac{R_1 - \hat{R}_1}{R_1} \right| \times 100 = 0.0575 \, \% \\
\varepsilon_{R_2} &= \left| \frac{R_2 - \hat{R}_2}{R_2} \right| \times 100 = 0.1370 \, \% \\
\varepsilon_{R_3} &= \left| \frac{R_3 - \hat{R}_3}{R_3} \right| \times 100 = 0.0175 \, \% \\
\varepsilon_{C_1} &= \left| \frac{C_1 - \hat{C}_1}{C_1} \right| \times 100 = 0.9996 \, \% \\
\varepsilon_{C_2} &= \left| \frac{C_2 - \hat{C}_2}{C_2} \right| \times 100 = 0.0506 \, \% \\
\varepsilon_{R_5} &= \left| \frac{R_5 - \hat{R}_5}{R_5} \right| \times 100 = 8.5441 \, \% \\
\varepsilon_{L_1} &= \left| \frac{L_1 - \hat{L}_1}{L_1} \right| \times 100 = 0.5965 \, \%
\end{align*}
\]

(5.49)
Based on the error between both curves and each parameter’s individual error, it is concluded that the algorithm is adequate.

5.4 Modified Randles circuit – estimation algorithm

This section refers to the algorithm developed for the second approach circuit. However, it was reformed into the one in figure 5.13.

![Figure 5.13 - Modified Randles circuit and corresponding Nyquist curve (38 points) for a particular case (R_1 = 1.741 mΩ, R_2 = 0.5697 mΩ, R_3 = 1.007 mΩ, R_4 = 22.11 mΩ, C_1 = 5.206 F, C_2 = 71.39 F, C_3 = 1172 F)](image)

With the following transfer function (eq. 5.50):

$$
Z_3(s) = R_1 + \frac{1}{sC_1} \left[ \frac{R_2 + \frac{R_3}{1 + sR_3C_2} + \frac{R_4}{1 + sR_4C_3}}{1 + \frac{R_3}{1 + sR_3C_2} + \frac{R_4}{1 + sR_4C_3}} \right]
$$

(5.50)

The second approach circuit was arranged to separate the phenomena in each electrode but the information in a Nyquist curve is related to the whole circuit. Even with the software’s fitting tools used previously in this work, it is not possible to distinguish weather a pair of RC values is associated to a specific electrode. The modified version preserves both RC circuits associated with diffusion and capacitance $C_1$ now represents the double layer capacitance in the anode and cathode. $R_2$ is the charge transfer resistance, again, for both electrodes.

5.4.1 $R_1$ estimation

The determination of $R_1$ follows the scheme of the non-modified Randle’s circuit because there is no inductive component. Hence (eq. 5.51),

$$
\lim_{s \to \infty} Z'(s) = R_1, \ s = j\omega
$$

(5.51)
5.4.2 R₂ and C₁ estimation

Again, as in the first algorithm, these parameters are estimated knowing that for high frequencies some elements can be neglected and the circuit reduced into the one in figure 5.14.

![Figure 5.14 - Shortened circuit, neglecting R₃C₂ and R₄C₃ time constants](image)

As so (eqs. 5.52 and 5.53),

\[
Z_{R₁R₂C₁}(s) = \frac{R₂}{1 + sR₂C₁} = R₁ + \frac{R₂}{1 + \omega²R₂²C₁²} - j \frac{\omega R₂²C₁}{1 + \omega²R₂²C₁²} = Z_r + jZ_i
\] (5.52)

\[
\begin{align*}
R₁ + \frac{R₂}{1 + \omega²R₂²C₁²} &= Z_r \\
- \frac{\omega R₂²C₁}{1 + \omega²R₂²C₁²} &= Z_i
\end{align*}
\]

\[
\begin{align*}
R₂ &= \frac{\left(R₁² - 2R₁Z_r + Z_i² + Z_r²\right)}{R₁ - Z_r} \\
C₁ &= -\frac{\omega\left(R₁² - 2R₁Z_r + Z_i² + Z_r²\right)}{Z_i}
\end{align*}
\] (5.53)

Where \(Z_r\) and \(Z_i\) are the real and imaginary parts of the point from the curve in the considered region and \(\omega\) its angular frequency. Once again, it is better to test every point in the curve to achieve the best result.

