Modeling a Proton Exchange Membrane Fuel Cell using Non-Equilibrium Thermodynamics

A Second Law analysis of assumptions and parameters

Julio César García Navarro





Challenge the future

Modeling a Proton Exchange Membrane Fuel Cell using Non-Equilibrium Thermodynamics

A Second Law analysis of assumptions and parameters

by

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in partial fulfillment of the requirements for the degree of

Master of Science in Sustainable Energy Technology

at the Faculty of Applied Sciences, Delft University of Technology, to be defended publicly on Monday June 30th, 2014 at 2:30 PM.

Student number: 4243919

Report number:2627Supervisor:Prof. dr. techn. et dr. ing. S. KjelstrupTU DelftTU DelftTU Delft Thesis committee: Prof. dr. ir. P. V. Aravind Prof. dr. ir. D. Bedeaux Prof. dr. ir. B. J. Boersma Prof. dr. ir. T. J. H. Vlugt

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Preface

The thesis that stands before your eyes right now, dear reader, is the result of nine months of work; some months went smoother than others, but I (and this thesis) managed to survive and live another day.

As far as I can see it, there were three major difficulties I encountered: first, I had to understand the language of Simulink[®]. Despite the fact that I had already worked with Simulink in previous years and with different projects, I never stopped (and I still do not) learning about how many ways there are for Simulink[®] not to work. In the end, I had to develop a computer program in which I told MatlabTM to tell Simulink[®] what to do because it turned out that I did not quite understood Simulink[®]'s language. It also appeared to be that MatlabTM and Simulink[®] are not as good at communicating with each other as I expected them to be (and yes, I am looking at you, "nested functions not allowed in MatlabTM blocks") so I had, in the end, to produce a Simulink[®] program filled with MatlabTM code blocks; it ended up not very pretty but boy does it run fast.

The second difficulty I had was actually understanding the model I utilized. It turns out that scientists do not make the best communicators (maybe that is why people still believe in Creationism and in Global Warming being a lie) which made the documentation produced by the sources I cite here pretty hard to understand. This was also a reason why I wrote the whole Chapter two as clear as possible, defining, in every section, all the variables and assumptions I utilized, and the model implementation diagram at the end of the chapter. I aimed at reproducibility and understandability of the model and I hope to have achieved it, so that, if another person wants to improve the model (or at least verify my findings) they could do so with the computer program of their preference or with the methodology they find more suitable.

The third difficulty I had was in the actual writing of this document. The $\[Mathbb{E}]_X$ language is actually very hard to fully understand; it is a bit like jazz music: unless you actually play it, it is highly likely that you do not really get it. I began using LyX, a graphic interface for $\[Mathbb{E}]_X$ for the writing of the thesis (and did the most part with that software), but the document did not look attractive enough, so I had to migrate all of the work to the simple non-graphic interface from which I am writing these lines. The toughest part was, though, the making of all the tables and figures you will find in this document. The programs that I use for those images are, in my opinion, very esoteric (given the fact that I became a $\[Mathbb{M}]_X$ user only a couple of months ago) and thus changing even the smallest bit of the figures takes a lot of time and effort, not to mention code errors here and there. Another very tough part of the writing of this thesis was using the custom TUDelft template (in case you were wondering why there was so much cyan color, that is the reason) because I had to browse through a code that I barely understand in order to make the document look as nice as possible.

Despite all the problems encountered, this thesis was finished; it may not be the prettiest thesis ever written (in my opinion it is, but that is because this is my baby and I love her no matter how she looks like, although she is pretty good looking) but it is the result of my hard work and I am proud of it. I am glad I chose this topic because I am aware now how complicated a fuel cell actually is and hope that I had contributed, at least in the smallest way, to the scientific world and to the incursion of fuel cells in our lives.

If you were wondering, dear reader, that I am an ungrateful human being, wonder no more: here comes my gratitude made text. I would like to thank the Engineering Thermodynamics group for letting me be a part of them; despite the fact no one else was working in a similar topic and thus I had no other fellow student to talk to about what I was doing, it was nice to know what the rest of the group members were doing, along with the technical and administrative problems that surround (almost)

every human organization I have seen. I guess that Molecular Simulations and Carbon Dioxide capture have to do, in their own way, with fuel cells and it felt nice to be part of a group. I would like to thank my exam committee for being there and validating my work, because I feel that, without them, this could never be acknowledged as science. My gratitude goes to TUDelft as well: thank you for admitting me into one of your Master programs, although I feel like the TUDelft should express some gratitude as well because, after all, I paid (a substantial amount of) money to receive education and, where I come from, business owners thank the customers for buying rather than the latter for being given the opportunity to buy. Thus, thank you and you're welcome, TUDelft.

My greatest share of gratitude lies with my parents. You see, I grew up not in a typical, Hollywoodesque home but in a place where I had the blessing of having some of the best role models there can ever exist. My father taught me that, despite all that can happen to you, a smile on the face is the best way to go, because the future will always be full of surprises and many good things can come. He is the person that is always telling jokes and laughing at life with such a good spirit that he irradiates some kind of aura that very few people can. I think I inherited his good spirit and warm heart, not to mention a great deal of his personality. My father is the kindest person I know; I will be eternally grateful for raising me the way he did, for I have tried to carry on with his teachings and I believe that the world is a better place because of his existence in it. Thank you father, for showing me that, even if the world can sometimes seem to be obscure and desolate, there is a flame in everyone's heart that one ought to unleash, and this flame will light up even the darkest corner of life and fill up the largest void; this flame is fueled by kindness one has towards others, especially to the ones that cannot do anything for you in return.

My mother is one of my personal heroes (she is at the same level with Iron Man and King Arthur Pendragon or even higher) because her story is a tale of conquest, of victory over life, and also over selflessness. She taught me that, in life, one should have four virtues: one ought to be respectful, honest, responsible and hard working, and I have tried to rule my life following her teachings and her example. She came out from a very poor village in a very poor part of Mexico (the level of poorness that First World inhabitants will never understand) and she had nothing, not even a father to raise her and her five brothers. She did not go to school beyond six years of elementary school and a year of secondary education because she could not afford to go. She had to endure sometimes not having anything to eat nor hot water to bathe with; sometimes not even footwear. She came to Mexico City and, through discipline and hard work, she managed to overcome all the difficulties life gave her, raising and educating three children, and I am blessed to be one of them. If there is something I admire the most about her is her selflessness: she has never stopped giving and not asking anything in return. She paid for my education at TUDelft and is willing to pay for a thousand more TUDelfts just to see me prepare well enough so that my children do not have ever to live what she lived (I am fortunate to never have lived that either). Thank you mother, for giving me the best example there can ever be about how life is a quest that never ends and you will always succeed if you follow a path of righteousness and magnanimity. Thank you, mother and father: you have given me the responsibility to carry on your teachings to my children and to their children as well, and I will dedicate my life to make you proud. I love you mom and dad.

I believe that I could not have come this far in life without the support of the rest of my family members, to whom I would like to dedicate these lines: thank you, Paco and Montse, you guys are the best brother and sister a guy like me can have. I admire your ambition, Paco, may you one day find yourself to be the most successful businessman in the world (or at least in the catering world), and hope that one day we can work together in the family business. If there is another example of a person that has found her inner flame, that would be my sister Montse. Please never lose your kind spirit, because more people look up to you than what you think. I love you guys. Tío Chino: I never got a change to thank you for supporting me in my first years of studying in Mexico a few years ago. You are one of the pillars of the family and one of the main reasons I am here, in Europe, writing this document. Thank you, Tío Chino, I love you. Another piece of gratitude flies to the rest of my family, for I know that, without them, I would be lost in the sea of madness this world can sometimes become. Thank you cousins, uncles, aunts, grandmas (may you rest in peace, Mama Ney) and grandpas (I never forgot you and never will, Abuelo Quicho). Finally, to Sebas: dude, you will be as great a man as you

want to be; I am honored to be your role model, and I hope you become the man you are destined to become, for I have great hopes on you. I love you, dude.

This preface would not feel completed unless I give a word of gratitude to my friends. I really miss all of you, guys and gals, I wish you were with me over here. Even though I might have reduced or even lost contact with some of them, I really appreciate their support; I know I would have never dared leave the nest if my friends would not have been there to show their support. They are the family I picked and I am sure that I chose the best: you are my friends because I admire each and every one of you guys; you have taught me many things I did not know about life and about people and I feel like I could not have made it this far if I had no one to look up to as I had you. I love all of you, may I forever remain a part of your lives, for it has been a pleasure sharing this Earth with you. Thank you, my friends.

I do not know if you still follow me, oh dearest of readers, for I have written a very personal preface and it is highly likely that I lost you somewhere in the process. If you are with me at this point, feel glad about yourself: you have succesfully read two pages of my thesis; kudos for you! I will reward you with a very precious thing: a short guide to reading my thesis and not die trying. You see, this thesis consists of more than sixty figures and tables and it is easy for a person to become confused between those lines, so I will tell you the best way to browse this document. This thesis is about, as you might have guessed when reading the title, a computer model of a fuel cell. Chapter one tells you what in God's name I am talking about, so, unless you have no idea what a fuel cell is, you can skip it. Chapter two documents the model I utilized and how I did it. If you are interested in that, please be my guest and carefully read the ninety four equations, along with all the definitions I use. Chapter three shows the results, which basically is me repeating myself, for I simply ran the computer model by changing a few numbers here and there and maybe adding a couple more equations, but the simulations are in essence the same. Chapter four summarizes what I found which is, in simple words, that I improved the model. The simplest way of addressing this document is reading the Abstract and Chapter four. Thank you, reader, for being here with me at this moment. I hope that you find this document at least slightly amusing; if you did not, you can still make this thesis useful; if you have a hard copy, you can use it to level that table in your living room that looks kind of crooked or if you happen to have an electronic version, I suggest you use the name of the thesis as a folder name where you can safely hide files from potential privacy invaders.

Thank you, reader, and I wish you good luck with the rest of this document.

Julio César García Navarro Delft, June 2014

Abstract

In this work, a model derived from Non-Equilibrium Thermodynamics, for the Proton Exchange Membrane Fuel Cell, was utilized in order to explore the effect of the assumptions and the transport parameters in the consistency of the model; that is, the compliance of the model with the Second Law of Thermodynamics.

This thesis begins with a short overview of the fuel cells as well as an introduction to Non-Equilibrium Thermodynamics. The model utilized is thoroughly depicted, along with all the assumptions made and the parameter set utilized in previous works. In order to numerically evaluate the consistency of the model, the entropy production departure was introduced, which accounts for the difference between the entropy production calculated with Non-Equilibrium Thermodynamics and the entropy production calculated with the entropy flux at the boundaries of each layer of the fuel cell. An optimization scheme was also introduced, where the transport parameters were varied in order to find the minimal entropy production departures, leading to a better consistency of the model with the Second Law of Thermodynamics.

It was found that the parameter set utilized by previous publications lead to entropy production departures as high as 80% and, after implementing the optimization scheme, these figures decreased to 22%. A model was introduced to take into account the water transport across the electrodes of the PEMFC. This model was utilized as a replacement for the water equilibrium assumption made in the electrodes, and it was found that the inclusion of this water transport across the electrodes increased the consistency of the PEMFC model with the Second Law of Thermodynamics, calculating entropy departures as low as 8%.

Further simulations of the model were carried out, in order to evaluate the effect of the relative humidity of the hydrogen and air streams on the voltage produced by a PEMFC. It was found that low relative humidity of the inlet gases leads to a substantial decrease in the voltage of the fuel cell, with corresponding decreases in the power produced by as much as 67% when operating at high current densities. In this work, a new transport parameter was introduced, namely the electrode water diffusivity, and the optimization scheme was introduced in order to estimate the value of this parameter, in the interval between 2.6×10^{-3} m/s and 5.8×10^{-3} m/s.

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1

Introduction

1.1. Fuel cells in the industry

Fuel cells have gotten, in recent years, a significant amount of attention from the media, partially because automobile manufacturers have gotten on board of the hydrogen venture: Mercedes-Benz presented in 2010 its Fuel Cell Drive Technology vehicle (the F-CELL), while Toyota and Hyundai plan to incorporate to the market hydrogen-powered versions of some of their most popular vehicles, the Camry and the Tucson, respectively, by 2015. The Japanese car manufacturer Honda has, however, opened the market for fuel cell vehicles in the United States with the incursion of the FCX Clarity (Figure 1.1), which became the first fuel cell-powered vehicle produced in series and available to the market.



Figure 1.1 – The Honda FCX Clarity: the world's first fuel cell vehicle available to the market. Source: Honda (2014).

The incursion of fuel cell vehicles requires, as one might expect, the coordination of private companies with the public sector, mainly in terms of infrastructure for the hydrogen supply because, due to technical deterrents, hydrogen cannot be transported in the mainstream gas pipes that have already been built. Nevertheless, fuel cell vehicles are seemed as a possible alternative to overcome the main issues that arise with the use of battery-powered cars, namely limited range and long charging times (Chan, 2007). The two competing storage technologies for transportation applications (fuel cells and batteries) are in different stages of development. Batteries have experienced a rather accelerated evo-

The image at the cover of this document was taken from NASA (2014).

lution, driven by the gigantic increase of the share of the portable electronics in the commodity market in the past few decades. Still, the main issues of batteries as energy storage for vehicles, limited range and long charging times, have remained largely unaddressed, despite the fact that current research has been trying to solve those problems. Fuel cells, on the other hand, have received less attention from the industry due to the lack of a widespread hydrogen supply infrastructure, which has hindered the progress needed for the technology to become both technically and economically feasible on a large scale. von Helmolt and Eberle (2007) provide a review of the current stance of the fuel cell technology in transportation applications.

Transportation is not the only application for which the market is in favor of welcoming hydrogen and fuel cells: backup applications (especially intended for telecommunications towers) have been in the scope of the major fuel cell manufacturers in the market. Companies such as Ballard Power, Proton Power Systems, ITM Power and Plug Power have aimed at backup applications with their products, although, not surprisingly, neither company has reached a profitability state. The main reason for this is the harsh competition for backup power: due to the current market status, the opportunity cost for a backup application is the use of mainstream fuel (namely diesel, gasoline or gas) which, as one may expect, offers net present values larger than zero and much lower capital costs. The main technical disadvantage a backup fuel cell system has, especially when it is intended for off-grid applications, is the need for a fuel reforming device, in order to switch the problem of supplying hydrogen to a much more manageable problem of supplying methanol, natural gas or even liquefied petroleum gas (LPG). Even a battery system would represent a smaller expenditure for on-grid applications, such as energy backup for computer servers and other systems in which access to the grid is ensured. However, wherever there is need for a resilient energy supplier and access to the electric grid is not an option, fuel cell systems can be utilized to successfully fill that market gap.

Fuel cell systems can be thought of as energy storage devices and, therefore, their natural competitors are batteries. In which applications can a fuel cell system fulfill the requirements needed for an energy storage system in order to be profitable? One of the main arguments in favor of fuel cell devices is related to the energy storage capacity as a function of size. Figure 1.2 shows the comparison of storage capacity and system volume for two types of storage technologies: Lithium-ion batteries and Direct Methanol Fuel Cells.



Figure 1.2 – System volume as a function of the electrical energy stored, for Li-ion batteries and Direct Methanol Fuel Cells (DMFC), and energy requirements of two portable electronics. Source: Larminie et al. (2003), page 159.

From Figure 1.2, it is clear that a lithium battery is more suitable to fulfill small energy requirements, such as mobile telephones, and that it is even smaller than low power DMFC's. For larger energy storage requirements (portable computers), however, a 5W DMFC would occupy a smaller volume than a Li-ion battery. Figure 1.2 depicts one of the main competitive advantages of the fuel cells over batteries: smaller system sizes for medium-scale power applications; the other main advantage of fuel cells over batteries are the (much) faster recharging times.

According to an interview done to Stephen Karaffa, Ballard Power's COO, "[...] the catalysts for future growth will be off-grid continuous power, distributed generation and zero emission transportation" (Forbes, 2014). It is with the help of those future growth catalysts that fuel cell systems can position themselves as the benchmark in the energy storage market, and I am certain that, with the lobbying of the automotive industry, we will see fuel cells become a major player in the renewable energy landscape of the short-term future.

1.2. What is a fuel cell system?

Fuel cells are electrochemical devices that convert chemical energy of a reaction directly into electrical energy (Hirschenhofer et al., 1998, page 1-1). In electrochemistry, such a device is called a *Galvanic cell*, in honor of one of the scientists that helped in their development and understanding, Luigi Galvani. The chemical reactions that occur in a fuel cell are always of the reduction-oxidation type, and the physical setup of a fuel cell is relatively simple: it consists of two electrodes, one anode (where the oxidation of a chemical compound takes place) and one cathode (where the reduction of a different chemical compound takes place); both electrodes are separated by a bulk phase, whose purpose is to maintain electric contact in the system by exchanging ions between both electrodes. Figure 1.3 shows the schematics of a galvanic cell.



Figure 1.3 – A galvanic cell, consisting of a zinc anode and a copper cathode. Source: Brown et al. (2011), page 836.

In Figure 1.3, the oxidation of zinc and the reduction of copper ions take place, creating a flow of electrons that can be used to produce work. It is important to remark that, according to the definition of a fuel cell (given in the previous paragraph), devices such as batteries fit into the description of a fuel cell: in a lithium battery, for example, lithium is oxidized at the anode and cobalt (present in the cathode in the form of cobalt oxide) is reduced, in order to form lithium cobaltate. Other galvanic cells, such as the one depicted in Figure 1.3 can also be regarded as fuel cells: the definition given by Hirschenhofer et al. (1998) applies to the different types of electrochemical cells where spontaneous reactions (that is, reactions in which the entropy increases) take place. The concept of a fuel cell is related, however, to galvanic cells whose reactants would combust (that is, react with oxygen) and, as such, the reactants consist of fluid phases that are constantly supplied to both electrodes, maintaining

a continuous reduction-oxidation process inside the cell. A fuel cell, as has just been described, consists of different layers: an anode, a cathode, both with a porous layer intended to distribute the reacting gases in the whole surface of each electrode, a separating and ion conducting phase and two current collectors (one at each electrode), whose purpose is, as can be deduced from their name, to collect the electric current produced in the fuel cell. Figure 1.4 shows the schematics of a Proton Exchange Membrane Fuel Cell.



Figure 1.4 – Schematics of a Proton Exchange Membrane Fuel Cell (PEMFC), with its five distinctive layers and a current collector at each side. Source: Kjelstrup and Røsjorde (2005).

The main feature that distinguishes one type of fuel cell from the rest is the ion conducting phase, and, in this sense, there are five different types of fuel cells. Alkaline Fuel Cells (AFC) utilize alkaline phases as ion conducting layers, and the ion that is transported between cathode and anode is typically the hydroxide ion (⁻OH), since the main compound that is oxidized is hydrogen. Proton Exchange Membrane Fuel Cells (PEMFC) transport protons (H⁺) from the anode to the cathode through a membrane that usually consists of an organic, solid polymer with functional groups that can release protons when hydrated. Phosphoric Acid Fuel Cells (PAFC) use, as the name suggests, phosphoric acid that is contained within a carbon matrix and, again, protons are conducted from the anode to the cathode of the fuel cell. Molten Carbonate Fuel Cells (MCFC) operate under transport of carbonate ions (CO_3^{2}) that flow from the cathode to the anode and, thus, the ion conducting phase consists of a molten carbonate phase. Solid Oxide Fuel Cells (SOFC) transport oxide ions (O²⁻) between the cathode and the anode of the fuel cell, and their electrolyte is a solid phase (usually a ceramic material) through whose crystalline structure, oxide ions can travel. Other classifications for the different fuel cells rely on their typical operation temperatures, which range from less than 100°C for PEMFCs to nearly 1000°C for SOFCs, and this is determined by the type of ion conducting phase that is utilized in each one: PEMFCs are bound to operate at relatively low temperatures because of material impediments of the electrolyte (large temperatures would cause dehydration and eventually destruction of the proton conducting membrane), and their operation would stop if subject to high temperatures. High temperature fuel cells, like SOFCs, are required to reach high temperatures due to the fact that their electrolyte can only conduct ions when subject to those operating conditions. A special remark must be done here: many people talk about a sixth type of fuel cells, namely the Direct Methanol Fuel Cells (DMFC), although they are basically PEMFC whose reducer phase is methanol (CH_3OH) and, given the classification stated in this paragraph, they fall into the PEMFC category.

The main products of a fuel cell are chemically stable compounds, which, according to the fact that a fuel cell operates with reactants that would combust, consist mainly on water and carbon oxides (depending on the fuel used, of course); the other products are electric energy and, according to the Second Law of Thermodynamics, waste heat. It is because of this that a fuel cell cannot operate by itself: it needs several auxiliary components in order to receive a continuous supply of reactants and to get rid of the waste heat and the chemical compounds produced. These components are called *Balance of Plant* components and their choice is determined solely by the operation requirements of the fuel cell. Balance of plant components utilized in typical fuel cell operation schemes include oxidant suppliers (air blowers and compressors, mainly, since air is the most common oxidant used in fuel cells), reducer suppliers (methanol pumps, for example, are utilized for DMFCs) and heat removal systems.

In PEMFCs, the types of fuel cells which concern this work, there is a crucial balance of plant component utilized: the air humidifier. Since PEMFCs operate with hydrogen as a reducer and oxygen as oxidant, water is the product of the operation of these fuel cells. As it will be seen in this work, water is needed in order to achieve a correct operation of the PEMFC; in particular, water is needed in order for the Proton Exchange Membrane to actually be able to exchange protons between the anode and the cathode. An air humidifier is a device that exchanges the water carried by the exiting oxidant phase and delivers it to the entering stream, so as to maintain a closed water cycle in the system. Other balance of plant components might include fuel cleaning (so as to avoid the deterioration of the electrodes or the ion conducting phase) and devices utilized to transform the direct current produced by the fuel cell into alternating current, depending on the requirements of the electric load the fuel cell system will supply.

There could be, as well, devices whose purpose is to recover the waste heat and transform it into a useful form of energy, such as the production of steam to use in steam turbines or the heating up of working fluids intended for residential or industrial heating. The choice of the balance of plant components depends on the type of fuel cell utilized (as was said before) as well as on the end use of the produced material and energy streams. The bundle of fuel cell and balance of plant components is called a *Fuel Cell System*. Figures 1.5 and 1.6 show two examples of fuel cell systems intended, respectively, for stationary and transportation applications.





From Figures 1.5 and 1.6, it is clear that the choice of balance of plant components for a fuel cell system depend exclusively on the final use of the energy streams produced and, thus, there is no universal choice but rather a series of guidelines a system designer should follow in order to properly adapt fuel cell technologies to a particular application.



Figure 1.6 – Schematic diagram of a hydrogen-fueled, Polymer Electrolyte Fuel Cell (PEFC) system for automotive applications. The PEFC (which is the same as a PEMFC) Stack depicted here could correspond, for example, to the image presented in the cover of this document. Source: Ahluwalia and Wang (2005).

1.3. Modeling of the fuel cell

The design of a fuel cell system, as was stated before, involves the selection of, besides the appropriate materials for the fuel cell itself, adequate balance of plant components and the correct operating conditions. If the designer does not foresee the effects of the selection of a particular set of components and materials on the performance of a fuel cell, the system is bound to fail, causing economic losses and even endangering human lives. There is a tool available to scientists and industrial system designers, which is able to help in the prevention of the consequences of a faulty design: the modeling of the fuel cell system.

A model for a fuel cell is merely a mathematical representation of the physical and chemical phenomena that occurs inside it, but there can (and there are) a vast number of modeling possibilities, depending on what the desired level of understanding one wants to gain. There are, for example, mathematical models that focus on the transport processes that occur inside a fuel cell, while others focus on the effect of the balance of plant components on the performance of a fuel cell system.

One of the most relevant models that have been developed for PEMFCs is the model presented by Springer et al. (1991), which, among other things, provided experimental data on the water and charge transport of the ion conducting membrane. This particular model is perhaps the benchmark in the scientific community when it comes to modeling the PEMFC because it provided experimental measurements on transport parameters, which were, at the time of publication, not quite known. Other modeling efforts, such as that of Rowe and Li (2001) deviate from Springer et al. in the sense that they assume a non isothermal operation of the fuel cell, which is a more logical assumption but more difficult to model. The multidimensionality of the fuel cell is taken into account in models such as the one presented by Dutta et al. (2001). Models of the likes of Wöhr et al. (1998) and van Bussel et al. (1998) propose models for the dynamic variations of the transport of water and heat in the PEMFC, thus increasing the complexity of the modeling. Some modelers are more interested in the effect of the gas supply and distribution in the fuel cell (Jung and Nguyen, 1998), while others, such as Pukrushpan (2003) focus their modeling efforts towards the balance of plant components. Weber and Newman

(2004) offer a more comprehensive on the different models for PEMFCs.

Modeling of a fuel cell can bring substantial advantages to the design of the system, given the fact that a model can predict the effect of different operating conditions and thus aid on the selection of appropriate balance of plant components. Modeling can increase the understanding of the physical and chemical phenomena that occur in a fuel cell, so as to give guidelines on the construction of fuel cell devices and provide room for improvement.

1.4. What is Non-Equilibrium Thermodynamics?

Non-Equilibrium Thermodynamics (or NET) is a theory that was first described by Onsager (1931). In his work, Onsager provides a framework to explain, with fundamental physical principles, the experimental results obtained by some of the forefathers of thermodynamics such as Lord Kelvin and Helmholtz.

Non-Equilibrium Thermodynamics is based on the fundamental assumption that a macroscopic process is irreversible, but consists of a series of microscopic processes which are, however, reversible. According to Onsager, the main driver of a physical process is the rate of increase of entropy; that is, any physical process that leads to the degradation of energy can happen spontaneously. This principle was already known by Classical Thermodynamics, and is summarized in the Second Law, but the main difference between the Classical and the Non-Equilibrium Thermodynamics is the fact that, according to the latter, any two (irreversible) transport processes that take place simultaneously, are likely to interfere with each other to some extent (Onsager, 1931).

The main postulate of Non-Equilibrium Thermodynamics is that the transport processes that occur within a system are coupled. For example: Fourier's Law states that, whenever there is a temperature gradient in a system, heat will be conducted from the high temperature region to the low temperature one. The addition brought by Onsager is that this same gradient can lead to electric charge or mass being conducted along the same path heat is transported (but not necessarily having the same direction). Kjelstrup et al. (2010) provides a more thorough explanation of Non-Equilibrium Thermodynamics.

The postulates of Non-Equilibrium Thermodynamics might seem, for some, difficult to understand, but it has been proven experimentally that the transport processes are coupled within a system: consider, for example, the operation of a thermocouple. A thermocouple consists of two metals with different transport properties, which are joined in one of their ends, while the other remains separated from one another, and is utilized as a temperature measuring device. Figure 1.7 shows the schematics of a thermocouple.



Figure 1.7 – Texas Instruments Inc. ADS 1118 Thermocouple junction diagram. The operation of this sort of devices is explained by Non-Equilibrium Thermodynamics. Source: Texas Instruments (2014).

In a thermocouple, both metals are subject to the same temperature gradient and, as can be expected, this would cause the transport of heat from one side to the other. The interesting property of a thermocouple is that the coupling of the transport processes leads to charge transport in each of the metals (this is predicted by Non-Equilibrium Thermodynamics). Since the electric circuits are open, this charge transport leads to an electric potential difference across the two metals (caused by the different material properties of each metal), and this electric potential difference can be measured with a voltmeter (see Figure 1.7). This potential difference depends on the temperature gradient at which both metals are subject; thus, a thermocouple can be used as a temperature measuring instrument. The operation of a thermocouple would be impossible for Classical Thermodynamics to predict; therefore, Non-Equilibrium Thermodynamics is needed in order to give an explanation for the physical phenomena that occur in such a device.

There is an extension of the Non-Equilibrium Thermodynamics theory, called Extended Irreversible Thermodynamics, in which the microscopic transport processes are no longer regarded as reversible. In this sense, Extended Irreversible Thermodynamics is a more general theory than Non-Equilibrium Thermodynamics. It was found by Pavelka and Maršík (2013) that this extended theory of Non-Equilibrium Thermodynamics is only relevant for processes that happen at very high temperatures (such as the ones under which a SOFC operates), and the coupling of transport processes is treated in the same way as the original Non-Equilibrium Thermodynamics theory postulated by Onsager.

The relevance of Non-Equilibrium Thermodynamics in this work is that, like thermocouples, there is coupling of the transport processes that occur in a fuel cell. In a PEMFC, electric charge is being transported across the proton conducting membrane; it has been found experimentally that water is also transported and thus the transport of water and electric charge are coupled. This effect is commonly regarded as *electro-osmotic drag* and is essential for the performance of the PEMFC. Coupling of heat and mass, and heat and charge transport has also been found to happen in a fuel cell (Kjelstrup et al., 2013), and the understanding of this coupling is essential in order to be able to correctly predict the temperature, concentration and electric potential gradients throughout the fuel cell. The comprehension of the coupling of the transport processes is, as has been said before, not possible for Classical Thermodynamics to achieve, which means that Non-Equilibrium Thermodynamics is fundamental for the modeling of fuel cells. PEMFCs have been studied under Non-Equilibrium Thermodynamics: see, for example, the works of Glavatskiy et al. (2013), Kjelstrup and Røsjorde (2005) and Burheim et al. (2010).

1.5. Assumptions and parameters and the consistency of a fuel cell model with the Laws of Thermodynamics

In the mathematical modeling world, it is common knowledge that a model is only as good as the assumptions it makes, and the more unreasonable they are, the less relevant the model becomes. The choice of parameters utilized in the model also plays a fundamental role on the fuel cell modeling. One of the most common assumptions made in the modeling of a PEMFC refers to isothermal operation; as was commented in Section 1.3, models have been developed that incorporate this assumption, as well as models that get rid of it. Assumptions can be useful for the model, mostly in order to reduce its complexity, to save on computational time or to simplify the solution of the equations that it containes. Nature, however, does not know of any assumptions: actual physical and chemical processes that occur all around us consist of a bundle of many transport processes occurring at the same time, whether we can perceive them (either through the senses or with measuring instruments) or not. The role of an assumption is, then, to help fit a mathematical model to reality.

Much of the work done around PEMFCs involves the calculation of transport parameters from experiments, especially the parameters of the proton exchange membrane. Springer et al. (1991) and Zawodzinski Jr et al. (1991) published a series of experimental results to predict the diffusion coefficient and the electric conductivity of the ion conducting membrane of a PEMFC. Burheim et al. (2010), Khandelwal and Mench (2006) and Vie and Kjelstrup (2004) present results that lead to the calculation of the heat conductivity of the membrane of the PEMFC, while Ge et al. (2006) provides experimental values of the electro-osmotic drag coefficient. Attention has also been given to the electrodes of the PEMFC,

which, as has been said in Section 1.2, are the central components of a fuel cell. Publications from Ramousse et al. (2009) and Thomas et al. (2013) show interest in the experimental measurement of the heat and water flows between the anode and the cathode of a fuel cell, while Herrera et al. (2012) experimentally determines the voltage losses that occur in a PEMFC due to, among other phenomena, the chemical kinetics at both electrodes. The coupling of heat, mass and charge in a PEMFC has also been experimentally demonstrated in works such as the one of Kjelstrup et al. (2013).

The publications cited in the previous paragraph are but a sample of the amount of experimental data available (many more can be found in the scientific publications databases); the amount of data is as numerous as diverse the authors and the research groups can be, each one of them focused on specific layers and/or processes inside a fuel cell. Some publications, while focusing on the same process or layer, arrive at different conclusions or propose different transport parameters; this can be a consequence of different material and setup choices, and most of the time the experimental methodology varies. Regardless of the differences in the experimental setups and measuring techniques utilized, the conclusions at which different publications arrive happen to sometimes deviate substantially, originating debates among those research groups. It is clear, then, that the parameter choices available for use in a fuel cell model are wide and, thus, a significantly relevant part of the modeling is the correct choice of the parameter set. How can a modeler know precisely which parameter set and which assumptions to make, in order to accurately model a fuel cell?

One of the greatest advantages of Non-Equilibrium Thermodynamics is that it gives the possibility to calculate the entropy production in a system by looking at the heat, mass and charge fluxes, as well as the temperature, electric potential and chemical potential gradients. The steady state entropy production in a system can be calculated, according to Classical Thermodynamics, as the difference between the entropy that leaves and the one that enters the system. Combining these two ways to calculate the entropy production in a system, results in a method to verify the consistency of the model with the Laws of Thermodynamics: the produced entropy, calculated with Non-Equilibrium Thermodynamics, should be identical to the produced entropy, calculated with the difference in the exiting and the entering entropy flows in the system. Although the transport parameters play a role in the calculation of the material and energy flows in a fuel cell and thus affect both methods of calculating the produced entropy, it is highly possible that an incorrect set of parameters could lead to a deviation between the produced entropy, calculated with both methods. The same applies to the assumptions utilized: different assumptions would lead to leaving out certain effects in the model of the fuel cell, which would cause an incorrect prediction of the temperature gradient across the fuel cell, for example, and this can, in turn, lead to a deviation between the entropy production calculated using both methods. Non-Equilibrium Thermodynamics can be used, then, to guide the correct choice of parameters and assumptions of a model that intends to describe the transport processes that occur in a fuel cell.

1.6. Objective of this work

In this work, the Non-Equilibrium Thermodynamics model for the Proton Exchange Membrane Fuel Cell, presented by Kjelstrup and Røsjorde (2005), will be utilized to provide insight of the heat, mass and charge transport that occur in such a device. The model will utilize assumptions that are common in the PEMFC modeling literature (see Springer et al., 1991, Pukrushpan, 2003, Rowe and Li, 2001 and Kjelstrup and Røsjorde, 2005), namely the assumption of water equilibrium across the anode of the PEMFC, the assumption of a membrane saturated with water at the interface between membrane and cathode, and the assumption of operation with water saturated hydrogen and air flows into the PEMFC.

The model utilized in this work follows the set of equations derived by Kjelstrup and Røsjorde (2005), although the boundary conditions utilized by Kjelstrup and Røsjorde are different from the ones used in this work: the temperature of the cathode side porous transport layer was allowed to vary in this work, while in the publication of Kjelstrup and Røsjorde (2005), the temperature of both the cathode and the anode side porous transport layer was set to be equal. The modeling of the PEMFC done in this work is similar to the one presented by Kolstad (2013) (Membrane processes relevant for the polymer electrolyte fuel cell), and the parameter set used for the simulations has also been taken from this reference.

The objective of this work is to test the effect of the parameter set and assumptions utilized in previous publications (Kolstad, 2013) on the consistency of the model with the Second Law of Thermodynamics. The consistency criteria that will be utilized is the entropy production departure: that is, the entropy production calculated with Non-Equilibrium Thermodynamics and with an entropy balance on the system. This work will provide an optimization scheme, in which transport parameters and boundary conditions utilized with the model are going to be tested, in order to obtain a set of values with which the entropy production departure of the model gets to a minimum.

Finally, this work will quantify the entropy produced in a PEMFC, as well as provide temperature, water concentration, voltage and heat flux profiles throughout the fuel cell. A guideline will be produced, so as to improve the understanding of the balance of plant component choices of a PEMFC system, as well as for the operation conditions under which this type of fuel cell should operate, in order to ensure a high performance and optimal power production.

2

Mathematical modeling of the Proton Exchange Membrane Fuel Cell

2.1. Anode-side porous transport layer

2.1.1. Coupled transport in the anode-side porous transport layer

In the anode-side porous transport layer (or anode-side PTL), a mixture of hydrogen and water enters the fuel cell from the flow fields of the current collector (the empty spaces of the current collector in Figure 1.4) and are transported towards the anode through a porous carbon matrix. Heat and electric current also enter the porous transport layer (coming from the current collector) and have the same direction as the flow of hydrogen and water; this is illustrated in Figure 2.1.



Figure 2.1 – Schematics of a fuel cell, that shows the different fluxes that are present in the anode-side porous transport layer. The term J'_q represents transported heat, J_{H_2} represents transported hydrogen, *j* represents electric current and J_{H_2O} represents transported water.

2.1.2. Mathematical model of the anode-side porous transport layer

The steady state mass balance in the system can be expressed as follows:

$$J_{H_2} = \frac{j}{2F} \tag{2.1}$$

Where J_{H_2} is the molar hydrogen flux, *j* is the electric current density and *F* is Faraday's constant (96485 C/mol).

The complete set of equations that represent the transport processes that happen in the anode-side porous transport layer is the following:

$$\frac{dT_{AP}}{dx} = -\frac{1}{\lambda_{AP}} \left[J'_{q,AP} - q^*_{w,AP} \left(J_{D,AP} - t_{w,AP} \frac{j}{F} \right) - \pi_{AP} \frac{j}{F} \right]$$
(2.2)

$$\frac{dx_{w,AP}}{dx} = -\frac{q_{w,AP}^* x_{w,AP}}{RT_{AP}^2} \frac{dT_{AP}}{dx} - \frac{1}{D_{w,AP}} \left(J_{D,AP} - t_{w,AP} \frac{j}{F} \right)$$
(2.3)

$$\frac{d\phi_{AP}}{dx} = -\frac{\pi_{AP}}{FT_{AP}}\frac{dT_{AP}}{dx} - \frac{t_{w,AP}RT_{AP}}{Fx_{w,AP}}\frac{dx_{w,AP}}{dx} - r_{AP}^{ohm}j$$
(2.4)

$$\frac{dJ'_{q,AP}}{dx} = -j\frac{d\phi_{AP}}{dx} - \left(J_{H_2}Cp_{H_2,AP} + J_{w,AP}Cp_{w,AP}\right)\frac{dT_{AP}}{dx}$$
(2.5)

$$\frac{d\sigma_{AP}}{dx} = -\left(\frac{J'_{q,AP}}{T^2_{AP}}\frac{dT_{AP}}{dx} + \frac{j}{T_{AP}}\frac{d\phi_{AP}}{dx} + \frac{J_{D,AP}R}{x_{w,AP}}\frac{dx_{w,AP}}{dx}\right)$$
(2.6)

Where T_{AP} is the temperature of the system, λ_{AP} is the heat conductivity, $J'_{q,AP}$ is the measurable heat flux, $x_{w,AP}$ is the water mole fraction, R is the universal gas constant (8.314 J/mol K), $D_{w,AP}$ is the diffusivity of water in hydrogen, ϕ_{AP} is the electric potential, $t_{w,AP}$ is the transference coefficient for water, r_{AP}^{ohm} is the electric resistivity of the layer, $Cp_{H_2,AP}$ and $Cp_{w,AP}$ are the specific heat capacities of hydrogen and water, respectively and σ_{AP} is the entropy production of the layer. It is clear, then, that the subindex AP depicts the values at the anode-side porous transport layer.

 π_{AP} is the Peltier heat of the layer, defined as:

$$\pi_{AP} = -T_{AP} \left(\frac{1}{2} S_{H_2,AP} + S_{e,AP} \right)$$
(2.7)

With $S_{H_2,AP}$ being the entropy of the hydrogen and $S_{e,AP}$ the transported entropy of electrons.