5.4.3 R₃, R₄, C₂ and C₃ estimation

These are the parameters where its estimation is different from all other ones and that will affect the whole algorithm.

About a Nyquist curve created by the circuit in figure 5.13, it can reveal three curvatures, depending on the parameters’ values. The next figure shows the overall and each individual curve if the circuit was segmented according to each time constant.
Figure 5.15 - Complete Randles' circuit, its simplifications according to each time constant and corresponding Nyquist curves (38 points) \( (R_1 = 1.741 \, m\Omega, R_2 = 0.5697 \, m\Omega, R_3 = 1.007 \, m\Omega, R_4 = 22.11 \, m\Omega, C_1 = 5.206 \, F, C_2 = 71.39 \, F, C_3 = 1172 \, F) \)

In figure 5.15 is marked a point A, whose real part is close to the sum of \( R_1, R_2 \) and \( R_3 \). Therefore, there is a point in the curve which is possible to know the sum of \( R_1, R_2 \) and \( R_3 \), but is not exactly point A. Since, at this point, \( R_1 \) and \( R_2 \) are no longer unknowns (eqs. 5.54 and 5.55),

\[
Re[A] \cong R_1 + R_2 + R_3 \quad (5.54)
\]

\[
\Leftrightarrow R_3 \cong R_1 + R_2 - Re[A] \quad (5.55)
\]

Point C corresponds to the maximum imaginary point (absolute value) of the semicircle it belongs to. That semicircle transfer function is (eqs. 5.56 and 5.57):

\[
Z_{R1,R2,R3,C2}(s) = R_1 + R_2 + \frac{R_3}{1 + sR_3C_2} \quad (5.56)
\]

\[
\Leftrightarrow Z_{R1,R2,R3,C2}(\omega) = R_1 + R_2 + \frac{R_3}{1 + \omega^2R_3^2C_2} - j\frac{\omega R_3^2C_2}{1 + \omega^2R_3^2C_2} \quad (5.57)
\]

Hence, solving the following equation (eq. 5.58),

\[
\frac{\partial}{\partial \omega} Im\{Z_{R1,R2,R3,C2}(\omega)\} = 0 \quad (5.58)
\]

It yields the following relation (eq. 5.59):

\[
\Rightarrow \omega_C R_3 C_2 = 1 \quad (5.59)
\]
Where \( \omega_c \) is the angular frequency of point C. That point and point B’s real parts are not necessarily the same, but are close which provides the next equation:

\[
C_2 \approx \frac{1}{\omega_c R_3}
\]  
(5.60)

Recapitulating, the equations that provide the values for \( R_3 \) and \( C_2 \) are (eq. 5.61):

\[
\begin{align*}
R_3 & \approx R_1 + R_2 - \text{Re}(A) \\
C_2 & \approx \frac{1}{\omega_c R_3}
\end{align*}
\]  
(5.61)

With \( R_1, R_2 \) and approximately \( R_3 \), it is possible to determine \( R_4 \) as (eq. 5.62):

\[
R_4 \approx R_{DC} - R_1 - R_2 - R_3
\]  
(5.62)

And the last capacitance \( C_3 \) (eq. 5.63),

\[
C_3 \approx \text{Re} \left( \frac{R_4}{R_2} + \frac{1}{sC_1 + \frac{1}{R_1} + \frac{R_3}{sC_2 R_3} + 1} \right) \frac{1}{\omega R_4}
\]  
(5.63)

Neither one of these last relations is an equality. Yet, they can serve as an initialization and those values corrected later on. Once again, every point of the curve should be tested in order to achieve the best results (it is evaluated the real part because there will always be a residual error, which will result in a small imaginary component).

### 5.4.4 Additional adjustment

Following these initializations, the parameters are individually adjusted resulting in the following pseudocode.

```matlab
num_iterations = 0;  % initialization
num_max = 100;       % maximum number of iterations (100, for example)
error = 1;           % initialization
error_max = 1e-10    % error’s maximum number (1e-10, for example)

while error > error_max && num_iterations < num_max
    adjustment of \( \bar{R}_3 \) and \( \bar{R}_4 \);
    adjustment of \( \bar{C}_2 \);
    estimation of \( \bar{C}_3 \);
    error = error calculation;
end
```

57
\[
\text{num\_iterations} = \text{num\_iterations} + 1;
\]

end

The algorithm is summarized by a flowchart in attachment 5.

5.4.5 Simulation

Regarding the Matlab simulation, it was conducted the same way as the other ones. The values attributed to every parameter were: \( R_1 = 1.741 \text{ m}\Omega \), \( R_2 = 0.5697 \text{ m}\Omega \), \( R_3 = 1.007 \text{ m}\Omega \), \( R_4 = 22.11 \text{ m}\Omega \), \( C_1 = 5.206 \text{ F} \), \( C_2 = 71.39 \text{ F} \), \( C_3 = 1172 \text{ F} \). Figure 5.16 displays both curves.

![Figure 5.16](image)

**Figure 5.16** - Simulation results for 38 points: estimated (red crosses) and to be estimated (blue line) curves

The error obtained for this simulation was \( 7.3643 \times 10^{-11} \) and the estimated parameters were (eq. 5.64):

\[
\begin{align*}
\hat{R}_1 &= 1.741029239327 \text{ m}\Omega \\
\hat{R}_2 &= 0.5704671752393833 \text{ m}\Omega \\
\hat{R}_3 &= 0.9897815386047011 \text{ m}\Omega \\
\hat{R}_4 &= 22.126422046829 \text{ m}\Omega \\
\hat{C}_1 &= 5.231218156880273 \text{ F} \\
\hat{C}_2 &= 71.960265043469590 \text{ F} \\
\hat{C}_3 &= 1169.192448820339 \text{ F}
\end{align*}
\] (5.64)

Since this simulation is conducted by attributing a value to each parameter beforehand, it is also possible to determine the error for every parameter. Thus (eq. 5.65),
Based on the error between both curves and each parameter’s individual error, it is concluded that the algorithm is adequate.

## 5.5 Modified Randles circuit with inductive part – estimation algorithm

This last algorithm has a slight modification of the previous one caused by the introduction of the inductive component, shown in the next figure.

![Modified Randles circuit with inductive component](image)

### Figure 5.17 - Modified Randles circuit with inductive component and corresponding Nyquist curve (38 points) for a particular case \( (R_1 = 1.741 \, m\Omega, R_2 = 0.5697 \, m\Omega, R_3 = 1.007 \, m\Omega, R_4 = 22.11 \, m\Omega, C_1 = 5.206 \, F, C_2 = 71.39 \, F, C_3 = 1172 \, F, R_5 = 0.02023 \, \Omega \) and \( L_1 = 53.59 \, nH \)

With the following transfer function (eq. 5.66):

\[
Z_4(s) = \frac{sR_5L_1}{R_5 + sL_1} + R_1 + \frac{1}{sC_1} \left[ \frac{R_2}{1 + sR_2C_2} + \frac{R_3}{1 + sR_3C_2} + \frac{R_4}{1 + sR_4C_2} \right]
\]  

(5.66)
5.5.1 $R_1$ estimation

As the previous algorithm (eq. 5.67),

$$R_1 = \frac{Re\{Z_a\} + Re\{Z_b\}}{2} \quad (5.67)$$

Being $Z_a$ and $Z_b$ points with the lowest imaginary absolute values, that is, the real axis’ closest points.

5.5.2 $R_5$ and $L_1$ estimation

Likewise (eqs. 5.68 and 5.69),

$$Z_{R_1,R_5,L_1}(s) = R_1 + \frac{sR_5L_1}{R_5 + sL_1} = R_1 + \frac{\omega^2 R_5 L_1^2}{R_5^2 + (\omega L_1)^2} + j \frac{\omega^2 R_5^2 L_1}{R_5^2 + (\omega L_1)^2} = Z_r + jZ_i \quad (5.68)$$

$$\iff \begin{cases} R_1 + \frac{\omega^2 R_5 L_1^2}{R_5^2 + (\omega L_1)^2} = Z_r \\ \frac{\omega^2 R_5^2 L_1}{R_5^2 + (\omega L_1)^2} = Z_i \end{cases} \iff \begin{cases} R_5 = -\frac{R_1^2 - 2R_1Z_r + Z_i^2 + Z_r^2}{R_1 - Z_r} \\ L_1 = \frac{R_1^2 - 2R_1Z_r + Z_i^2 + Z_r^2}{\omega Z_i} \quad (5.69) \end{cases}$$