 $q_{w,AP}^*$ is the heat of transfer for water in this layer, which is assumed to have the following form (Kjelstrup and Røsjorde, 2005):

$$q_{w,AP}^* = -T_{AP}S_{w,AP}$$
(2.8)

 $J_{D,AP}$ is called the interdiffusional flux; it represents the fact that water and hydrogen are both diffusing through the anode-side PTL. The interdiffusional flux depicts the net water flux, taking as a frame of reference the hydrogen flux; it is defined as (Kjelstrup and Røsjorde, 2005):

$$J_{D,AP} = \left(\frac{J_{w,AP}}{x_{w,AP}} - \frac{J_{H_2}}{x_{H_2,AP}}\right) x_{w,AP}$$
(2.9)

With $x_{w,AP}$ and $x_{H_2,AP}$ being the water and hydrogen mole fraction, respectively.

2.1.3. Model consistency of the anode-side porous transport layer

The model for the anode-side porous transport layer can be validated using two different equations: the entropy production equation and the entropy flux difference. The entropy production equation corresponds to equation 2.6, and the calculated value at the boundaries of the layer has to be equal to the difference between the entropy flux that exits and the entropy flux that enters this part of the fuel cell. The entropy flux difference is defined as:

$$\Delta J_{s,AP} = \frac{J'_{q,AP,exit}}{T_{AP,exit}} - \frac{J'_{q,AP,entrance}}{T_{AP,entrance}} + J_{w,AP} \left(S_{w,AP,exit} - S_{w,AP,entrance} \right) + J_{H_2} \left(S_{H_2,AP,exit} - S_{H_2,AP,entrance} \right)$$
(2.10)

Where the values with an *exit* subindex represent the values of the depicted variables, at the exit of the layer; that is, the result of the set of differential equations 2.2 to 2.6 for the full thickness of the membrane. Similarly, the values with an *entrance* subindex represent the initial conditions of the same system of equations. $S_{w,AP,exit}$ and $S_{w,AP,entrance}$ refer to the entropy of the water at the exit and entrance of the layer, while $S_{H_2,AP,exit}$ and $S_{H_2,AP,entrance}$ are entropy values for hydrogen calculated at the same locations in the layer (that is, with $T_{AP,exit}$ and $T_{AP,entrance}$, respectively).

In order to quantify the degree of validity of the model (and thus of the parameters), the *entropy production departure* is introduced:

$$S_{dev,AP} = \frac{\sigma_{AP,exit} - \Delta J_{s,AP}}{\Delta J_{s,AP}} * 100\%$$
(2.11)

Where $\sigma_{AP,exit}$ represents the entropy production calculated at the total thickness of the anode-side PTL. The closer the value of $S_{dev,AP}$ is to zero, the more consistent the model is (and are thus the chosen parameters and assumptions). Moreover, this parameter can give an idea of which value is larger (the entropy production or the entropy flux difference) and of the order of magnitude of the deviation.

2.2. Anode

2.2.1. Role of the anode in the operation of the fuel cell

In the anode, hydrogen is dissociated with the help of a catalyst (usually it consists of platinum deposited on a carbon support) and protons (H⁺) are formed, according to the half-cell reaction:

$$\frac{1}{2}H_2 \rightleftharpoons H^+ + e^-$$

In order for the anode half-cell reaction to happen, there needs to be a junction between the anodeside porous transport layer, the catalyst and the membrane (the so-called *triple junction*). In the anode, for which an illustration is provided in Figure 2.2, the heat, hydrogen, water and charge are transported through the porous carbon matrix (black lines); hydrogen needs to reach the catalyst (white circles), where it will be oxidized into protons, which will furthermore be transported to the membrane (gray surface).

It is important to be noted that water undergoes a phase change in this layer: water is carried in the vapor state by the humidified hydrogen that comes from the anode-side PTL, but it enters the proton-conducting membrane in the liquid state; ths condensation of water causes an increase in the measurable heat flux produced in the anode.

2.2.2. Mathematical model of the anode

The steady state mass balances of hydrogen and water are expressed as follows:

$$J_{H_2} = \frac{J}{2F}$$
(2.12)

Where J_{H_2} is the molar hydrogen flux, *j* is the electric current density and *F* is Faraday's constant (96485 C/mol).

$$J_{w,AR} = J_{w,AL} = J_{w,AP}$$
(2.13)

Where $J_{w,AR}$ represents the water flux at the right hand side of the anode (the value closer to the membrane) and $J_{w,AL}$ represents the left-most value, namely the value at the exit of the anode-side porous transport layer.

The temperature of the anode surface can be calculated with:

$$T_{AS} = T_{AL} - \frac{1}{\lambda_A} \left[J'_{q,AL} - q^*_{w,AL} \left(J_{w,AL} - t_{w,AL} \frac{j}{F} \right) - \pi_{AL} \frac{j}{F} \right]$$
(2.14)



Figure 2.2 – Schematics of a fuel cell anode, that shows the different material and energy fluxes. The term J'_q represents transported heat, J_{H_2} represents transported hydrogen, *j* represents electric current, J_{H_2O} represents transported water and J_{H^+} represents transported protons. The black lines represent the anode side porous transport layer, the small white circles (catalyst) and large black circles (support) represent the anode surface, and the gray, continuous area, is the membrane. Source: Larminie et al. (2003), page 74.

Where T_{AL} represents the temperature at the left hand side of the anode (the value at the exit of the anode-side PTL), λ_A is the heat conductivity of the anode and $t_{w,AL}$ is the transference coefficient of the left hand side of the anode (thus the transference coefficient of the anode-side PTL).

 $q_{w,AL}^*$ is the heat of transfer of water in the anode, calculated as:

$$q_{w,AL}^* = -T_{AL}S_{w,AL}$$
(2.15)

With $S_{w,AL}$ being the entropy of the water at the left hand side of the anode.

 π_{AL} is the Peltier heat of the left hand side of the anode, calculated as:

$$\pi_{AL} = -T_{AL} \left(\frac{1}{2} S_{H_2, AL} + S_{e, AL} \right)$$
(2.16)

Where $S_{H_2,AL}$ is the entropy of the hydrogen at the left hand side of the anode and $S_{e,AL}$ is the transported entropy of electrons.

The temperature of the right hand side of the anode (which will be the initial condition of the membrane) is calculated as follows:

$$T_{AR} = T_{AS} - \frac{1}{\lambda_A} \left[J'_{q,AR} - q^*_{w,AR} \left(J_{w,AR} - t_{w,AR} \frac{j}{F} \right) - \pi_{AR} \frac{j}{F} \right]$$
(2.17)

Where $t_{w,AR}$ is the transference coefficient of the right hand side of the anode (the electro-osmotic drag of the membrane) and the values of $q_{w,AR}^*$ and π_{AR} are calculated as follows:

$$q_{w,AR}^* = -T_{AR} S_{w,AR} \tag{2.18}$$

Where $S_{w,AR}$ is the entropy of the water at the right hand side of the layer.

The Peltier heat of the right hand side of the anode was experimentally determined by Kjelstrup and Røsjorde (2005):

$$\pi_{AR} = 13 * T_{AR} \tag{2.19}$$

The total electric potential difference across the anode can be split into two parts: an *effective* potential difference that is solely related to the coupled transport processes and the electric resistance of the layer, and a part that is related exclusively to the Gibbs energy change due to the electrochemical reaction that happens in this layer. The equation for the electric potential is the following:

$$\Delta \phi_A = \phi_{AR} - \phi_{AL} = \Delta \phi_{A,eff} - \frac{\Delta G_A}{2F}$$
(2.20)

Where ϕ_{AR} and ϕ_{AL} are, respectively, the electric potential values at the right and left hand sides of the anode. $\Delta \phi_{A,eff}$ (the *effective* electric potential difference) is defined as:

$$\Delta \phi_{A,eff} = -\frac{\pi_{AL}}{T_{AL}F} \left(T_{AS} - T_{AL} \right) - \frac{\pi_{AR}}{T_{AR}F} \left(T_{AR} - T_{AS} \right) - r_S^{ohm} j$$
(2.21)

Where r_{S}^{ohm} is the electric resistivity of the anode.

 ΔG_A refers to the Gibbs free energy change due to the half-cell reaction occurring at the anode, and is defined as:

$$\Delta G_A = -\mu_{H_2,AS} \tag{2.22}$$

Where $\mu_{H_2,AS}$ is the chemical potential of the hydrogen at the anode surface, which is, in turn, calculated as:

$$\mu_{H_2,AS} = H_{H_2,AS} - T_{AS}S_{H_2,AS} \tag{2.23}$$

With $H_{H_2,AS}$ and $S_{H_2,AS}$ being, respectively, the enthalpy and entropy of the hydrogen, evaluated at the anode surface conditions, using as a standard state pure gas at a pressure of 1 atm.

The heat flux at the right hand side of the anode is obtained with an energy balance for the anode:

$$J'_{q,AR} = J'_{q,AL} + j\phi_{AL} + J_{H_2}H_{H_2,AL} + J_{W,AL}H_{W,AL} - j\phi_{AR} - J_{W,AR}H_{W,AR}$$
(2.24)

Where $J'_{q,AL}$ is the measurable heat flux at the left hand side of the anode (thus the final values from the anode-side PTL), $H_{H_2,AL}$ is the enthalpy of the hydrogen, evaluated at the anode left hand side conditions, and $H_{w,AL}$ and $H_{w,AR}$ are the enthalpies of the water, evaluated at the left and right hand side of the anode, respectively.

For the calculation of the entropy production, it was assumed that the chemical potential (at constant temperature) of the water is constant (see Section 2.7.2). The entropy production at the anode is calculated as follows:

$$\sigma_{A} = J'_{q,AR} \left(\frac{1}{T_{AR}} - \frac{1}{T_{AS}} \right) + J'_{q,AL} \left(\frac{1}{T_{AS}} - \frac{1}{T_{AL}} \right) - \frac{j}{T_{AS}} \Delta \phi_{A,eff}$$
(2.25)

2.2.3. Model consistency of the anode

As was the case with the anode-side PTL, the model can be validated with the comparison between the calculated entropy production and the entropy flux difference; the latter can be calculated using the following equation:

$$\Delta J_{s,A} = \frac{J'_{q,AR}}{T_{AR}} - \frac{J'_{q,AL}}{T_{AL}} + J_{w,AR} \left(S_{w,AR} - S_{w,AL} \right) - J_{H_2} S_{H_2,AL}$$
(2.26)

Where $S_{w,AL}$ is the entropy of water, calculated at the left hand side of the anode (that is, with T_{AL}).





As was done in the previous layer, the *entropy production departure* is introduced:

$$S_{dev,A} = \frac{\sigma_A - \Delta J_{s,A}}{\Delta J_{s,A}} * 100\%$$
(2.27)

2.3. Membrane

In the fuel cell membrane, protons that are produced in the anode, along with water and heat, are transported through a matrix of sulphonated Teflon[®] (Nafion[®]), to the cathode. Figure 2.3 shows the structure of Nafion[®].

A phenomenon that occurs in the membrane is that water, being a dipolar molecule (due to the difference in electronegativity between hydrogen and oxygen), is subject to being dragged along with the transported protons (which are essentially electric charges). This phenomenon is called *electro-osmotic drag* and is related to the coupled water and charge transport through the membrane. As well as with any solid material, the membrane is capable of conducting heat, which means that there are three fluxes and forces in the system: those related to heat, charge and water transport. Figure 2.4 shows the aforementioned fluxes.

2.3.1. Mathematical model of the membrane

The steady state water balance of the system is:

$$J_{w,M} = J_{w,AR} \tag{2.28}$$

Where $J_{w,AR}$ is the water flux at the right hand side of the anode.

The temperature, water fraction, electric potential, heat flux and entropy production profiles of the membrane can be calculated with the following set of equations:

$$\frac{dT_M}{dx} = -\frac{1}{\lambda_M} \left[J'_{q,M} - q^*_{w,M} \left(J_{w,M} - t_{w,M} \frac{j}{F} \right) - \pi_M \frac{j}{F} \right]$$
(2.29)

$$\frac{da_{w,M}}{dx} = -\frac{q_{w,M}^* l_{w,M}}{\frac{dl_{w,M}}{da_{w,M}} RT_M^2} \frac{dT_M}{dx} - \left(J_{w,M} - t_{w,M} \frac{j}{F}\right) \frac{M_M}{\frac{dl_{w,M}}{da_{w,M}} \rho_M D_{w,M}}$$
(2.30)



Figure 2.4 – Schematics of a fuel cell, that shows the different fluxes that are present in the fuel cell membrane. The term J'_q represents transported heat, J_{H_2O} represents transported water and j represents transported electric current (protons).

$$\frac{d\phi_M}{dx} = -\frac{\pi_M}{T_M F} \frac{dT_M}{dx} - \frac{t_{w,M} R T_M}{F a_{w,M}} \frac{da_{w,M}}{dx} - r_M^{ohm} j$$
(2.31)

$$\frac{dJ'_{q,M}}{dx} = -j\frac{d\phi_M}{dx} - J_{w,M}Cp_{w,M}\frac{dT_M}{dx}$$
(2.32)

$$\frac{d\sigma_M}{dx} = -\left(\frac{J'_{q,M}}{T_M^2}\frac{dT_M}{dx} + \frac{j}{T_M}\frac{d\phi_M}{dx} + \frac{J_{w,M}}{Ra_{w,M}}\frac{da_{w,M}}{dx}\right)$$
(2.33)

Where T_M is the temperature of the system, λ_M is the heat conductivity, $J'_{q,M}$ is the measurable heat flux, $t_{w,M}$ is the transference coefficient of water (or electro-osmotic drag), $a_{w,M}$ is the activity of the water in the membrane, M_M is the molar mass of the membrane, ρ_M is the dry density of the Nafion[®] membrane, $D_{w,M}$ is the diffusivity of water in the membrane, ϕ_M is the electric potential, R is the universal gas constant (8.314 J/mol K), r_M^{ohm} is the electric resistance of the layer, $Cp_{w,M}$ is the specific heat capacity of (liquid) water, and σ_M is the entropy production of the layer. It is clear, then, that the subindex M depicts the values at the membrane.

 π_M is the Peltier heat of the layer, experimentally defined as (Kjelstrup and Røsjorde, 2005):

$$\pi_M = 13 * T_M$$
 (2.34)

 $q_{w,M}^*$ is the heat of transfer for water in this layer, calculated as:

$$q_{w,M}^* = -T_M S_{w,M} (2.35)$$

The quantity $l_{q,M}$ refers to the water content of the membrane; that is, the amount of water molecules absorbed by the membrane per sulphonic acid group present in the membrane structure (Figure 2.3). The following experimental relationship between the water content and the water activity in the membrane was published by Springer et al. (1991) and has been widely used in the fuel cell modeling:

$$l_{w,M} = 0.043 + 17.81 * a_{w,M} - 39.85 * a_{w,M}^2 + 36 * a_{w,M}^3$$
(2.36)

The derivative of equation 2.36 with respect to the water activity is, then:

$$\frac{dl_{w,M}}{da_{w,M}} = 17.81 - 79.7 * a_{w,M} + 108 * a_{w,M}^2$$
(2.37)

2.3.2. Model consistency of the membrane

The entropy flux difference can be defined in this layer in a similar way as it was defined for the anode-side PTL (equation 2.10):

$$\Delta J_{s,M} = \frac{J'_{q,M,exit}}{T_{M,exit}} - \frac{J'_{q,M,entrance}}{T_{M,entrance}} + J_{w,M} \left(S_{w,M,exit} - S_{w,M,entrance} \right)$$
(2.38)

Where the values with the subindex *exit* refer to the final values obtained with the system of equations 2.29, 2.30, 2.31, 2.32 and 2.33 (thus the values evaluated at the thickness of the membrane), while the subindex *entrance* refers to the initial values of that system of differential equations; $S_{w,M,exit}$ and $S_{w,M,entrance}$ for example, refer to the entropy of the water at the exit and entrance of the layer, respectively (that is, with $T_{M,exit}$ and $T_{M,entrance}$). The *entropy production departure* is defined as:

$$S_{dev,M} = \frac{\sigma_{M,exit} - \Delta J_{s,M}}{\Delta J_{s,M}} * 100\%$$
(2.39)

Again, σ_{Mexit} represents the entropy production calculated at the total thickness of the membrane.

2.4. Cathode

2.4.1. Role of the cathode in the operation of the fuel cell

In the cathode of a fuel cell, the electrons that were produced at the anode are utilized to reduce oxygen, which will thereafter combine with protons that were transported through the membrane in order to produce water, according to the reactions:

$$e^{-} + \frac{1}{4}O_2 \rightleftharpoons \frac{1}{2}O^{2-}$$
$$\frac{1}{2}O^{2-} + H^+ \rightleftharpoons \frac{1}{2}H_2O$$

The cathode has a similar composition as the anode (platinum supported on carbon) and, as was said in Section 2.2.1, also requires the physical connection between the membrane, the catalyst and the cathode-side porous transport layer in order to ensure the correct operation of the fuel cell. Figure 2.5 depicts an image of the cathode and the different material and energy fluxes that flow into and out of it.

The main property that differentiates the anode and the cathode of the fuel cell is their kinetic properties: the cathode of a Proton Exchange Membrane Fuel Cell has slower kinetics than the anode (Larminie et al., 2003, pages 51 and 52) and thus creates a resistance in the system, that will be one of the causes behind the electric potential losses that occur in a PEMFC; this electric potential loss is called *activation overpotential* because it is related to the activation energy the system needs to overcome in order for the reaction to take place.

2.4.2. Mathematical model of the cathode

The steady state mass balances for oxygen and water are expressed as follows:

$$J_{O_2} = -\frac{J}{4F}$$
(2.40)

Where *j* is the electric current density and *F* is Faraday's constant (96485 C/mol). The minus sign indicates that the oxygen flows to the left (as shown in Figure 2.5).

$$J_{w,CR} = J_{w,CL} + \frac{j}{2F}$$
(2.41)



Figure 2.5 – Schematics of a fuel cell cathode, that shows the different material and energy fluxes. The term J'_q represents transported heat, J_{0_2} represents transported oxygen, *j* represents electric current, J_{H_20} represents transported water and J_{H^+} represents transported protons. The gray, continuous area, represents the Nafion[®] membrane, the small white circles (catalyst) and large black circles (support) represent the cathode surface, and the black lines represent the cathode side porous transport layer. Source: adapted from Larminie et al. (2003), page 74.

 $J_{w.CL}$ represents the water flux in the left hand side of the cathode, calculated as:

$$J_{w,CL} = J_{w,M}$$
 (2.42)

The term j/2F in equation 2.41 accounts for the water production in this layer.

The temperature of the cathode surface can be calculated with the following equation:

$$T_{CS} = T_{CL} - \frac{1}{\lambda_C} \left[J'_{q,CL} - q^*_{w,CL} \left(J_{w,CL} - t_{w,CL} \frac{j}{F} \right) - \pi_{CL} \frac{j}{F} \right]$$
(2.43)

Where T_{CL} represents the temperature at the left hand side of the cathode (the value at the exit of the membrane), λ_c is the heat conductivity of the cathode and $t_{w,CL}$ is the transference coefficient of the left hand side of the cathode (thus the transference coefficient of the membrane).

 $q_{w,CL}^*$ is the heat of transfer of water in the cathode, calculated as:

$$q_{w,CL}^* = -T_{CL}S_{w,CL}$$
(2.44)

With $S_{w,CL}$ being the entropy of the water at the left hand side of the cathode.