Where $Z_r$ and $Z_i$ are the real and imaginary parts of the chosen point, respectively. Similarly to the Randles’ algorithm without an inductive component, $R_1$ is corrected. The pseudocode is:

```python
num_iterations = 0;  # initialization
num_max = 100;      # maximum number of iterations (100, for example)
error = 1;          # initialization
error_max = 1e-10   # error's maximum number (1e-10, for example)

while error > error_max && num_iterations < num_max
    calculation of $\tilde{R}_5$ and $\tilde{L}_1$;
    adjustment of $\tilde{R}_1$;
    error = error calculation;
    num_iterations = num_iterations + 1;
end```

60
5.5.3 \( R_2 \) and \( C_1 \) estimation

Knowing \( R_1, R_5 \) and \( L_1 \) (eq. 5.70),

\[
Z_{R2,C1,R5,L1}(s) = R_1 + \frac{R_2}{1 + sR_2C_1} + \frac{sR_5L_1}{R_5 + sL_1} = Z, s = j\omega
\]  

(5.70)

Being \( Z \) the chosen point. Hence (eqs. 5.71 to 5.78),

\[
\begin{align*}
R_1 + \frac{R_2}{1 + \omega^2 R_2^2 C_1^2} + \frac{\omega^2 R_5 L_1^2}{R_5^2 + (\omega L_1)^2} &= Z_r \\
- \frac{\omega R_5^2 C_1}{1 + \omega^2 R_2^2 C_1^2} + \frac{\omega^2 R_5^2 L_1^2}{R_5^2 + (\omega L_1)^2} &= Z_i
\end{align*}
\]  

(5.71)

\[
\begin{align*}
R_2 &= -\frac{A + B}{C} \\
C_1 &= -\frac{D}{\omega(E + F)}
\end{align*}
\]  

(5.72)

\[
A = \omega^2 L_1^2 R_1^2 + 2\omega^2 L_1^2 R_1 R_5 - 2\omega^2 L_1^2 R_5 Z_r + \omega^2 L_1^2 R_5^2 - 2\omega^2 R_5 L_1^2 Z_r + \omega^2 L_1^2 Z_r^2
\]  

(5.73)

\[
B = \omega^2 L_1^2 Z_r^2 - 2\omega R_5^2 L_1 Z_i + R_5^2 R_5^2 - 2R_1 R_5^2 Z_r + R_5^2 Z_i^2 + R_5^2 Z_r^2
\]  

(5.74)

\[
C = R_1 R_5^2 - R_5^2 Z_r + \omega^2 L_1^2 R_1 + \omega^2 L_1^2 R_5 - \omega^2 L_1^2 Z_r
\]  

(5.75)

\[
D = \omega^2 Z_i L_1^2 - \omega R_5^2 L_1 + R_5^2 Z_i
\]  

(5.76)

\[
E = \omega^2 L_1^2 R_1^2 + 2\omega^2 L_1^2 R_1 R_5 - 2\omega^2 L_1^2 R_5 Z_r + \omega^2 L_1^2 R_5^2 - 2\omega^2 L_1^2 R_5 Z_r + \omega^2 L_1^2 Z_i^2
\]  

(5.77)

\[
F = \omega^2 L_1^2 Z_r^2 - 2\omega L_1 R_5^2 Z_i + R_1^2 R_5^2 - 2R_1 R_5^2 Z_r + R_5^2 Z_i^2 + R_5^2 Z_r^2
\]  

(5.78)

Where \( Z_r \) and \( Z_i \) are the real and imaginary components of \( Z \) and \( \omega \) its angular frequency.
5.5.4 $R_3, R_4, C_2$ and $C_3$ estimation

Once again (eqs. 5.79 and 5.80),
\[ Re(A) \equiv R_1 + R_2 + R_3 \]  
(5.79)
\[ \Rightarrow R_3 \equiv R_1 + R_2 - Re\{A\} \]  
(5.80)

Being A the point referred previously and shown in figure 5.15 (the only difference between the Nyquist curves in figures 5.15 and 5.16 is the addition of an inductive part in the latter). To determine $C_2$ (eqs. 5.81 and 5.82),
\[ Z_{R_1,R_2,R_3,C_2}(s) = R_1 + R_2 + \frac{R_3}{1 + sR_3C_2}, s = j\omega \]  
(5.81)
\[ \Rightarrow Z_{R_1,R_2,R_3,C_2}(\omega) = R_1 + R_2 + \frac{R_3}{1 + \omega^2R_3C_2^2} - j\frac{\omega R_3^2C_2}{1 + \omega^2R_3C_2^2} \]  
(5.82)

Hence, solving the following equation (eq. 5.83),
\[ \frac{\partial}{\partial\omega} Im\{Z_{R_1,R_2,R_3,C_2}(\omega)\} = 0 \]  
(5.83)

It yields the following relation (eq. 5.84):
\[ \Rightarrow \omega_cR_3C_2 = 1 \]  
(5.84)

Thus (eq. 5.85),
\[ C_2 \equiv \frac{1}{\omega_bR_3} \]  
(5.85)

Recapitulating again, the equations that provide the values for $R_3$ and $C_2$ are (eq. 5.86):
\[ \begin{cases} 
R_3 \equiv R_1 + R_2 - Re\{A\} \\
C_2 \equiv \frac{1}{\omega_bR_3} 
\end{cases} \]  
(5.86)

With $R_1$, $R_2$ and approximately $R_3$, it is possible to determine $R_4$ as (eq. 5.87):
\[ R_4 \equiv R_{DC} - R_1 - R_2 - R_3 \]  
(5.87)

The last capacitance $C_3$ is determined as (eq. 5.88):
Once again, these expressions can serve as an initialization and the values corrected later on. Every point of the curve should be verified in order to achieve the best results.

\[ C_3 \approx \Re \left\{ \left( \frac{R_4}{R_2} + \frac{1}{sC_1 + \frac{1}{R_1 - Z + \frac{sL_1R_5}{sL_1 + R_5}}} \right) + R_3 + \frac{R_3}{sR_2C_2} + 1 \right\} \] (5.88)

5.5.5 Additional adjustment

Following these initializations, the parameters are individually adjusted resulting in the following pseudocode.

\begin{verbatim}
num_iterations = 0;  % initialization
num_max = 100;       % maximum number of iterations (100, for example)
error = 1;           % initialization
error_max = 1e-10;   % error's maximum number (1e-10, for example)

while error > error_max && num_iterations < num_max
    adjustment of \( \hat{R}_3 \) and \( \hat{R}_4 \);  
    adjustment of \( \hat{C}_2 \);  
    estimation of \( \hat{C}_5 \);  
    error = error calculation;  
    num_iterations = num_iterations + 1;
end
\end{verbatim}

The algorithm is summarized by a flowchart in attachment 6.

5.5.6 Simulation

The values attributed to every parameter were: \( R_1 = 1.741\, m\Omega \), \( R_2 = 0.5697\, m\Omega \), \( R_3 = 1.007\, m\Omega \), \( R_4 = 22.11\, m\Omega \), \( C_1 = 5.206\, F \), \( C_2 = 71.39\, F \), \( C_3 = 1172\, F \), \( R_5 = 0.02023\, \Omega \), \( L_1 = 53.59\, nH \). Figure 5.18 displays both curves.
Figure 5.18 - Simulation results for 38 points: estimated (red crosses) and to be estimated (blue line) curves.

The error obtained for this simulation was $2.5072 \times 10^{-10}$ and the estimated parameters were (eq. 5.89):

\[
\begin{align*}
\tilde{R}_1 &= 1.766531244175 \, m\Omega \\
\tilde{R}_2 &= 0.5749918824741048 \, m\Omega \\
\tilde{R}_3 &= 0.9790690688923046 \, m\Omega \\
\tilde{R}_4 &= 22.107107804459 \, m\Omega \\
\tilde{C}_1 &= 6.192048942906515 \, F \\
\tilde{C}_2 &= 73.793133531442690 \, F \\
\tilde{C}_3 &= 1171.216632417863 \, F \\
\tilde{R}_5 &= 0.023753544543986 \, \Omega \\
\tilde{L}_1 &= 53.30134909038835 \, nH
\end{align*}
\] (5.89)

The error for every parameter was (eq. 5.90):
Based on the error between both curves and each parameter’s individual error, it is concluded that the algorithm is adequate.

\[
\begin{align*}
\varepsilon_{R_1} &= \left| \frac{R_1 - \bar{R}_1}{R_1} \right| \times 100 = 1.4665 \% \\
\varepsilon_{R_2} &= \left| \frac{R_2 - \bar{R}_2}{R_2} \right| \times 100 = 0.9289 \% \\
\varepsilon_{R_3} &= \left| \frac{R_3 - \bar{R}_3}{R_3} \right| \times 100 = 2.7737 \% \\
\varepsilon_{R_4} &= \left| \frac{R_4 - \bar{R}_4}{R_4} \right| \times 100 = 0.0131 \% \\
\varepsilon_{C_1} &= \left| \frac{C_1 - \bar{C}_1}{C_1} \right| \times 100 = 18.9406 \% \\
\varepsilon_{C_2} &= \left| \frac{C_2 - \bar{C}_2}{C_2} \right| \times 100 = 3.3662 \% \\
\varepsilon_{C_3} &= \left| \frac{C_3 - \bar{C}_3}{C_3} \right| \times 100 = 0.0668 \% \\
\varepsilon_{R_5} &= \left| \frac{R_5 - \bar{R}_5}{R_5} \right| \times 100 = 17.4174 \% \\
\varepsilon_{L_1} &= \left| \frac{L_1 - \bar{L}_1}{L_1} \right| \times 100 = 0.5386 \% 