 π_{CL} is the Peltier heat of the left hand side of the cathode, calculated as (Kjelstrup and Røsjorde, 2005):

$$\pi_{CL} = 13T_{CL} \tag{2.45}$$

The temperature of the right hand side of the cathode (which will be the initial condition of the cathode-side porous transport layer) is calculated as follows:

$$T_{CR} = T_{CS} - \frac{1}{\lambda_C} \left[J'_{q,CR} - q^*_{w,CR} \left(J_{w,CR} - t_{w,CR} \frac{j}{F} \right) - \pi_{CR} \frac{j}{F} \right]$$
(2.46)

Where $t_{w,CR}$ is the transference coefficient of the right hand side of the cathode (the transference coefficient of the cathode-side PTL), defined as:

$$t_{w,CR} = t_{w,AP} + 0.5 \tag{2.47}$$

With $t_{w,AP}$ being the transference coefficient of the anode-side PTL. The reasoning behind this definition is the fact that there are two sources from where the water that exits the cathode comes: the water transported through the membrane and the water produced from the reaction between the protons and the oxide ions. When there is no water being transported through the membrane, there is still transport of water due to the transport of charge because there is water produced at the cathode, which means that the smallest value the transference coefficient at the right hand side of the cathode can acquire is 0.5 (due to the stoichiometry of the half-cell reactions).

The values of $q_{w,CR}^*$ and π_{CR} are calculated as follows:

$$q_{w,CR}^* = -T_{CR}S_{w,CR}$$
(2.48)

With $S_{w,CR}$ being the entropy of the water at the right hand side of the cathode.

$$\pi_{CR} = -T_{CR} \left(\frac{1}{4} S_{O_2,CR} - S_{e,CR} - t_{w,CR} S_{w,CR} \right)$$
(2.49)

Where $S_{O_2,CR}$ is the entropy of the oxygen at the right hand side of the cathode and $S_{e,CR}$ is the transported entropy of the electrons.

The total electric potential difference across the cathode can be split into three parts: an *effective* potential difference that is solely related to the coupled transport processes and the electric resistance of the layer, a part that is related exclusively to the Gibbs energy change due to the electrochemical reaction that happens in this layer and a part that accounts for the activation overpotential, mentioned in Section 2.4.1. The equation for the electric potential is the following:

$$\Delta\phi_C = \phi_{CR} - \phi_{CL} = \Delta\phi_{C,eff} - \frac{\Delta G_C}{2F}$$
(2.50)

Where ϕ_{CR} and ϕ_{CL} are, respectively, the electric potential values at the right and left hand sides of the cathode. $\Delta \phi_{C,eff}$ (the *effective* electric potential difference) is defined as:

$$\Delta \phi_{C,eff} = -\eta_C - \frac{\pi_{CL}}{T_{CL}F} \left(T_{CS} - T_{CL} \right) - \frac{\pi_{CR}}{T_{CR}F} \left(T_{CR} - T_{CS} \right) - r_S^{ohm} j$$
(2.51)

Where r_{S}^{ohm} is the electric resistivity of the cathode. The term η_{C} represents the cathode overpotential (as explained in Section 2.4.1), and is calculated as (Kjelstrup and Røsjorde, 2005):

$$\eta_C = \frac{2RT_{CS}}{F} ln\left(\frac{j}{j_0}\right) \tag{2.52}$$

Where j_0 represents the exchange current density, which is a parameter that depicts the current produced due to the half-cell reactions when they are in equilibrium, and in this sense, is a parameter that measures the kinetics of the cathodic reactions: the larger the exchange current density, the faster the kinetics of this electrode are (Larminie et al., 2003, pages 51 and 52).

 ΔG_c is the Gibbs free energy change due to the half-cell reaction at the cathode and is defined as:

$$\Delta G_C = \mu_{w,CS} - \frac{\mu_{O_2,CS}}{2}$$
(2.53)

With $\mu_{O_2,CS}$ and $\mu_{w,CS}$ being, respectively, the chemical potentials of the oxygen and the water, evaluated at the cathode surface conditions; each chemical potential is defined as:

$$\mu_{O_2,CS} = H_{O_2,CS} - T_{CS}S_{O_2,CS} \tag{2.54}$$

$$\mu_{w,CS} = H_{w,CS} - T_{CS}S_{w,CS} \tag{2.55}$$

Where $H_{O_2,CS}$ and $H_{w,CS}$ are the enthalpies of the oxygen and the water, respectively, evaluated at the cathode surface conditions, using as a standard state pure gases at a pressure of 1 atm.

The heat flux at the right hand side of the cathode is obtained with an energy balance in the cathode:

$$J'_{q,CR} = J'_{q,CL} + j\phi_{CL} + J_{w,CL}H_{w,CL} - j\phi_{CR} - J_{w,CR}H_{w,CR} - J_{O_2,CR}H_{O_2,CR}$$
(2.56)

Where $J'_{q,CL}$ is the measurable heat flux at the left hand side of the cathode (thus the final values from the membrane), and $H_{w,CL}$ and $H_{w,CR}$ are the enthalpies of the water, evaluated at the left and right hand side of the cathode, respectively (using T_{CL} and T_{CR}).

For the calculation of the entropy production, it was assumed that the chemical potential (at constant temperature) of the water is constant (see Section 2.7.4). The entropy production at the cathode is calculated as follows:

$$\sigma_{C} = J'_{q,CR} \left(\frac{1}{T_{CR}} - \frac{1}{T_{CS}} \right) + J'_{q,CL} \left(\frac{1}{T_{CS}} - \frac{1}{T_{CL}} \right) - \frac{j}{T_{CS}} \Delta \phi_{C,eff}$$
(2.57)

2.4.3. Model consistency of the cathode

As was the case with the anode, the model can be validated with the comparison between the calculated entropy production and the entropy flux difference; the latter can be calculated using the following equation:

$$\Delta J_{s,C} = \frac{J'_{q,CR}}{T_{CR}} - \frac{J'_{q,CL}}{T_{CL}} + J_{O_2,CR} S_{O_2,CR} + J_{w,CR} S_{w,CR} - J_{w,CL} S_{w,CL}$$
(2.58)

Where $S_{w,CL}$ is the entropy of water, calculated at the left hand side of the cathode (that is, with T_{CL}).

As was done in the previous layer, the *entropy production departure* is introduced:

$$S_{dev,C} = \frac{\sigma_C - \Delta J_{s,C}}{\Delta J_{s,C}} * 100\%$$
(2.59)

2.5. Cathode-side porous transport layer

2.5.1. Layout of the transported fluxes in the cathode-side porous transport layer

The cathode-side porous transport layer (or cathode-side PTL) does an analogous work to its anodeside counterpart: it is the layer through which humidified air (coming from the flow fields in the current collector) enters the system, and oxygen is transported to the cathode, while water, heat and electric current are transported from the cathode to the exiting air (which will be depleted in oxygen and thus richer in nitrogen). Figure 2.6 shows a depiction of the aforementioned fluxes.

2.5.2. Mathematical model of the cathode-side porous transport layer

The steady state mass balances in the system can be expressed as follows:

$$J_{O_2} = -\frac{j}{4F}$$
(2.60)



Figure 2.6 – Schematics of a fuel cell, that shows the different fluxes that are present in the cathode-side porous transport layer. The term J'_q represents transported heat, J_{O_2} represents transported oxygen, *j* represents electric current, J_{H_2O} represents transported water and J_{N_2} represents the nitrogen flux that enters the system.

The steady state water balance of the system is:

$$J_{w,CP} = J_{w,CR} \tag{2.61}$$

Where $J_{w,CP}$, the water flux through the cathode-side PTL, is equal to $J_{w,CR}$, the water flux calculated at the right hand side of the cathode (see Section 2.4.2)

The temperature, water fraction, electric potential, heat flux and entropy production profiles of the membrane can be calculated with the following set of equations (assuming that the oxygen flux is independent from the water flux, see Section 2.7.5):

$$\frac{dT_{CP}}{dx} = -\frac{1}{\lambda_{CP}} \left[J'_{q,CP} - q^*_{w,CP} J_{D,CP} - \pi_{CP} \frac{j}{F} \right]$$
(2.62)

$$\frac{dx_{w,CP}}{dx} = -\frac{j}{4FD_{0_2,CP}}$$
(2.63)

$$\frac{d\phi_{CP}}{dx} = -\frac{\pi_{CP}}{T_{CP}F}\frac{dT_{CP}}{dx} - r_{CP}^{ohm}j$$
(2.64)

$$\frac{dJ'_{q,CP}}{dx} = -j\frac{d\phi_{CP}}{dx} - \left(J_{w,CP}Cp_{w,CP} + J_{O_2}Cp_{O_2}\right)\frac{dT_{CP}}{dx}$$
(2.65)

$$\frac{d\sigma_{CP}}{dx} = -\left(\frac{J'_{q,CP}}{T^2_{CP}}\frac{dT_{CP}}{dx} + \frac{j}{T_{CP}}\frac{d\phi_{CP}}{dx} + \frac{J_{D,CP}R}{x_{w,CP}}\frac{dx_{w,CP}}{dx}\right)$$
(2.66)

Where T_{CP} is the temperature of the system, λ_{CP} is the heat conductivity, $J'_{q,CP}$ is the measurable heat flux, $x_{w,CP}$ is the water mole fraction in the cathode-side PTL, $D_{O_2,CP}$ is the diffusivity of oxygen in nitrogen in the cathode-side PTL, ϕ_{CP} is the electric potential, R is the universal gas constant (8.314 J/mol K), r_{CP}^{ohm} is the electric resistivity of the layer, $Cp_{w,CP}$ is the specific heat capacity of (vapor) water, $Cp_{O_2,CP}$ is the specific heat capacity of oxygen and σ_{CP} is the entropy production of the layer. It is clear, then, that the subindex CP depicts the values at the cathode-side porous transport layer.

 π_{CP} is the Peltier heat of the layer, calculated as:

$$\pi_{CP} = -T_{CP} \left(\frac{1}{4} S_{O_2, CP} - S_{e, CP} - t_{w, CP} S_{w, CP} \right)$$
(2.67)

Where $S_{O_2,CP}$ and $S_{w,CP}$ are the entropy of, respectively, oxygen and water, $S_{e,CP}$ is the transported entropy of the electrons and $t_{w,CP}$ is the transference coefficient of water in this layer, defined as:

$$t_{w,CP} = t_{w,AP} + 0.5 \tag{2.68}$$

Where $t_{w,AP}$ is the transference coefficient for water at the anode-side PTL. The origin of this equation was already discussed in Section 2.4.2.

 $q_{w,CP}^{*}$ is the heat of transfer for water in this layer, defined as:

$$q_{w,CP}^* = -T_{CP}S_{w,CP}$$
(2.69)

 $J_{D,CP}$ is called the interdiffusional flux, which, in a same fashion as was done in the anode-side PTL, represents the fact that water and oxygen are both diffusing through the cathode-side PTL, and this quantity represents the net water flux, taking as a frame of reference the oxygen flux; is defined as (Kjelstrup and Røsjorde, 2005):

$$J_{D,CP} = \left(\frac{J_{w,CP}}{x_{w,CP}} - \frac{J_{O_2}}{x_{O_2,CP}}\right) x_{w,CP}$$
(2.70)

Where $x_{O_2,CP}$ is the oxygen mole fraction.

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2.5.3. Model consistency of the cathode-side porous transport layer

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The entropy flux difference can be defined in this layer similarly to the entropy flux differences of the anode-side PTL and the membrane (equations 2.10 and 2.38):

$$\Delta J_{s,CP} = \frac{J_{q,CP,exit}}{T_{CP,exit}} - \frac{J_{q,CP,entrance}}{T_{CP,entrance}} + J_{w,CP} \left(S_{w,CP,exit} - S_{w,CP,entrance} \right) + J_{O_2,CP} \left(S_{O_2,CP,exit} - S_{O_2,CP,entrance} \right)$$
(2.71)

Where the values with the subindex *exit* refer to the final values obtained with the system of equations 2.62, 2.63, 2.64, 2.65 and 2.66 (thus the values evaluated at the total thickness of the cathode-side PTL), while the subindex *entrance* refers to the initial values of that system of differential equations; $S_{w,CP,exit}$ and $S_{w,CP,exit}$, for example, refer to the entropy of the water at the exit and entrance of the layer, while $S_{02,CP,exit}$ and $S_{02,CP,entrance}$ do so for the oxygen (that is, with $T_{CP,exit}$ and $T_{CP,entrance}$, respectively).

The *entropy production departure* is defined as:

$$S_{dev,CP} = \frac{\sigma_{CP,exit} - \Delta J_{s,CP}}{\Delta J_{s,CP}} * 100\%$$
(2.72)

Where $\sigma_{CP,exit}$ represents the entropy production calculated at the total thickness of the anode-side PTL.

2.6. Total entropy production and total entropy production departure

In sections 2.1, 2.2, 2.3, 2.4 and 2.5, the model for the thermodynamic description of a fuel cell was depicted, as well as the parameters that are going to be utilized for its validation; the entropy

production departures were also defined for each layer. A final verification parameter will be presented in this section, namely the *total entropy production departure*. In order to define the total entropy production departure, the total entropy flux difference in the fuel cell has to be calculated:

$$\Delta J_{s,total} = \frac{J'_{q,CP,exit}}{T_{CP,exit}} - \frac{J'_{q,AP,entrance}}{T_{AP,entrance}} + J_{w,CP}S_{w,CP,exit} - J_{w,AP}S_{w,AP,entrance} + J_{O_2}S_{O_2,CP,exit} - J_{H_2}S_{H_2,AP,entrance}$$

$$(2.73)$$

Where $J'_{q,CP,exit}$, $T_{CP,exit}$, $S_{w,CP,exit}$ and $S_{O_2,CP,exit}$ are, respectively, the measurable heat flux, the temperature and the entropy of the water and the oxygen (calculated with $T_{CP,exit}$), obtained at the total thickness of the cathode-side PTL (see equation 2.71), $J'_{q,AP,entrance}$, $T_{AP,entrance}$, $S_{w,AP,entrance}$ and $S_{H_2,AP,entrance}$ are the initial values for heat flux, temperature and entropy of the water and the hydrogen (calculated with $T_{AP,entrance}$), in the anode-side PTL (see equation 2.10). $J_{w,CP}$ and $J_{w,AP}$ represent the water fluxes at the cathode and anode-side PTL, while J_{O_2} and J_{H_2} are the oxygen and hydrogen fluxes, respectively.

Having defined the total entropy flux difference, we can now define the total entropy production departure:

$$S_{dev,total} = \frac{\sigma_{total} - \Delta J_{s,total}}{\Delta J_{s,total}} * 100\%$$
(2.74)

Where the term σ_{total} represents the total entropy production in the system:

$$\sigma_{total} = \sigma_{AP,exit} + \sigma_A + \sigma_{M,exit} + \sigma_C + \sigma_{CP,exit}$$
(2.75)

With $\sigma_{AP,exit}$, σ_A , $\sigma_{M,exit}$, σ_C and $\sigma_{CP,exit}$ being the individual entropy productions of each one of the layers described in the previous Sections of this chapter.

2.7. Assumptions and parameters

The list of all assumptions, utilized for the implementation of the model described in this Chapter, will be listed in this Section.

2.7.1. Assumptions in the anode-side porous transport layer

- The interaction between water and hydrogen was assumed to be in correspondence with the Lennard-Jones model, which was utilized to calculate the diffusion coefficient of water in hydrogen (with kinetic theory of gases); see Section 2.7.6 for the diffusion coefficient model.
- The incoming hydrogen to the anode-side PTL was assumed to have a relative humidity of 100%.
- All thermodynamic and transport parameters were calculated using the initial conditions for temperature and composition.
- The gas stream (comprised of hydrogen and water) was assumed to be at a total pressure of 1 atm.

2.7.2. Assumptions in the anode

- All thermodynamic and transport parameters were calculated using the initial conditions for temperature and composition.
- It was assumed that the catalyst was equally distributed in the anode and thus the layer can be modeled in one dimension.
- There is water equilibrium between the anode-side PTL exit and the membrane entrance (see Section 2.8.5).
- It was assumed that the chemical potential at constant temperature was equal at both sides of the anode ($\Delta \mu_{w,T,AL} = \Delta \mu_{w,T,AR}$) (see Kjelstrup and Røsjorde, 2005).

2.7.3. Assumptions in the membrane

• It was assumed that the water content of the membrane can only acquire values between 0 and 14, in order to ensure smoothness of the relationship between water content and activity (see
equation 2.36), and thus a continuous derivative in equation 2.37. The model found by Springer et al. (1991) is a continuous function of the water activity, but in that model, the water content of the membrane was allowed to go up to 16.8 (although this did not span from actual experimental results but rather, as here, as an assumption made by mathematical reasons), and the relationship between the water content and water activity in the range 14-16.8 followed a different relationship in comparison with equation 2.36, which makes its derivative a non-continuous function.

- The water content of the membrane at the total thickness of the membrane was assumed to be 14 (thus the water activity was assumed to be 1 in the membrane-cathode interface).
- All thermodynamic and transport parameters were calculated using the initial conditions for temperature but with the average value for the water content in the membrane. This was done because a large water content difference was expected between both sides of the membrane and it was assumed that the transport parameters of the membrane are more sensitive to changes in the water content than to changes in temperature.
- The adsorption and absorption enthalpy of water in the membrane was assumed to be negligible compared to the condensation enthalpy of water. Moreover, it was assumed that water is transported in the membrane in the liquid phase.

2.7.4. Assumptions in the cathode

- All thermodynamic and transport parameters were calculated using the initial conditions for temperature and composition.
- It was assumed that the catalyst was equally distributed in the cathode and thus the layer can be modeled in one dimension.
- It was assumed that the water chemical potential at constant temperature was equal at both sides of the cathode ($\Delta \mu_{w,T,CL} = \Delta \mu_{w,T,CR}$) (see Kjelstrup and Røsjorde, 2005).

2.7.5. Assumptions in the cathode-side porous transport layer

- The interaction between oxygen and nitrogen was assumed to be in correspondence with the Lennard-Jones model, which was utilized to calculate the diffusion coefficient of oxygen in nitrogen (with kinetic theory of gases); see Section 2.7.6 for the diffusion coefficient model.
- The incoming air to the cathode-side PTL was assumed to have a relative humidity of 100%.
- All thermodynamic and transport parameters were calculated using the initial conditions for temperature and composition.
- It was assumed that the fuel cell operates with an excess of air, which means that the exiting air will have a similar composition as the incoming air.
- It was assumed that the oxygen flux is not coupled to the rest of the fluxes in this layer (water, heat and electric current).
- The gas stream (comprised by nitrogen, oxygen and water) was assumed to be at a total pressure of 1 atm.
- A dry air mole composition of $x_{0_2,dry} = 0.21$ and $x_{N_2,dry} = 0.79$ was utilized.

2.7.6. Parameters utilized

Diffusion coefficients at the backings

As it was already stated in the assumptions, the diffusion coefficients of water in hydrogen and oxygen in nitrogen were determined using kinetic theory of gases, assuming both pairs of gases to interact as Lennard-Jones gases. The diffusion coefficient (and the rest of the calculation procedure followed in this section) was taken from Bird et al. (2007), pages 526 and 527. The diffusion coefficient of a gas A in a gas B can be calculated as:

$$D_{AB} = 1.8583 x 10^{-7} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \frac{T^{1.5}}{p \Sigma_{AB}^2 \Omega_{D,AB}} [=] \frac{m^2}{s}$$
(2.76)

Where M_A and M_B represent the molar masses, in g/mol, of the components A and B, T is the temperature of the system in K, p is the pressure of the system, in atm, Σ_{AB} represents the mean hard

sphere radius in the mixture of A and B, defined as¹:

$$\Sigma_{AB} = \frac{1}{2} \left(\Sigma_A + \Sigma_B \right) [=] \mathring{A}$$
(2.77)

With Σ_A and Σ_B being the hard sphere radius of the components A and B, respectively, in Å.