\end{align*}
\] (5.90)

5.6 Advantages and Disadvantages

The classic technique to estimate the parameters from the internal impedance of a cell is through an optimization algorithm, usually implemented in software as the one used earlier in this work. These computer programs can solve a set of non-linear equations using numerical methods. It is, therefore, required a good initialization of each parameter to be estimated in order to get a good convergence which constitutes a major disadvantage of such methods. Furthermore, the processing capacity needed to run these algorithms might be too much for a microcontroller.

The algorithms developed in this work do not require any initialization of the parameters’ values and can easily be implemented in a microcontroller because of their simplicity.

On the other hand, each algorithm was established for a certain circuit which is a disadvantage when comparing to a computer program. This type of software can estimate every parameter for any established circuit.

Another possible drawback is the obligatory evaluation of the internal resistance \( R_{DC} \), which requires a separated experiment from the EIS. Such assessment is not needed in a computer program of this type. However, the internal resistance can provide more information about the circuit itself. For instance, in the case that it is not measured, the internal resistance is still, for the first two algorithms (eq. 5.91),
Or, for the final two (eq. 5.92),

\[ R_{DC} = R_1 + R_2 + R_3 + R_4 \]  \hspace{1cm} (5.92)

If \( R_{DC} \) was directly measured as described previously, its value must be equal to each of the expressions mentioned right above. If not, it means the circuit considered does not describe the internal impedance truthfully.
6 Conclusions

This thesis had three major goals to be developed: an electrical lumped parameter model of a LiFePO$_4$ battery cell's impedance; a thermal lumped parameter model of a LiFePO$_4$ battery cell and an online estimation algorithm of the internal battery parameters.

The thermal model developed to characterize a single cell revealed itself precise, when compared to a study made in a scientific paper and experimental analysis.

Regarding the electrical lumped parameter model, the final approach developed revealed itself accurate, since its Nyquist curve was almost identical with the experimental one. The diffusion phenomenon was particularly difficult to model, since it required a total of 3 RC circuits in each electrode to do it. Although the data provided was insufficient and, in some cases, incomplete, some conclusions were still able to be collected, such as the charge transfer and electrolyte resistances that might be approximately equal. Nevertheless, it was not possible to identify any signs of degradation in the battery cell.

The estimation algorithms developed were based on the first two approaches due to its importance in the modeling of a cell’s internal impedance, unlike the third approach, and each one of them was simulated in Matlab environment.

After the algorithms’ development, the next step would be to implement them in a microcontroller and test them.
References and Bibliography