The term $\Omega_{D,AB}$ represents the collisional integral for diffusion, of the gas pair A-B, which is a parameter that depends on the dimensionless temperature of the pair A-B. The collisional integral is defined as (Bird et al., 2007, page 866):

$$\Omega_{D,AB} = \frac{1.06036}{T_{ad}^{0.15610}} + \frac{0.193}{exp\left(0.47635T_{ad}\right)} + \frac{1.03587}{exp\left(1.52996T_{ad}\right)} + \frac{1.76474}{exp\left(3.89411T_{ad}\right)} [=]1$$
(2.78)

Where T_{ad} is the dimensionless temperature of the gas pair A-B, calculated as:

$$T_{ad} = \frac{T}{\varepsilon_{AB}} [=]1 \tag{2.79}$$

Where *T* is the system temperature, in K, and ε_{AB} is the normalized Lennard-Jones potential well depth of the system A-B (the well depth divided by the Boltzmann factor *k*), defined as the geometric average of the individual Lennard-Jones potential well depths for component A and component B:

$$\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B} [=] K \tag{2.80}$$

Finally, a correction to the diffusion coefficient was introduced, that allowed for the use of the Fick's first law in the form $J_A = -D_{AB} \frac{dx_A}{dx}$ (thus as a function of mole fractions rather than concentration):

$$D_{AB,corrected} = D_{AB} \frac{p * 1.01325 \times 10^5}{RT} [=] \frac{mol}{ms}$$
(2.81)

Where p is the system pressure, in atm, R is the universal gas constant (8.314 J/mol K) and T is the system temperature, in K.

The values of the parameters M, Σ and ε for water, hydrogen, oxygen and nitrogen are depicted in Table 2.1.

	$M\left[g/mol\right]$	$\Sigma [\text{\AA}]$	$\varepsilon \left[K \right]$
Water	18	$3.166^{(*)}$	$78.166^{(*)}$
Hydrogen	2	2.915	38
Oxygen	32	3.433	113
Nitrogen	28	3.667	99.8

Table 2.1 – Parameters used for the calculation of the diffusion coefficients of the gas pairs water-hydrogen and oxygennitrogen. Source: Bird et al. (2007), pages 864 and 866. ^(*)The values for water were not present in the previous reference since it is a polar molecule; the values here were obtained from Berendsen et al. (1987) and refer to Lennard-Jones parameters of water calculated with an extended simple point charge model.

Relative humidity and water content in the backings

As was stated in the assumptions, the relative humidity of both hydrogen and air at the entrances of the system (thus at the entrance of the anode-side PTL and the exit of the cathode-side PTL) was assumed to be 100%. The relationship between the relative humidity and the water mole fraction of either stream (hydrogen and air) is the following:

$$x_w = \frac{RH}{100\%} \frac{p_{w,sat}}{p} [=] mole fraction$$
(2.82)

¹Although, in the original text, this equation is only valid for non-polar pairs of gases, it was assumed to hold for the waterhydrogen system as well, (one does not expect strong polar interactions between a polar and a nonpolar gas). Where *RH* is the relative humidity, in %, *p* is the system pressure, in atm and $p_{w,sat}$ is the vapor pressure of water, calculated with Antoine's equation:

$$p_{w,sat} = \frac{1}{1.01325} * 10^{\left(5.11564 - \frac{1687.537}{(T - 273.15) + 230.17}\right)} [=]atm$$
(2.83)

With *T* being the system temperature, in K. The parameters shown in equation 2.83 were obtained from Poling et al. (2001), page A.59.

Calculation of enthalpies and entropies

The enthalpy and entropy of the water, hydrogen and oxygen were calculated as follows:

$$H = H^{0} + Cp \left(T - 298\right) \left[=\right] \frac{J}{mol}$$
(2.84)

$$S = S^{0} + Cp \ln\left(\frac{T}{298}\right) - R \ln(x) [=] \frac{J}{mol K}$$
(2.85)

Where H^0 and S^0 are the standard enthalpy and entropy, respectively, in J/mol and J/mol K, when the reference temperature is 298 K, Cp is the specific heat capacity, in J/mol K, R is the universal gas constant (8.314 J/mol K) and x represents the mole fraction of the substance in the gas mixture.

Transport properties in the membrane

The following equations calculate the electric resistivity, the water diffusivity and the heat conductivity of the membrane:

$$r_M^{ohm} = \left\{ exp\left[1268\left(\frac{1}{303} - \frac{1}{T}\right) \right] \left(0.5139l_{w,M} - 0.326 \right) \right\}^{-1} [=]\Omega m$$
(2.86)

$$D_{w,M} = 10^{-10} exp \left[2416 \left(\frac{1}{303} - \frac{1}{T} \right) \right] \left(2.563 - 0.33 l_{w,M} + 0.0264 l_{w,M}^2 - 6.71 \times 10^{-4} l_{w,M}^3 \right) [=] \frac{m^2}{s}$$
(2.87)

$$\lambda_M = 0.177 + 3.7x 10^{-3} l_{w,M} [=] \frac{W}{m K}$$
(2.88)

In the equations above, *T* is the system temperature, in K, and $l_{w,M}$ is the water content of the membrane, in mol_{water}/mol_{sulphonic acid group}. Equations 2.86 and 2.87 were obtained from Springer et al. (1991), while equation 2.88 was calculated from the results published by Burheim et al. (2010). Table 2.2 shows the rest of the parameters of the Nafion[®] membrane.

Membrane parameter	Symbol	Value	Unit
Dry density Dry molar mass Total acid capacity	$\begin{array}{c} \rho_M \\ M_M \\ A_c \end{array}$	$1,640 \\ 1.1 \\ 0.91$	kg/m^3 kg/mol eq/kg

Table 2.2 – Nafion® membrane material parameters. Sources: Kjelstrup and Røsjorde (2005) and DuPont (2009).

Overview of the parameters utilized

Table 2.3 shows the thermodynamic parameters (standard enthalpy, entropy and specific heat capacity) for water (in vapor and liquid state), hydrogen and oxygen. The specific heat capacity was assumed to be constant over the range of temperatures simulated in this work.

Table 2.4 shows the transport parameters utilized to define the base case simulation scenario (see Section 3.1).

Table 2.5 shows the layer thickness values utilized in the model.

	$H^0\left[J/mol ight]$	$S^0\left[J/(molK)\right]$	$Cp\left[J/(molK) ight]$
Vapor water	-242,000	189	34
Hydrogen	1,000	135	29
Liquid water	-285,000	70	75
Oxygen	1,000	205	29

Table 2.3 – Thermodynamic parameters utilized in this work, for a reference temperature of 298 K. Source: Kjelstrup and Røsjorde (2005).

Parameter	Symbol(s)	Value	Unit
Transported en-	$S_{e,AP} = S_{e,AL} =$	-2	J/(molK)
tropy of electrons	$S_{e,CR} = S_{e,CP}$		
Anode-side PTL transfer-	$t_{w,AP} = t_{w,AL}$	0	-
PTL thermal conductivity	$\lambda_{AP} = \lambda_{CP}$	0.42	W/(mK)
PTL electric resistivity	$r_{AP}^{ohm}=r_{CP}^{ohm}$	0.0001	Ωm
Electrode thermal conduc-	$\lambda_A = \lambda_C$	1710	$W/(m^2K)$
Electrode electric resistivity	$r_A^{ohm} = r_C^{ohm}$	$7.2x10^{-6}$	Ωm^2
Membrane transference coef- ficient (electro esmotic drag	$t_{w,M}$	1.2	-
coefficient)		0 F 10-3	A / 2
Cathode exchange current density	$\mathcal{J}0$	$2.5x10^{-5}$	A/m^2

Table 2.4 – Transport parameters utilized to define the base case scenario. Source: Kolstad (2013).

Layer	Thickness $[m]$
Anode-side PTL	$246x10^{-6}$
Anode	_(*)
Membrane	$192x10^{-6}$
Cathode	_(*)
Cathode-side PTL	$246x10^{-6}$

Table 2.5 – Transport parameters utilized in this work. Source: Kolstad (2013). ^(*)These values are not shown here because the thickness of both electrodes has already been included in the transport parameters shown in Table 2.4.

Finally, the initial value of the inlet heat flux to the anode-side PTL was left as a parameter that can be optimized, whose base case value will be zero:

$$J'_{q,AP,entrance} = 0 (base \, case) \tag{2.89}$$

As was explained earlier, it is possible to optimize this parameter by searching for the minimum value of the entropy production departures, defined in equations 2.11, 2.27, 2.39, 2.59, 2.72 and 2.74.

2.8. Model implementation

After the model has been described and the assumptions and parameters have been stated, the implementation will be described in the rest of this Section.

2.8.1. Numerical solution and procedure

The sets of equations corresponding to the anode-side PTL (2.2, 2.3, 2.4, 2.5 and 2.6), the membrane (2.29, 2.30, 2.31, 2.32 and 2.33) and the cathode-side PTL (2.62, 2.63, 2.64, 2.65 and 2.66) represent systems of coupled first-order differential equations, and in this sense, cannot be solved analytically. Moreover, it is important to emphasize on the fact that the initial conditions of some layers of the fuel cell depend on the final values of the previous layer (as can be seen in Figure 1.4) and thus the model should be implemented in a modular computational environment, preferably one in which a visualization of the information flow is possible. Because of these reasons, the model was implemented in the MatlabTM Simulink[®] software, which allowed for visualization of the data flows through the different sets of equations present in the described model.

The differential sets of equations were solved using a Fourth Order Runge-Kutta solution procedure, that allowed for fast computation and a better approximation to the real solution than lower-order numerical integration algorithms. Each set of differential equations was implemented with 100 steps between the initial conditions and the final values obtained.

Whenever there was an iterative procedure needed to be implemented, it was implemented directly in Simulink[®], using a Trust-Region Dogleg iterative procedure (Mathworks, 2014).

2.8.2. Iterative inlet water flux calculation

The model presented in this work has one main initial system input required, namely the inlet water flux to the anode-side PTL. Inherently, the model does not have an algorithm to calculate this quantity, hence the assumption made in Section 2.7.3 about the water content in the membrane-cathode interface to be equal to 14. This assumption allows for the model to calculate the water flux required by the system to maintain the water content at the right hand side of the membrane always equal to 14. An iterative procedure was thus implemented, that allows for the calculation of the correct water flux.

The iteration procedure operates as follows: an initial assumption of the water flux that enters the left hand side of the anode-side PTL is done; the model carries on with the simulations of the anode-side PTL, the anode and the membrane, and the final value of the water activity in the membrane (the integration of equation 2.30 over the whole thickness of the membrane) is calculated. The calculated water content, using the initial assumption for the water flux, is then compared with the value assumed (which is 1 for the water activity or 14 for the water content, according to Section 2.7.3) and the iteration process continues until the two water content values are equal (which is restricted by the numerical tolerance set in Simulink[®].

2.8.3. Iterative procedure in the electrodes

Although the systems of equations presented in Sections 2.2 and 2.4 are purely algebraic, another iterative algorithm needs to be implemented: note how the calculations of the temperature at the right hand side of each electrode (equations 2.17 and 2.46) require the knowledge of the heat flux, but at the same time, the calculation of the heat fluxes at the right hand side of each electrode (equations 2.24 and 2.56) need the calculation of the enthalpies, which need the values of the temperatures at this same location. Therefore, an iterative procedure for the temperature, the electric potential and the heat flux was implemented, although knowledge about the results coming from rest of the layers is not necessary since these sets of equations are mathematically self-contained.

The iteration procedure is simple: initial assumptions of the temperature, the electric potential and the heat flux at the right hand side of each electrode are done (which were initially estimated to be 10% above the inlet values), and these are verified, respectively, with equations 2.17, 2.20 and 2.24 for the anode, and equations 2.46, 2.50 and 2.56 for the cathode.

2.8.4. Iterative procedure in the cathode-side PTL

As can be seen in Section 2.7.5, an assumption has been made regarding the air composition at the exit of the fuel cell (see Figure 2.6), which means that, contrary to an initial value assumption, as it

was done in Section 2.7.1, an iterative procedure is required in order to ensure that the model complies with the assumption made. In the same fashion as Section 2.8.3, the model of the cathode-side PTL is mathematically self-contained and thus the results of the simulations done with the models for the rest of the layers is not necessary to solve this particular set of equations.

The iteration procedure went as follows: initial assumptions for the initial water and the oxygen mole fractions are done, and the final values of the set of differential equations, namely the integration of equation 2.63 over the total thickness of the cathode-side PTL, is compared with the calculation of the composition of humid air at the temperature at the exit of the cathode-side PTL (resulting from the integration of equation 2.62).

2.8.5. Water equilibrium and calculation of the initial water activity in the membrane

It was already stated in Section 2.7.3 that the water activity of the membrane was assumed to be 1 (that corresponds to a water content of 14) and that it was assumed that there is water equilibrium between the anode-side PTL exit and the membrane entrance (see Section 2.7.2). What does this assumption imply? It implies that the chemical potential of the water at the exit of the anode-side PTL will be equal to the chemical potential of the water at the entrance of the membrane. The water chemical potential at the exit of the anode-side PTL can be calculated as follows:

$$\mu_{w,AP,exit} = H_{w,AP,exit} - T_{AP,exit} S_{w,AP,exit}$$
(2.90)

Where $H_{w,AP,exit}$ is the enthalpy of the water at the exit of the anode-side PTL (calculated with equation 2.84), $T_{AP,exit}$ is the exit temperature of the anode-side PTL, that is, the integrated result of equation 2.2 through the total thickness of the layer, and $S_{w,AP,exit}$ is the entropy of the water, evaluated at $T_{AP,exit}$.

The chemical potential of the water that enters the membrane is calculated as follows:

$$\mu_{w,M,entrance} = H_{w,M,entrance} - T_{M,entrance} S_{w,M,entrance}$$
(2.91)

Where $H_{w,M,entrance}$ is the enthalpy of the water evaluated at $T_{M,entrance}$ (the initial temperature of the membrane), and $S_{w,M,entrance}$ is the entropy of the water, defined as:

$$S_{w,M,entrance} = S_{w,M,entrance}^{0} + Cp_{w,M} \ln\left(\frac{T_{M,entrance}}{298}\right) - R \ln\left(a_{w,M,entrance}\right)$$
(2.92)

With $S_{w,M,entrance}^{0}$ being the standard entropy of the water at 298 K and $Cp_{w,M}$ being the specific heat capacity of water in the membrane (both obtainable from Table 2.3), *R* is the universal gas constant (8.314 J/mol K) and $a_{w,M,entrance}$ is the initial water activity in the membrane. Since equations 2.90 and 2.91 are equal (due to the equilibrium assumption), it is possible to equate them and incorporate equation 2.92, which then yields the following equation, that calculates the initial water activity in the membrane:

$$a_{w,M,entrance} = exp \left[\frac{\mu_{w,M,entrance} - H_{w,M,entrance}}{R T_{M,entrance}} + \frac{S_{w,M,entrance}^0}{R} + \frac{Cp_{w,M}}{R} \ln \left(\frac{T_{M,entrance}}{298} \right) \right]$$
(2.93)

2.8.6. Implementation algorithm of the model

Figure 2.7 shows the algorithm implemented for the solution of the fuel cell model described in Sections 2.1, 2.2, 2.3, 2.4 and 2.5; the flowchart includes the implementation of the iterative algorithms explained in Sections 2.8.2, 2.8.3 and 2.8.4. The logic showed in Figure 2.7 was directly implemented in the MatlabTM Simulink[®] environment.



Figure 2.7 – Flow chart of the implementation of the model in the Matlab[™] Simulink[®] environment.

3

Simulation results

In the following pages, the results from the simulations carried out with the model described in Chapter 2 are displayed. Four different scenarios are depicted: simulations with the base case parameters (shown in Table 2.4, simulations with optimized transport parameters (the optimization scheme is explained in Section 3.2), simulations after removal of the water equilibrium assumption (see Section 2.7.2) and simulations carried out with different operation schemes, which were made in order to evaluate the performance of the fuel cell with varying relative humidity of the inlet hydrogen and the inlet air.

3.1. Base case scenario

3.1.1. Simulations with the base case parameters

Figures 3.1, 3.2, 3.3, 3.4 and 3.5 show the simulated temperature, water fraction (and membrane water content), voltage, heat flux and entropy production profiles, using the base case transport parameters depicted in Section 2.7.6.

Tables 3.1 and 3.2 show the final outcomes of the simulations done with the base case parameters.

$j \left[A/m^2 ight]$	$T_{CP,exit} - T_{AP,entrance} \left[K \right]$	$\phi_{CP,exit} - \phi_{AP,entrance} \left[V \right]$
500	2.08	0.450
1500	-3.32	0.347
3000	-11.94	0.243
5000	-24.39	0.124

Table 3.1 – Temperature and voltage differences between inlet (left hand side of the anode porous transport layer) and outlet (right hand side of the cathode porous transport layer), using base case parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m^2 .

$j \left[A/m^2 ight]$	$J_{w,AP}\left[mol/(m^2s)\right]$	$J_{w,CR}\left[mol/(m^2s)\right]$
500	-0.0097	-0.0071
1500	0.0021	0.0098
3000	0.0200	0.0356
5000	0.0445	0.0704

Table 3.2 – Water flux before and after the cathode, using base case parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m^2 .

Figure 3.6 shows the I-V curve of the fuel cell, obtained with the base case parameters.



Figure 3.1 – Temperature as a function of the fuel cell thickness, using base case parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$, $J'_{q,AP,entrance} = 0W/m²$ and $a_{w,M,exit} = 1$.

It can be seen in Figure 3.1 that the temperature increases along the fuel cell only at low current densities, and after that it follows a decreasing profile for larger current densities; this is caused by the choice of the initial heat flux: in Figure 3.4, the lowest current density is associated with a negative heat flux (thus, a heat flux that flows to the anode-side PTL), which is, in turn, a consequence of the negative water flux obtained (see Table 3.2). The larger current densities, in turn, have increasing water flux values and thus positive heat fluxes, which leads, in turn, to a decreasing temperature profile of the fuel cell.

It can be seen in Figure 3.1 that the electrode responsible for the largest temperature differences is the cathode and that the temperature is larger in the membrane than in the cathode-side PTL is caused by the evaporation of water in this electrode: water is transported in the liquid phase from the anode to the cathode (because of the transport of the H_3O^+ molecules through the Nafion[®] membrane), while water in the cathode-side PTL is in the vapor phase. In order for water to incorporate to the air flux that flows through the cathode-side PTL, it needs to be evaporated and thus it takes the heat that is produced in the cathode.

From Figure 3.2, one can conclude that, the higher the current density, the lower the water content in the membrane and the water fraction at the cathode-side PTL diminishes as well. These two phenomena are a sole consequence of the decreasing water profiles through the cell: lower temperatures lead to a lower water saturation pressure and thus the water fraction in the cathode-side PTL declines with higher current densities. The same happens to the initial membrane water content: a low temperature results in a low water activity at the left hand side of the membrane.

The voltage profile shown in Figure 3.3 shows that there are no voltage losses in either one of the porous transport layer, but there is a substantial loss through the membrane. The negative voltages in the anode are a result of the temperature in this electrode: temperatures higher than the standard



Figure 3.2 – Water fraction (left and right) and membrane water content (center) as a function of the fuel cell thickness, using base case parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$, $J'_{q,AP,entrance} = 0W/m^2$ and $a_{w,M,exit} = 1$.