[22] Birkl, C., & Howey, D. (2013). Model identification and parameter estimation for LiFePO4 batteries, IET Hybrid and Electric Vehicles Conference (HEVC), DOI.


### Attachment 1

Section 3.1.3 – figure 3.8

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Attachment 2

The following figures show the experimental results’ conclusions, the same in section 3.3.1 (chosen 25% SOC). Note that the experimental results regarding temperature 60°C are not displayed in figures, once that, as explained in section 8, the data was incomplete and was, therefore, useless.

Figure 9.1 - Experimental results for L1+L2

Figure 9.2 - Experimental results for R9+R10
Figure 9.3 - Experimental results for C6+C5

Figure 9.4 - Experimental results for R11+R12
Figure 9.5 - Experimental results for R2

Figure 9.6 - Experimental results for R3
Figure 9.7 - Experimental results for R4

Figure 9.8 - Experimental results for R6+R13+R15
Figure 9.9 - Experimental results for $R_7 + R_{14} + R_{16}$

Figure 9.10 - Experimental results for $C3 + C7 + C9$
Figure 9.11 - Experimental results for C1

Figure 9.12 - Experimental results for C2
Set \( k = 1 \)

Determine \( C^2(\text{block}) \)

\[ k > \text{number of points in the curve?} \]

Increment \( k \) by 1

Determine \( R^2(k) \) and \( C^1(k) \) (eq. 5.16)

Determine \( R^3(k) \) (eq. 5.19)

Determine \( C^2(k) \) block

**Figure 10.1 - Main flowchart**
Figure 10.2 - Determine $C_2$ block

Figure 10.3 - Adjustment block
Start

Input data: Nyquist plot(k)

Determine $R_{DC}$ (eq. 5.18) and $R_1$ (eq. 5.30)

Determine $R_5$ and $L_1$ block

Set $k = 1$

$k > \text{number of points in the curve}$?

False

Determine $R_2(k)$ and $C_1(k)$ (eq. 5.36)

Determine $R_3(k)$ (eq. 5.43)

Determine $C_2(k)$ block

Increment $k$ by 1

True

Error computation (eq. 5.23)

Choose $R_2, R_3 C_1, C_2$

Adjustment Block

End

Attachment 4

**Figure 11.1 - Main flowchart**
Figure 11.2 - Determine $R_5$ and $L_1$ block

Figure 11.3 - Computation of $R_5$ and $L_1$ block
Set $k = 1$

$k > \text{number of points in the curve?}$

False

Determine $R_2(k)$ and $C_1(k)$ (eq. 5.51)

Determine $R_3(k)$ and $R_4(k)$ block

Determine $C_2(k)$ block

Determine $C_3(k)$ block

True

Increase $k$ by 1

Determine $R_3(k)$ and $R_4(k)$ block

Error computation (eq. 5.23)

Choose $R_2, R_3, R_4, C_1, C_2, C_3$

Adjustment Block

End

Input data: Nyquist plot$(k)$

Figure 12.1 - Main flowchart
Figure 12.2 - Determine $R_3$ and $R_4$ block

Figure 12.3 - Determine $C_2$ block
Figure 12.4 - Determine $C_3$ block
Figure 12.5 - Adjustment block
Attachment 6

Figure 13.1 - Main flowchart
Figure 13.2 - Determine $R_5$ and $L_1$ block

Figure 13.3 - Computation of $R_5$ and $L_1$ block
Set $j = 1$

- $j >$ number of points in the curve?
  - False: Computation of $R_3(j)$ (eq. 5.77) and $R_4(j)$ (eq. 5.84)
  - True: Error computation (eq. 5.23)
    - Choose $R_3$ and $R_4$ False
      True
      Start
      End

Figure 13.4 - Determine $R_3$ and $R_4$ block

Set $j = 1$

- $j >$ number of points in the curve?
  - False: Computation of $C_2(j)$ (eq. 5.82)
  - True: Error computation (eq. 5.23)
    - Choose $C_2$ False
      True
      Start
      End

Figure 13.5 - Determine $C_2$ block
Figure 13.6 - Determine $C_3$ block
Figure 13.7 - Adjustment block