Figure 3.3 – Voltage as a function of the fuel cell thickness, using base case parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$, $J'_{q,AP,entrance} = 0W/m²$ and $a_{w,M,exit} = 1$.



Figure 3.4 – Heat flux as a function of the fuel cell thickness, using base case parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m². An inlet heat flux $J'_{q,AP,entrance} = 0W/m^2$ was utilized in the simulations (see Section 2.7.6). The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$.

temperature of 298 K cause a positive increase in the chemical potential of the hydrogen, which leads to a decrease in the voltage for this electrode (due to the negative relationship between the electrode voltage and the Gibbs free energy). The most interesting result comes in the membrane: it can be seen that all of the voltage losses in the system are caused by the proton (and water) transport through the membrane, and that these values scale with the electric current density. Moreover, one can see in Figure 3.3 that the voltage always decreases regardless of the sign of the water flux (see Table 3.2), which means that the voltage losses are caused primarily by the transport of protons.

In the I-V curve of the fuel cell (Figure 3.6), a value slightly lower than the reference open-circuit potential (1.23 V) was obtained; this was caused by the way the overpotential was calculated: equation 2.52 shows a logarithmic dependence on the current density and, moreover, the exchange current density is always a value larger than zero. The smallest value of the electric current density that can be simulated using the model is, effectively, the exchange current density: a smaller simulated current density would result in a prediction of negative electric potentials produced in the fuel cell, which is not physically feasible.

As for the entropy production profile (Figure 3.5), one can conclude that the major sources of entropy in the system are the cathode and the membrane; for the former, the large entropy production comes from the fact that an exothermic reaction happens and thus there is a large production of entropy; in the membrane, the entropy production is originated by the dissipation of heat associated with the transport of electric current (note that, in Figure 3.4, the heat flux always increases in the membrane, regardless of the current density). It is interesting to note that the entropy production at the anode becomes larger with higher current densities; this was caused by an increase in the term $j/T_{AS} \Delta \phi_{A,eff}$ of equation 2.25, which dominates at higher current densities.



Figure 3.5 – Entropy production as a function of the fuel cell thickness, using base case parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$, $J'_{q,AP,entrance} = 0W/m²$ and $a_{W,M,exit} = 1$.

3.1.2. Entropy production departures in the base case scenario

Tables 3.3 and 3.4 show the entropy production departures obtained for each layer of the fuel cell, as well as the total entropy production departure, using base case parameters.

$j[A/m^2]$	$S_{dev,AP} \left[\% ight]$	$S_{dev,A} \left[\% ight]$	$S_{dev,M} \left[\% ight]$	$S_{dev,C} \left[\% ight]$	$S_{dev,CP}$ [%]
500	-0.11	-83.32	-40.96	2.17	0.01
1500	-0.24	15.10	4.42	-1.01	0.00
3000	-0.59	40.44	13.45	-2.07	0.01
5000	-0.97	26.57	10.16	-2.94	0.02

Table 3.3 – Entropy production departures of each layer of the fuel cell, using base case parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m².

$j \left[A/m^2 ight]$	$S_{dev,total}$ [%]
500	5.72
1500	2.05
3000	3.60
5000	6.75

Table 3.4 – Total entropy production departures, using base case parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m^2 .



Figure 3.6 – Voltage of the fuel cell for different electric current densities (I-V curve), using base case parameters. The boundary conditions utilized are $T_{AP,entrance} = 330K$, $J'_{q,AP,entrance} = 0W/m^2$ and $a_{w,M,exit} = 1$.

In Table 3.4, it can be seen that the total entropy production departure in the system ranges between 2% and 6%, which would be an indication that the model is consistent with the Second Law of thermodynamics; however, table 3.3 tells a different story: the entropy production departures of both porous transport layer are well below 1% (thus the model used for these layers is consistent with the Second Law of Thermodynamics) and the same can be said of the cathode, while the models for the anode and the membrane show that there is a large deviation between the entropy production and the difference of the inlet and outlet entropy fluxes, most likely caused by an incorrect set of parameters, assumptions and boundary conditions, in the model. An interesting remark that can be done is the fact that most of the entropy is produced in the cathode, which has a small entropy production departure, while the rest of the layers produce a smaller amount of entropy; the total entropy production, which means that the total entropy production departure can hide large entropy production departures in layers where a small amount of entropy is produced.

The conclusion here is that the total entropy production departure is not sufficient for the verification of the consistency of the model and the parameters utilized, because of the fact that the total entropy production departure overlooks the contribution of the layers with small entropy productions, which can, nonetheless, have substantially large entropy production departures. There is, thus, opportunity to find an optimal set of parameters, which can make the model presented in Chapter 2 consistent with the Second Law of Thermodynamics.

3.2. Parameter optimization

3.2.1. Optimization procedure

In order to achieve the optimization of the parameters used in the model, a new optimization parameter was introduced, which is called the *individual global entropy production departure*:

Where $S_{dev,AP}$ denotes the entropy production departure of the anode-side PTL (equation 2.11), $S_{dev,A}$ is the entropy production departure of the anode (equation 2.27), $S_{dev,M}$ corresponds to the entropy production departure of the membrane (equation 2.39), $S_{dev,C}$ is the entropy production departure of the cathode (equation 2.59), $S_{dev,CP}$ denotes the entropy production departure of the cathode-side PTL (equation 2.72) and $S_{dev,total}$ corresponds to the total entropy production departure of the fuel cell (equation 2.74). The symbol || denotes the absolute value of the quantity. The sum of the absolute values was chosen in order to take into account solely the magnitude of the entropy production departures.

Simulations were run for four electric current densities: 500, 1500, 3000 and 5000 A/m² for all the parameters except for the optimization of the initial heat flux, for which the whole spectrum of electric current densities was utilized, from 0 to 5000 A/m² (in increases of 200 A/m²); these current density values were chosen in order to cover a broad range of the I-V curve and thus to evaluate the effect of the changes in the parameters for different current densities. While a larger number of current densities could have been chosen, they would not provide meaningful information of the individual global entropy production departure and it would therefore result in longer simulation times that would nevertheless yield similar results; these current density values provide thus an optimal simulation time and optimization accuracy.

The individual global entropy production departure values obtained were added, in order to yield the *global entropy production departure*:

$$S_{dev,global} = S_{dev,global,500A/m^{2}} + S_{dev,global,1500A/m^{2}} + S_{dev,global,3000A/m^{2}} + S_{dev,global,5000A/m^{2}}$$
(3.2)

The optimal parameters are, therefore, the ones for which the value of $S_{dev,global-total}$ reaches a minimum.

The optimization of the parameters followed the following logic: one parameter was proposed and simulations were done in order to calculate the global entropy production departure (equation 3.2), using the base case values for rest of the parameters, and this process was repeated until either a minimum was obtained or a definite trend appeared that no minimum was going to be found; this was the *first optimization stage*.

Simulations were then done with a second parameter, using base case parameters for rest of the parameters except for the parameter that was previously optimized, for which the optimal value was used instead. This process was repeated for each one of the parameters depicted in this Section, and a total of 5 optimization stages were reached, which means that an optimal value (or set of values) was found for five of the parameters of the model, out of the 11 parameters evaluated.

3.2.2. Optimal initial heat flux

Figure 3.7 shows the initial heat flux values ($J'_{q,AP,entrance}$) that yield the minimum global entropy production departure, defined in equation 3.2.

It can be seen that, for the whole range of electric current densities evaluated, the optimal initial heat flux is always negative, which will result in increasing temperatures between the anode-side PTL and the cathode-side PTL. It can be concluded thus that negative (and changing) initial heat fluxes in the model are more in accordance with the Second Law of Thermodynamics than a static value of 0 W/m^2 .

The shape of the curve in Figure 3.7 is not very clear without information on the actual heat flux profile in the fuel cell for different electric current densities. It will be shown that the behavior of the optimal initial heat flux is related to the location where heat is coming out of the system, which, in



Figure 3.7 – Optimal initial heat flux curve for electric current densities in the range between 0 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$.

turn, will be related to the location where heat must be removed from the fuel cell in order to avoid overheating.

3.2.3. Optimal parameters in the membrane

Figures 3.8, 3.9, 3.10 and 3.11 show the global entropy production departure (as defined in equation 3.2) for different membrane transport parameters.

It is clear from Figure 3.8 that the optimal water transference coefficient (thus the electro-osmotic drag) in the membrane should have a value of 1 rather than the value of 1.2 utilized in the base case scenario; the value of 1 is the minimum value the electro-osmotic drag can take, due to the fact that the molecule that is being transported is H_3O^+ , which means that, for every proton transported, there is one water molecule that is transported as well and thus a value of less than 1 is not physically feasible. Moreover, it is interesting to note that the behavior of the global entropy production departure is exponential with respect to the transference coefficient (note that the scale of the y-axis in Figure 3.8 is logarithmic), which means that this parameter has a decisive role in the consistency of the model for the membrane.

It was shown in Section 2.7.6 that the transport properties of the membrane (except the transference coefficient, $t_{w,M}$) are not constant values but rather functions that depend on the temperature of the membrane and its water content, and thus different simulations were done adding a scaling factor to each one of these parameters. The values depicted at the top x-axis of Figures 3.9, 3.10 and 3.11 are the average values for the different current densities utilized.

Figure 3.9 shows that there is a minimum in the global entropy production departure when a scaling factor of 1.5 is utilized, which means that the optimal water diffusivity is 1.5 times larger than the value predicted by equation 2.87, making the value predicted by the correlation by Springer et al. (1991) underestimated. The fact that a scaling factor was chosen for the optimization of this parameter means that it is unclear if the dependence on either the temperature or the water content is correct and only



Figure 3.8 – Global entropy production departure as a function of the membrane transference coefficient $(t_{w,M})$. The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

the values are underestimated, or if there is actually a different dependence on any of those variables.

The optimal membrane thermal conductivity (Figure 3.10) was found to be 0.5 times the correlation shown in equation 2.88, which could mean that either the dependence on the water content is smaller or that the intercept (the thermal conductivity at zero water content) should be lower.

As for the membrane electric resistivity (Figure 3.11), optimization could not be achieved, due to the fact that there was a decreasing global entropy production departure profile when the electric resistivity increased, to the point that the model predicted negative voltage increases (which is physically unfeasible for a galvanic cell such as the fuel cell modeled in this work). It is concluded thus that the proposed optimization scheme cannot optimize the membrane electric resistivity.

3.2.4. Optimal parameters in the electrodes

Figures 3.12, 3.13 and 3.14 show the global entropy production departure (as defined in equation 3.2) for different electrode parameters.

It can be seen in Figure 3.12 that the optimal thermal conductivity lies close to the base case value but is slightly smaller, thus giving an indication that this transport parameter was already close to its optimal value (which can be confirmed by the low cathode entropy production departure shown in Table 3.3). This is an early indication that the parameters might not be responsible for the large entropy production departure in the anode and that the problem lies therefore in the assumptions made.

The electric resistivity of the electrodes (Figure 3.13) has a similar behavior than that of the membrane electric resistivity: there is a steady decrease in the global entropy production departure for larger resistivity values, up to the point that the total voltage produced by the fuel cell becomes negative; this further proves that this optimization scheme is not suitable for the optimization of electric resistivities in the system.



Figure 3.9 – Global entropy production departure as a function of the membrane water diffusivity ($D_{w,M}$). The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

The cathode exchange current density is the only non-transport parameter for which optimization was attempted: it is a parameter that evaluates the kinetic performance of the fuel cell and is therefore a sole function of the catalyst properties, such as active surface area and type of catalyst. Nevertheless, optimization was attempted, with the expected result that this parameter cannot be optimized with the chosen scheme (primarily due to the fact that this is not a transport parameter). Another interesting remark that can be done is the impact of the exchange current density in the global entropy production departure: as it can be seen in Figure 3.14, the global entropy production departure values lie between 75% and 79% for changes in the cathode exchange current density of almost three orders of magnitude; this is an indication that the exchange current density has little effect on the consistency of the model.

3.2.5. Optimal parameters in the anode-side PTL and cathode-side PTL

Figures 3.15, 3.16 and 3.17 show the global entropy production departure (as defined in equation 3.2) for different transport parameters in both porous transport layers.

In Figure 3.15, it can be seen that the base case value of $t_{w,AP} = 0$ was already the optimal, and the same can be said about the thermal conductivity (Figure 3.16); these results confirm what was already visible in Table 3.3: the parameter set in the model for the porous transport layers already yielded minimum entropy production departure values (well below 1%).

The electric resistivity, contrary to what happened with the other transport parameters for the porous transport layer (but as was expected given the results of the optimization of the electric resistivities of the rest of the layers), optimization could not be achieved, because of the steady decrease in the global entropy production departure for increasing electric resistivities; this, in turn, would predict negative voltages generated in the fuel cell (which is physically unfeasible). Note that the effect of the



Figure 3.10 – Global entropy production departure as a function of the membrane thermal conductivity (λ_M). The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

porous transport layer electric resistivity on the global entropy production departure is very small: it lies between 78%*and*76% for an increase in four orders of magnitude; this is a consequence of the fact that there is negligible voltage losses in these layers and therefore their contribution to the global entropy production departure is very small.

3.2.6. Global entropy production departure in different optimization stages

Figure 3.18 aids in the visualization of the effect of each optimized parameter in the global entropy production departure.

It is clear from Figure 3.18 that the parameter with the highest influence in the global entropy production departure is the initial heat flux, $J'_{q,AP,entrance}$: note how the global entropy production departure decreased from 260% to approximately 150%; the second parameter with the highest influence was the membrane water transference coefficient (whose optimal value further reduced the global entropy production departure to approximately 100%). The membrane thermal conductivity and water diffusivity have a significantly reduced effect on the global entropy production departure in comparison with the rest of the parameters (reducing its value altogether from 100% to 80%) and the parameter with the smallest contribution to the reduction in the global entropy production departure was the electrode thermal conductivity (with a reduction of a few percent points).

Table 3.5 shows the optimal transport parameters found in the optimizations, along with the base case values and a comparison between them.

The conclusion of the results shown in Figure 3.18 is that the initial heat flux plays a fundamental role in the consistency of the Non-Equilibrium Thermodynamics model for the fuel cell, and that, of all the transport parameters in the system, the membrane parameters are the most relevant for the



Figure 3.11 – Global entropy production departure as a function of the membrane electric resistivity (r_M^{ohm}). The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

Parameter	Optimized value	Base case value	Deviation
$J'_{q,AP,entrance}$	Varies	0	N/A
$t_{w,M}$	1	1.2	-20%
$D_{w,M}$	1.5x equation $2.7.13$	1x equation $2.7.13$	50%
λ_M	0.5x equation $2.7.14$	1x equation $2.7.14$	-50%
$\lambda_{A(C)}$	1539	1710	-10%

Table 3.5 – Optimal transport parameters found, base case transport parameters and the deviation between the optimal and the base case parameters.

compliance of the model with the Second Law of Thermodynamics.

3.2.7. Simulations with the optimal parameters

Figures 3.19, 3.20, 3.21, 3.22 and 3.23 show the simulated temperature, water fraction (and membrane water content), voltage, heat flux and entropy production profiles, using the optimized transport parameters found (see Table 3.5).

Tables 3.6 and 3.7 show the final outcomes of the simulations done with the optimized parameters.

Figure 3.24 shows the I-V curve of the fuel cell, obtained with the optimized parameters.

It can be seen in Figure 3.19 that the temperature profile of the cell at any electric current density is positive: there is a larger temperature in the cathode-side PTL than in the anode-side PTL, which is primarily caused by the negative optimal initial heat flux. What is interesting to note in Figure 3.19 is



Figure 3.12 – Global entropy production departure as a function of the electrode thermal conductivity ($\lambda_{A(C)}$). The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

$j \left[A/m^2 ight]$	$T_{CP,exit} - T_{AP,entrance} \left[K \right]$	$\phi_{CP,exit} - \phi_{AP,entrance} \left[V\right]$
500	25.99	0.412
1500	10.53	0.329
3000	5.69	0.228
5000	4.69	0.112

Table 3.6 – Temperature and voltage differences between inlet (left hand side of the anode porous transport layer) and outlet (right hand side of the cathode porous transport layer), using optimized parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m^2 .

$j \left[A/m^2 ight]$	$J_{w,AP}\left[mol/(m^2s)\right]$	$J_{w,CR}\left[mol/(m^2s)\right]$
500	-0.0003	0.0023
1500	-0.0029	0.0049
3000	0.0113	0.0269
5000	0.0339	0.0598

Table 3.7 – Water flux before and after the cathode, using optimized parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m^2 .

the behavior of the cell in both porous transport layers: although the optimal thermal conductivity was found to be equal to the base case scenario value, the temperature profile in the anode-side PTL is steadily increasing (regardless of the current density), while the cathode-side PTL shows a decreasing temperature from the cathode to the exit of the air; this is caused by a positive heat flux in this layer (see Figure 3.22). A positive heat flux in the cathode-side PTL means that heat is being conducted from the cathode to the exit air and there is a relationship between the electric current density and the value of the heat flux, which means that, at high current densities, heat exits the system through



Figure 3.13 – Global entropy production departure as a function of the electrode electric resistivity $(r_{A(C)}^{ohm})$. The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

both sides, which leads to the conclusion that cooling of the fuel cell has to happen through both the anode and the cathode when the current density is large. In a stack arrangement where several fuel cells are placed next to each other, this means that both exit heat fluxes converge in a single current collector (which also has channels through which coolant circulates), which leads to the conclusion that an external coolant supply is needed for large power applications: if the air that circulates through the cathode-side PTL were to be the only source of heat removal of the system, operation at large power applications would require a substantial amount of air in order to force all the heat to flow to the cathode, which would therefore require a large air supply system and thus large power demand, reducing the actual net power produced by a fuel cell system.

The water management of the fuel cell is a very important part of the operation of a fuel cell. Figure 3.20 shows that operation at large current densities leads to a decreasing membrane water content, which leads to large voltage losses in this layer (see Figure 3.21). According to Table 3.7, water exits through both sides of the fuel cell for the lower current densities, while, for larger currents, the water flows from the cathode to the exit air and, even though the temperature appears to be lower in this layer for large current densities (which leads to a low water saturation pressure), water keeps flowing to the exit air, which would therefore cause condensation of the water in the air, and this can lead unavoidably to blockage of the flow field through which air is supplied to the system. In conclusion, water needs to be removed from the cathode-side PTL to avoid blockage of the air path, in order to prevent increasingly high back pressures and thus the need for extra power in the air supply system, that would be required to overcome the blockages of the air flow field that are caused by the large amount of condensed water present in the cathode-side PTL.

As was said before, most of the voltage losses in the system are caused by the electric resistivity in the membrane (ohmic voltage losses), and these scale with the electric current density. According to Figure 3.24, it is only at current densities lower than 500 A/m² where the fuel cell has low voltage losses



Figure 3.14 – Global entropy production departure as a function of the cathode exchange current density (j_0). The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

caused by the charge transport in the membrane, which means that the operation window in which the main source of voltage losses is the low cathode exchange current density (thus the *activation overpotential*) is limited to low current densities.

The heat flux profile (Figure 3.22) is related to both the temperature and the water flux in the system: Figure 3.22 shows that, for the largest current density simulated (5000A/m²), the anode is the source of most of the heat produced in the system. This is caused by the large water flux that flows from the anode to the cathode, which causes a large amount of water condensation in the anode (since water enters from the hydrogen stream as a vapor and needs to enter the membrane as a liquid in order to be able to conduct protons). The temperature and heat flux profiles show the relevance of the water management of the fuel cell: if there happened to be a larger temperature gradient between the incoming hydrogen and the anode, water might condense in this electrode, because more heat would start to flow to the left and it might be absorbed by the water in order to evaporate again and incorporate itself to the hydrogen stream; since hydrogen is already at 100% relative humidity, the extra water would start condensing in the hydrogen flow field, leading to blockages of the hydrogen path. This is the reason behind the usage, in some fuel cell system setups, of a heat exchanger that warms up the inlet hydrogen to the fuel cell, using the larger temperature of the exiting hydrogen stream.

The entropy production profiles (Figure 3.23) show that, again, the cathode is the main source of the production of entropy in the system, while the membrane accounts for a substantial increase in the entropy production of the system when operating at high current densities (because of the dissipation of heat in this layer).

The voltage-current density characteristic (I-V curve) of the fuel cell, using optimized transport parameters, is depicted in Figure 3.24, and compared to the I-V curve shown in Figure 3.6, in order to show that the parameters obtained do not change significantly the electric characteristics of the



Figure 3.15 – Global entropy production departure as a function of the anode-side PTL transference coefficient ($t_{w,AP}$). The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

fuel cell. The fact that the curve obtained with optimized values lies slightly below the base case one is caused by a lower membrane thermal conductivity (Table 3.5), which causes a larger temperature gradient in the membrane, which, in turn, increases the electric resistivity of the membrane, leading to higher dissipation of heat and thus larger voltage losses.

3.2.8. Entropy production departures in the optimized scenario

Tables 3.8 and 3.9 show the entropy production departures obtained for each layer of the fuel cell, as well as the total entropy production departure, using optimized parameters.

$j \left[A/m^2 ight]$	$S_{dev,AP}\left[\% ight]$	$S_{dev,A} \left[\% ight]$	$S_{dev,M} \left[\% ight]$	$S_{dev,C} \left[\% ight]$	$S_{dev,CP}\left[\% ight]$
500	-0.11	-0.35	-0.15	-0.37	0.00
1500	-0.31	-8.77	-3.90	-0.40	0.47
3000	-0.53	18.76	6.37	-1.24	0.03
5000	-0.71	22.22	7.15	-1.78	0.04

Table 3.8 – Entropy production departures of each layer of the fuel cell, using optimized parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m^2 .

Table 3.9 shows that the total entropy production departures are close to 1% for the four electric current densities simulated during the optimization, and they are significantly lower than the total deviations found with the base case scenario (Table 3.4), which ranged from 2% to 6%. However, as was stated previously, the total entropy production departures do not depict the actual consistency of the model.



Figure 3.16 – Global entropy production departure as a function of the anode and cathode-side PTL thermal conductivity $(\lambda_{AP(CP)})$. The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

$j[A/m^2]$	$S_{dev,total} [\%]$
500	-1.28
1500	0.66
3000	-0.56
5000	-1.35

Table 3.9 – Total entropy production departures, using optimized parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m².

Comparing the results in Table 3.8 with those depicted in Table 3.3, one can notice that the models for both porous transport layers are still in compliance with the Second Law of Thermodynamics (with entropy production departures well below 1%), which was to be expected, since the transport parameters in these layers are already the optimal. The entropy production departure values of the cathode were reduced, from between 1% and 3% to less than 2% for current density of 5000 A/m², which is an initial sign that optimization was achieved. The entropy production departures of the anode and membrane show a much larger reduction: the anode, with the highest entropy production departures (from 15% to 83%), has now entropy production departures that span between 0.35% to 22%, while the membrane underwent a reduction from between 4% and 41%, to a range of values between 0.15% and 7%. Although optimization was reached, entropy production departures in the anode of 22% are still present, which leads to the conclusion that there must be an assumption made in this electrode that leads to a model that is not very consistent with the Second Law of Thermodynamics.



Figure 3.17 – Global entropy production departure as a function of the anode and cathode-side PTL electric resistivity ($r_{AP(CP)}^{ohm}$). The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

3.3. Water equilibrium assumption and optimization of the electrode water diffusivity

As was argued in the previous Section, the model developed for the fuel cell is not entirely in agreement with the Second Law of Thermodynamics, and the main source of this disagreement is the model for the anode. According to Section 2.7, the only different assumption between the anode and the cathode (for which the model and the parameter set complies with the Second Law of Thermodynamics) is the assumption that water is at equilibrium in the anode. The implication of this assumption is that the chemical potential of the water at the interface between the anode-side PTL and the anode (thus at the right hand side of the anode-side PTL) is identical to the chemical potential of the water at the interface between the anode and the membrane (thus at the left hand side of the membrane).

The water equilibrium assumption has been utilized in order to calculate the water activity at the left hand side of the membrane (see Section 2.8.5) and so far it has yielded results that agree with what was expected: at higher current densities, more water is transported across the membrane and therefore there is a lower amount of water at the interface anode-membrane. However, with anode entropy production departures that are as high as 22% with optimized transport parameters, it appears as if that assumption might not hold. In this Section, the assumption of water equilibrium will be removed from the model and, instead, another model will be proposed, namely for the water transport across the electrodes, along with the optimization of the water diffusivity.

3.3.1. Model for the water transport across the electrodes

According to Kjelstrup and Røsjorde (2005), the chemical potential difference of the water at the interfaces between the electrodes and the backings/membrane, as a function of the coupled mass-charge and mass-heat transfer, can be depicted as follows:



Figure 3.18 – Global entropy production departure for the different optimization stages. Each optimization stage illustrates which set of parameters were optimized in each case.

$$\Delta\mu = -\frac{q_w^*}{T}\Delta T - \frac{\left(J_w - t_w \frac{j}{F}\right)}{l_{\mu\mu}}$$
(3.3)

Where q_w^* represents the heat of transfer (that represents the coupling between the water and the heat transport), *T* is the temperature of the interface, J_w represents the water flux through the electrode, t_w is the water transference coefficient of the interface, *j* is the electric current density, *F* represents Faraday's constant (96485 C/mol) and the term $l_{\mu\mu}$ is the Onsager mass transport coefficient (Kjelstrup and Røsjorde, 2005). The relationship between the Onsager mass transport coefficient and the water diffusivity is the following (Kjelstrup et al., 2010, pages 50 and 51):

$$l_{\mu\mu} = \frac{c_w D_w}{R} \tag{3.4}$$

Where c_w is the total concentration of water in the interface, D_w is the water diffusivity and R is the universal gas constant (8.314 J/mol K). Equation 3.3 can be used for al four electrode interfaces. At the interface anode-side PTL-anode:

$$\mu_{w,T,AS} = \mu_{w,T,AL} - \frac{q_{w,AL}^*}{T_{AL}} \left(T_{AS} - T_{AL} \right) - \frac{R \left(J_{w,AL} - t_{w,AL} \frac{j}{F} \right)}{c_{w,AL} D_{w,A}}$$
(3.5)

Where $\mu_{w,T,AS}$ is the chemical potential (at constant temperature) of the water at the anode surface, $\mu_{w,T,AL}$ is the chemical potential (at constant temperature) of the water at the anode left hand side (thus the value at the right hand side of the anode-side PTL), $q_{w,AL}^*$ is the heat of transfer at the anode left hand side, T_{AL} is the temperature at the anode left hand side, T_{AS} is the temperature at the anode surface, $J_{w,AL}$ is the water flux at the anode left hand side, $t_{w,AL}$ is the water transference coefficient



Figure 3.19 – Temperature as a function of the fuel cell thickness, using optimized parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

at the anode left hand side (thus the transference coefficient of the anode-side PTL) and $D_{w,A}$ is the water diffusivity at the anode. The value $c_{w,AL}$ represents the total concentration of water at the anode left hand side and, given the fact that water at the anode-side PTL is inn the vapor state, the total concentration can be calculated (assuming the hydrogen-water mixture to behave as ideal) as follows:

$$c_{w,AL} = x_{w,AL} \frac{p_{AL}}{RT_{AL}}$$
(3.6)

Where $x_{w,AL}$ is the water mole fraction at the anode left hand side and p_{AL} is the total system pressure at the anode left hand side.

In a similar fashion, the water chemical potential difference at the interface anode-membrane can be calculated:

$$\mu_{w,T,AR} = \mu_{w,T,AS} - \frac{q_{w,AR}^*}{T_{AR}} \left(T_{AR} - T_{AS} \right) - \frac{R \left(J_{w,AR} - t_{w,AR} \frac{J}{F} \right)}{c_{w,AR} D_{w,A}}$$
(3.7)

Where $\mu_{w,T,AR}$ is the chemical potential (at constant temperature) of the water at the anode right hand side, $q^*_{w,AR}$ is the heat of transfer at the anode right hand side, T_{AR} is the temperature at the anode right hand side, $J_{w,AR}$ is the water flux at the anode right hand side and $t_{w,AR}$ is the water transference coefficient at the anode right hand side (thus the value of the transference coefficient of the membrane). The total water concentration at the interface anode-membrane, $c_{w,AR}$, is a bit more complicated and less intuitive to calculate.

In order to know the water concentration at the membrane left hand side, two membrane parameters are needed: the dry density of the Nafion[®] membrane and its acid capacity. The first parameter



Figure 3.20 – Water fraction (left and right) and membrane water content (center) as a function of the fuel cell thickness, using optimized parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are: $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.



Figure 3.21 – Voltage as a function of the fuel cell thickness, using optimized parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.



Figure 3.22 – Heat flux as a function of the fuel cell thickness, using optimized parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

(membrane dry density, ρ_M) shows the density of the material, while the second one represents the amount of sulphonic acid groups present in the membrane. It was shown in Figure 2.3 that the Nafion[®] membrane consists of chains of polytetrafluoroethylene, with side chains that end with a —HSO₃ radical group; the amount of acid groups of the membrane, called *total acid capacity* (represented in Table 2.2 with the symbol A_C), represents the number of H⁺ groups that can be released by the membrane (therefore expressed in eq/kg); since the —HSO₃ radical groups can release one proton per molecule, the units of the total acid capacity can be expressed in mol_{acid groups}/kg_{membrane}, and, according to Table 2.2, there is a concentration of 0.91 moles of acid groups per kilogram of membrane. Finally, the amount of water molecules that are present in the membrane is a value introduced in Section 2.3, namely the water content of the membrane (represented by the symbol l_w), and is expressed in mol_{water}/mol_{sulphonic acid group; subsequently, the total concentration of water in the membrane can be expressed as:}

$$c_{w,AR} = \rho_M A_c l_{w,AR} \tag{3.8}$$

Where $l_{w,AR}$ represents the water content at the membrane left hand side, which is a function of the water activity at the interface anode-membrane (and is calculated using equation 2.36).

The difference in the water chemical potential across the interfaces anode-side PTL-anode and anodemembrane has an effect on the effective potential difference in that electrode; the total effective potential difference of the anode can be, then, written as follows:

$$\Delta \phi_{A,eff} = -\frac{\pi_{AL}}{T_{AL}F} (T_{AS} - T_{AL}) - \frac{\pi_{AR}}{T_{AR}F} (T_{AR} - T_{AS}) - r_{S}^{ohm} j - \frac{t_{w,AL}}{F} (\mu_{w,T,AS} - \mu_{w,T,AL}) - \frac{t_{w,AR}}{F} (\mu_{w,T,AR} - \mu_{w,T,AS})$$
(3.9)



Figure 3.23 – Entropy production as a function of the fuel cell thickness, using optimal parameters, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

Where π_{AL} and π_{AR} are the Peltier heat due to charge transport at the anode left and right hand sides, respectively, and r_s^{ohm} represents the electrode resistivity.

The entropy production is also affected by the non-zero chemical potential difference in the anode; the total entropy production in the anode can be calculated as follows:

$$\sigma_{A} = J'_{q,AR} \left(\frac{1}{T_{AR}} - \frac{1}{T_{AS}} \right) + J'_{q,AL} \left(\frac{1}{T_{AS}} - \frac{1}{T_{AL}} \right) - \frac{j}{T_{AS}} \Delta \phi_{A,eff} - \frac{J_{w,AL}}{T_{AL}} \left(\mu_{w,T,AS} - \mu_{w,T,AL} \right) - \frac{J_{w,AR}}{T_{AR}} \left(\mu_{w,T,AR} - \mu_{w,T,AS} \right)$$
(3.10)

Where $J'_{q,AL}$ and $J'_{q,AR}$ are the heat fluxes at the left and right hand side of the anode, respectively.

Since the model would not be consistent if the water transfer in the cathode were not to be modeled in a similar fashion to the anode (although, as has been seen earlier, this membrane already complies with the Second Law of Thermodynamics and thus any change might result in a deviation), analogue equations to 3.5 and 3.7 were developed for the cathode:

$$\mu_{w,T,CS} = \mu_{w,T,CL} - \frac{q_{w,CL}^*}{T_{CL}} \left(T_{CS} - T_{CL} \right) - \frac{R \left(J_{w,CL} - t_{w,CL} \frac{J}{F} \right)}{c_{w,CL} D_{w,C}}$$
(3.11)

$$\mu_{w,T,CR} = \mu_{w,T,CS} - \frac{q_{w,AR}^*}{T_{CR}} \left(T_{CR} - T_{CS} \right) - \frac{R \left(J_{w,CR} - t_{w,CR} \frac{j}{F} \right)}{c_{w,CR} D_{w,C}}$$
(3.12)



Figure 3.24 – Voltage of the fuel cell for different electric current densities (I-V curve), using optimized parameters and base case parameters. The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

All the variables and parameters in equations 3.11 and 3.12 are similar to those present in equations 3.5 and 3.7, and were introduced in Section 2.4. The total water concentrations for each of the interfaces in the cathode (membrane-cathode and cathode-cathode-side PTL) are defined as follows:

$$c_{w,CL} = \rho_M A_c l_{w,CL} \tag{3.13}$$

Where $l_{w,CL}$ represents the water content at the membrane right hand side, which is a function of the water activity at the interface membrane-cathode and, according to the assumption made in Section 2.7.3, is equal to 14.

Accordingly, the total water concentration at the interface cathode-cathode-side PTL can be expressed as follows (assuming the gas mixture water-oxygen-nitrogen to behave ideally):

$$c_{w,CR} = x_{w,CR} \frac{p_{CR}}{RT_{CR}}$$
(3.14)

Where $x_{w,CR}$ is the water mole fraction at the left hand side of the cathode-side PTL, p_{CR} is the cathode-side PTL pressure and T_{CR} is the temperature at the left hand side of the cathode-side PTL.

Similarly, the equations for the cathode effective potential difference and the total entropy production were found:

$$\Delta \phi_{C,eff} = -\eta_C - \frac{\pi_{CL}}{T_{CL}F} (T_{CS} - T_{CL}) - \frac{\pi_{CR}}{T_{CR}F} (T_{CR} - T_{CS}) - r_S^{ohm} j - \frac{t_{w,CL}}{F} (\mu_{w,T,CS} - \mu_{w,T,CL}) - \frac{t_{w,CR}}{F} (\mu_{w,T,CR} - \mu_{w,T,CS})$$
(3.15)



Figure 3.25 – Global entropy production departure as a function of the electrode water diffusivity ($D_{W,A(C)}$). The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{W,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

$$\sigma_{C} = J'_{q,CR} \left(\frac{1}{T_{CR}} - \frac{1}{T_{CS}} \right) + J'_{q,CL} \left(\frac{1}{T_{CS}} - \frac{1}{T_{CL}} \right) - \frac{j}{T_{CS}} \Delta \phi_{C,eff} - \frac{J_{w,CL}}{T_{CL}} \left(\mu_{w,T,CS} - \mu_{w,T,CL} \right) - \frac{J_{w,CR}}{T_{CR}} \left(\mu_{w,T,CR} - \mu_{w,T,CS} \right)$$
(3.16)

Where η_C is the cathode overpotential (equation 2.52), π_{CL} and π_{CR} are the Peltier heats of the cathode left and right hand side, respectively, and $J'_{q,CL}$ and $J'_{q,CR}$ are the heat fluxes at the cathode left and right hand side.

Equations 3.5, 3.7, 3.11 and 3.12 were incorporated to the model presented in Chapter 2, and the following equation substitutions were made: equation 3.9 substituted equation 2.21, equation 3.10 substituted equation 2.25, equation 3.15 substituted equation 2.51 and, finally, equation 3.16 substituted equation 2.57. The optimization scheme described in Section 3.2 was applied as well. The only assumption that was made in this Section is that the water diffusivities of both electrodes are identical, therefore:

$$D_{w,A} = D_{w,C}$$
 (3.17)

3.3.2. Optimization of the water diffusivity

Figure 3.25 shows the global entropy production departure (as defined in Section 3.2). A base case parameter value of $D_{w,A(C)} = 5.8 \times 10^{-3} m/s$ was utilized, and it is defined as the electrode water diffusivity that gives a similar global entropy production departure as the fifth optimization stage (see Section 3.2.6).



Figure 3.26 – Global entropy production departure for the different optimization stages, including optimization of the electrode water diffusivity. Each optimization stage illustrates which set of parameters were optimized in each case.

It can be seen in Figure 3.25 that optimization is not possible using the scheme presented in this work, due to the fact that the global entropy production departure decreases with steadily decreasing water diffusivities, while, as one could expect, lower diffusivities predict negative voltages produced by the fuel cell. An optimal value was found at 2.6×10^{-3} m/s, which corresponds to a water diffusivity that yields lower global entropy production departures than the base case parameter, while still predicting positive voltages out of the fuel cell. The optimal electrode water diffusivity would have to be confirmed experimentally (as it has never been introduced before), but this work is able to provide an estimation for this value, that could be used to confirm experimental results.

Figure 3.26 shows the global entropy production departure for the different optimization stages (see Figure 3.18) and includes the optimization done for the electrode water diffusivity.

From Figure 3.26, it is interesting to note that the electrode water diffusivity has a larger effect on the global entropy production departure than previously optimized parameters, namely the membrane water diffusivity and the thermal conductivities of both the membrane and the electrodes. As was said before, the optimized value of the electrode water diffusivity is an estimated value that yields lower global entropy production departures (thus increasing the numerical proximity between the entropy production calculated with Non-Equilibrium Thermodynamics and the difference in entropy fluxes in the electrodes) while still predicting positive voltages in the fuel cell (otherwise this value would lead to prediction of physically impossible operation in the fuel cell).

The reason behind the inability of this work to optimize the electrode water diffusivity using the optimization scheme presented in Section 3.2.1 is the fact that, despite the electrode water diffusivity being a transport parameter, it depends solely on the properties of the electrode, namely the type of catalyst support and its physical characteristics, such as its surface area and pore size and distribution, to name a few, and it is in this sense that an optimal value of the electrode water diffusivity can only be found for a particular type of catalyst. Moreover, the interface porous transport layer-electrode and



Figure 3.27 – Temperature as a function of the fuel cell thickness, using the optimized electrode water diffusivity, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

electrode-membrane is a rather complex system (see Figures 2.2 and 2.5) and, even for a well-defined catalyst, the electrode water diffusivity can change substantially, depending on how the fuel cell was prepared. This does not mean that the results obtained in this Section are meaningless; on the contrary, it has been found that, should experiments be conducted and electrode water diffusivities be obtained for a catalyst (and fuel cell layers in general) whose materials are the ones used in the simulations done in this work, values of the electrode water diffusivity between 2.6×10^{-3} m/s and 5.8×10^{-3} m/s should be found.

3.3.3. Simulations with the optimal electrode water diffusivity

Figures 3.27, 3.28, 3.29, 3.30 and 3.31 show the simulated temperature, water fraction (and membrane water content), voltage, heat flux and entropy production profiles, using the optimized electrode water diffusivity of 2.6×10^{-3} m/s.

$j[A/m^2]$	$T_{CP,exit} - T_{AP,entrance} \left[K \right]$	$\phi_{CP,exit} - \phi_{AP,entrance} \left[V \right]$
500	24.04	0.370
1500	9.02	0.294
3000	7.47	0.173
5000	8.60	0.019

Tables 3.10 and 3.11 show the final outcomes of the simulations done with the optimized parameters.

Table 3.10 – Temperature and voltage differences between inlet (left hand side of the anode porous transport layer) and outlet (right hand side of the cathode porous transport layer), using the optimized electrode water diffusivity, for electric current densities of 500, 1500, 3000 and 5000 A/m^2 .



Figure 3.28 – Water fraction (left and right) and membrane water content (center) as a function of the fuel cell thickness, using the optimized electrode water diffusivity, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.



Figure 3.29 – Voltage as a function of the fuel cell thickness, using the optimized electrode water diffusivity, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.


Figure 3.30 – Heat flux as a function of the fuel cell thickness, using the optimized electrode water diffusivity, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

$j \left[A/m^2 ight]$	$J_{w,AP}\left[mol/(m^2s)\right]$	$J_{w,CR}\left[mol/(m^2s)\right]$
500	0.0047	0.0073
1500	0.0009	0.0086
3000	0.0061	0.0216
5000	0.0214	0.0473

Table 3.11 – Water flux before and after the cathode, using the optimized electrode water diffusivity, for electric current densities of 500, 1500, 3000 and 5000 A/m^2 .

The temperature, voltage, heat flux and entropy production profiles obtained for the optimized electrode water diffusivity are very similar to the ones obtained in Section 3.2.7 (where the rest of the optimal parameters are used in the simulations), which proves that the water equilibrium assumption is but a mere special case of a more general model, that takes into account the resistances to the transport of water in the fuel cell. The most meaningful result obtained was in the membrane water content profile (Figure 3.28), where a more clear distinction in the water content of the membrane at the left hand side is visible for the different electric current densities simulated. This result is in a better agreement to what is expected of the water content of the membrane: there should be a more clear reduction in the water activity at the membrane left hand side when the current density increases, due to the fact that more water is flowing towards the cathode (as can be seen in Table 3.11) and therefore there should be a lower water content in the membrane.

3.3.4. Entropy production departures in the optimized electrode water diffusivity scenario

Tables 3.12 and 3.13 show the entropy production departures obtained for each layer of the fuel cell, as well as the total entropy production departure, using optimized parameters.



Figure 3.31 – Entropy production as a function of the fuel cell thickness, using the optimized electrode water diffusivity, for electric current densities of 500, 1500, 3000 and 5000 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

$j \left[A/m^2 ight]$	$S_{dev,AP} \left[\% ight]$	$S_{dev,A} \left[\% ight]$	$S_{dev,M} \left[\%\right]$	$S_{dev,C} \left[\% ight]$	$S_{dev,CP} \left[\%\right]$
500	-0.10	4.84	1.94	-5.83	0.00
1500	-0.30	0.96	1.10	-5.43	0.22
3000	-0.57	2.74	3.72	-4.93	0.02
5000	-0.90	4.77	3.14	-3.28	0.03

Table 3.12 – Entropy production departures of each layer of the fuel cell, using the optimized electrode water diffusivity, for electric current densities of 500, 1500, 3000 and 5000 A/m^2 .

$j \left[A/m^2 ight]$	$S_{dev,total}$ [%]
500	-7.87
1500	-4.31
3000	-3.62
5000	-2.45

Table 3.13 – Total entropy production departures, using the optimized electrode water diffusivity, for electric current densities of 500, 1500, 3000 and 5000 A/m^2 .

According to Table 3.13, the total entropy production departure of the model is larger than even the results obtained with the base case parameters (see Table 3.4), which, in turn, were already larger than the optimized scenario (Table 3.9); this could be an indication that the model of one of the layers of the fuel cell might not be correct but, as was argued before, the total entropy production departure is not a parameter that can be interpreted by itself: the entropy production departures of each one of the layers should be utilized in order to draw conclusions from the results.

Tables 3.12 and 3.13 show that the entropy production departure of every layer in the fuel cell is below 5% (in fact, the only value above 5% is the total entropy production departure of the simulations done at 500 A/m²); there is a clear reduction in the entropy production departures in the anode (which acquired values, in the optimized scenario, of up to 22%) and in the membrane as well: in the optimized parameters scenario (Table 3.8), membrane entropy production departures reached up to 7%, while the introduction of the water transport through the electrodes decreased the departures to a maximum of 4%. The reduction in the anode and membrane entropy production departures came at the expense of an increase in the cathode entropy production departures (which had values of less than 2%). The reason behind the larger total entropy production departures are the larger cathode entropy production departures and the fact that the cathode is the largest entropy producer (see Figure 3.31) and is therefore a consequence of the alteration of the model in this layer. Nevertheless, the entropy production departures for every layer, as well as the total departure, acquired values well below 10%, which indicates that, within the expected numerical error propagation (remembering that the implementation of the model in a computational environment requires the usage of numerical integrators and algebraic iteration methods, which have numerical errors inherent to their nature and this, in turn, will cause accumulation of errors in the final outcomes, leading to deviations between the entropy production departure calculated with one way or the other), the obtained model (and parameter set) is closer to agreement with the Second Law of Thermodynamics.

3.4. Hydrogen and air relative humidity: effect on the performance of the PEMFC

After having obtained a Non-Equilibrium Thermodynamics model that is more consistent with the Second Law of Thermodynamics (in comparison with the base case scenario model), the next part of this work will explore the effect of two different operational assumptions in the model, namely the effect of using hydrogen and air with different relative humidities, in the voltage and water profiles of the fuel cell.

The relative humidity is a parameter that depicts the water content in a gas at a certain temperature and is mainly affected by the temperature of said gas. The transport of water to and from a gas stream is affected by both thermodynamic and transport parameters (see, for example, Perry et al. (1999), chapter 12, page 12-3). Nevertheless, it was assumed in this work that the main property that affects the relative humidity of a gas is the saturation pressure of the water at a certain temperature; therefore, equation 2.82 is used as the relationship between relative humidity and the water mole fraction in a gas stream.

3.4.1. Hydrogen relative humidity

Figures 3.32 and 3.33 show, respectively, the water and voltage profiles of the fuel cell at different hydrogen RH (relative humidity) values, simulated with an electric current density of $500A/m^2$.

Figure 3.34 shows the I-V curves of the fuel cell at different hydrogen relative humidities.

The results are clear: the usage of low hydrogen relative humidities leads to low membrane water contents at the left hand side (Figure 3.32), which, in turn, cause a lower water content throughout the whole membrane, that leads to a higher membrane electric resistivity. Although this effect appears not to be very relevant in the simulations done with 500 A/m², the I-V curve (Figure 3.34) shows that this effect is consistent regardless of the electric current density at which the fuel cell is operated.

Apparently, a loss of voltage of 0.1 V might not be as important as one may think, because one might expect this to be the uncertainty of the device with which the voltage produced by the fuel cell is measured. We can put this voltage loss in perspective: when operating at 500 A/m², the power loss of the fuel cell corresponds to 50 W/m² with a 25% relative humidity hydrogen; this power production corresponds to one fourth of the value when operating at 100% relative humidity (with a power output of 200 W/m²). When the current demanded from the fuel cell increases to 5000 A/m², the power losses become significantly higher: operation with 100% relative humidity hydrogen leads to a power



Figure 3.32 – Water fraction (left and right) and membrane water content (center) as a function of the fuel cell thickness, using optimized parameters (excluding the electrode water diffusivity), for hydrogen relative humidity values of 100%, 75%, 50% and 25%, and an electric current density of 500 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

output of 750 W/m², while the lowest relative humidity value (25%) simulated, can produce only one third of the fully-humidified value (250 W/m²), resulting in a power loss of 67%.

The conclusion that can be drawn from these simulations is that operation with high hydrogen relative humidities is mandatory in order to ensure that the fuel cell produces the maximum possible power and, therefore, that it is operated at an optimal efficiency.

3.4.2. Air relative humidity

Figures 3.35 and 3.36 show, respectively, the water and voltage profiles of the fuel cell at different air RH (relative humidity) values, simulated with an electric current density of 500 A/m².

Figure 3.37 shows the I-V curves of the fuel cell at different air relative humidities.

According to Figures 3.35 and 3.36, the operation of the fuel cell with different air relative humidities results in an almost negligible difference in both the voltage profile and the water content of the membrane, and the only difference in the profiles lies in the cathode-side PTL (as expected). Simulation with different current densities results in a slight (almost not perceivable in Figure 3.37) increase in the voltage produced in the fuel cell, which is primarily caused by an increase in the oxygen partial pressure. It was expected, however, that operation with decreasing air relative humidities would have at least the same effect as operation with decreasing hydrogen relative humidities (see Section 3.4.1) because of an expected increase in the driving force that leads to a higher water flux that exits the fuel cell.

The conclusion that can be drawn from the simulations carried out with different air relative humidities is that the model presented in Chapter 2 cannot predict the effect of different inlet air conditions in the fuel cell, mainly because of the fact that drying out of the fuel cell is caused by transport processes that are not taken into account in the model (the drag of condensed water, for example, was not included



Figure 3.33 – Voltage as a function of the fuel cell thickness, using optimized parameters (excluding the electrode water diffusivity), for hydrogen relative humidity values of 100%, 75%, 50% and 25%, and an electric current density of 500 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

in the model). The main consequence of the usage of air with lower humidity should be a decrease in the water content of the membrane at the right hand side (which was, as an assumption, set to 14), which carries, as a consequence, the fact that this assumption is coupled to the assumption of operation with air with 100% relative humidity. It was found, therefore, that this is a limitation on the model and, as such, it should not be used to perform any attempts on utilizing the model to simulate the effect low humidity air has on the performance of the fuel cell.

It is important to emphasize that the results that have been obtained with the model are not necessarily meaningless due to the sole fact that the model is incapable to simulate operation with dry air. On the contrary, the results that were already shown in previous Sections of this work are of extreme relevance in order to understand the coupling of the mass, heat and charge transport in a fuel cell, and the only conclusion that arises from the results in this Section is that the model, as any other model that attempts to give insight on the operation of a fuel cell, has its limitations and is therefore capable of producing meaningful results on some of the operational choices a fuel cell system designer has to make in terms of materials and balance of plant components, but not every one of them.



Figure 3.34 – Voltage of the fuel cell for different electric current densities (I-V curve), using optimized parameters (excluding the electrode water diffusivity), for hydrogen relative humidity values of 100%, 75%, 50% and 25%. The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.



Figure 3.35 – Water fraction (left and right) and membrane water content (center) as a function of the fuel cell thickness, using optimized parameters (excluding the electrode water diffusivity), for air relative humidity values of 100%, 75%, 50% and 25%, and an electric current density of 500 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.



Figure 3.36 – Voltage as a function of the fuel cell thickness, using optimized parameters (excluding the electrode water diffusivity), for air relative humidity values of 100%, 75%, 50% and 25%, and an electric current density of 500 A/m². The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.



Figure 3.37 – Voltage of the fuel cell for different electric current densities (I-V curve), using optimized parameters (excluding the electrode water diffusivity), for air relative humidity values of 100%, 75%, 50% and 25%. The boundary conditions utilized are $T_{AP,entrance} = 330K$ and $a_{w,M,exit} = 1$, while the initial heat flux utilized was taken from Figure 3.7.

4

Conclusions

In this work, a model derived from Non-Equilibrium Thermodynamics was utilized in order to gain insight on the transport processes that occur in a fuel cell. According to Non-Equilibrium Thermodynamics, the water, electric charge and heat fluxes are not independent but rather related to one another, and it was in this sense that Non-Equilibrium Thermodynamics was chosen as an appropriate framework within which the coupling of these transport processes was modeled. In the end, the model utilized provided insight on the effect of different transport processes on the overall performance of the fuel cell. The input that the model gave was valuable not only to understand phenomena such as the transport of water through the Nafion[®] membrane due to the transport of charge in this layer, or the temperature gradients present in the different layers of the fuel cell; the model was also useful for understanding the relevance of the water management in the fuel cell. The modeling exerts the importance of ensuring correct operation of the fuel cell and optimal power production, as well as the importance of choosing the appropriate balance of plant components and correct operational conditions (such as the temperature and water content of the inlet gas streams) for a fuel cell system.

The model utilized in this document is one-dimensional and, as such, does not predict the flow of material or heat in an orthogonal direction with respect to the thickness of the PEMFC. Modeling a multi-dimensional fuel cell might give a more accurate representation of the distribution of the heat and water in the fuel cell. Such a model would be able to predict, for example, where a leakage of water can occur (if water flows to the gas inlet or to the outlet) which can lead to the prediction of water blockages in the flow fields of the current collectors that can, in turn, cause the back pressure increases that often occur in a fuel cell. Moreover, a multi-dimensional model can be used to design an optimal cooling system for the fuel cell, in order to remove the heat more effectively from the fuel cell, according to the insight such a model can bring in terms of the direction of the heat flux produced in the cell e.g. a multi-dimensional model could predict if the heat is accumulated in the center of the fuel cell or if it tends to flow to the boundaries (orthogonal to the fuel cell thickness).

4.1. Consistency of the model with the Second Law of Thermodynamics

The model utilized in this work follows the Laws of Thermodynamics, it was derived from the principle of energy conservation and from the calculation of the entropy production in the fuel cell system. The choice of transport parameters is of utmost relevance for ensurinng that the model is consistent with the Second Law of Thermodynamics, because it may affect the set of assumptions that can be made. An evaluation parameter was proposed in this work, namely the entropy production departure, which was utilized for the calculation of the difference between the production of entropy in each layer of the fuel cell, calculated with two different methods: with the Non-Equilibrium Thermodynamics model and with the difference in the entropy fluxes (into and out of each layer). Although, in previous works, the total entropy production departure had already been utilized in order to prove the consistency of the model with the Second Law of Thermodynamics, it was proven that the total entropy production departure is insufficient to characterize the consistency of the model. The reason behind the insufficiency of the total

entropy production departure as a consistency-control parameter is that it gives a higher importance to the layers with the largest entropy production. The calculation of the entropy production departure of each layer was found to be a better approach for the determination of the consistency of the model utilized.

In this work, it was found that the set of parameters chosen for the first simulations of the model yield large entropy production departures in some of the layers of the fuel cell, which pointed out to the need of finding a set of parameters that decreased the entropy production departures of each one of the layers, as well as the total entropy production departure. An optimization variable was proposed, namely the Global Entropy Production Departure, that adds up the entropy production departures of each layer in the system with the total entropy production departure in order to give an oversight of the numerical consistency of the parameter set utilized. An optimization scheme was introduced: different values of each one of the eleven parameters used in the original model were simulated utilizing different electric current density values and an optimal was found whenever the global entropy production departure decreased to a minimum.

It was found in this work that out of the eleven evaluated parameters (the thermal conductivity and electric resistivity in the membrane, electrodes and porous transport layers, along with the transference coefficients of the membrane and porous transport layers, the cathode exchange current density and the initial heat flux), five of them could be successfully optimized utilizing the proposed optimization scheme. The initial heat flux into the system was the parameter that showed the largest impact on the global entropy production departure, which points out the relevance of the correct choice of the boundary conditions in the model for its agreement with the Second Law of Thermodynamics. In the end, the optimized set of parameters showed a deviation of up to 50% with respect to the base case parameter set, indicating that the interpretation of the experiments done in a fuel cell should be subject to evaluation in terms of their own agreement with the Second Law of Thermodynamics. The model utilized in this work can be utilized in order to provide such validation, giving it therefore yet another use. Moreover, it was found that six of the eleven parameters tested for optimization could not be optimized utilizing the scheme proposed in this work. The reason behind this optimization unfeasibility was found to be the nature of some of the parameters, some of which do not correspond to transport parameters but are rather kinetic parameters. The values these kinetic parameters can acquire are not bound by thermodynamic arguments for by chemical ones, which proves that a thermodynamic approach cannot be applied for parameters that are fundamentally not bound by thermodynamics but rather by chemical kinetics.

Simulations with the optimized set of parameters showed that large entropy production departures were still calculated for some layers of the fuel cell, namely the anode and the membrane, despite the fact that the global entropy production departure was smaller than the value obtained with simulations utilizing the base case parameter set. The conclusion that can be given is that, at least, one of the assumptions done in the modeling of one of these layers caused disagreement with the Second Law of Thermodynamics. It was determined that the assumption of water equilibrium originated large entropy production departures in the anode; therefore, an addition to the model was proposed, namely the modeling of the water transport across the electrodes.

The model proposed for the transport of water across the electrodes was based on the calculations of the water chemical potentials at the electrode surfaces and at the interfaces between the electrodes and the porous transport layers or the membrane; the transport parameter that was proposed is the water diffusivity through the electrodes. Despite the fact that no experimental data is available for the water diffusivity in the electrodes (which was assumed to be equal in both electrodes), it was found that the optimal value of the water diffusivity should lie between 2.6x10⁻³ m/s and 5.8x10⁻³ m/s or in the vicinity of that interval, in order to increase the consistency of the model with the Second Law of Thermodynamics.

Simulations with the water transport model proposed (and the water diffusivity found) showed a substantial improvement in the consistency of the model with the Second Law of Thermodynamics,

especially in the models for the anode and the membrane, despite slight entropy production departure increases in the cathode and the total entropy production departures.

The conclusion that was reached in this work is that a transport parameter set was obtained, which, along with the assumptions utilized, increases the consistency of the model with the Second Law of Thermodynamics.

4.2. Balance of plant components and operating conditions in a PEMFC fuel cell system

In this work, the behavior of different thermodynamic variables along the thickness of a PEMFC were obtained, which gave insight on the operational choices that need to be made in order to ensure that the fuel cell operates at high electric efficiency and with a large life cycle, both of which are of utmost importance for the PEMFC system. This Section will summarize the findings of this work, with respect to the balance of plant components of a fuel cell system and to the operating conditions, most of which have not been yet presented in the literature dedicated to the PEMFC modeling.

As for the heat management and the temperature gradients throughout the system, a detailed analysis was done in order to quantify the heat flux that comes out of the fuel cell, which can be translated into the amount of heat removal needed for the operation of the PEMFC. It was found that the cathodeside porous transport layer has usually a larger temperature than the anode-side, which is caused by the proximity of the former to the cathode, where a larger portion of the heat of the fuel cell is produced; this means that the operation of the cell is essentially non isothermal. Heat was found to come out of the anode of the fuel cell at all electric current densities, which calls for a cooling design for which the heat produced should be removed from this electrode. What the model also predicts is that, with operation at higher electric current densities, heat will also come out of the cathode. Both the effect of the temperature increase of the cell and the heat produced should be taken into account for the design of the cooling system required by the fuel cell in order to overcome overheating and loss of water in the system, which would have harmful consequences for the capacity of the Nafion[®] membrane to conduct protons.

Several conclusions were reached in terms of the water management of the fuel cell: it was found that operation at larger electric current densities leads to a reduction in the water content of the Nafion[®] membrane, which, in turn, causes an increase in its electric resistivity and thus leads to larger voltage losses in the fuel cell. The conclusion from these results is that the ohmic losses in the system are always caused by a low water content in the membrane, and that the system can suffer from dehydration when operating at large electric current densities. The results obtained are in agreement with the results of Kjelstrup and Røsjorde (2005). The model utilized quantifies the entropy production and the heat flux increase caused by the electric resistance in the membrane, which adds to the understanding of the irreversible heat production in the fuel cell, and concludes that a substantial amount of the total entropy production is due to this layer of the fuel cell.

Finally, simulations with different relative humidities of the inlet gases were performed. For the hydrogen stream, it was found that the reduction of the relative humidity of this gas results in a reduction in the voltage the fuel cell can produce; this effect is caused by a reduction in the water content of the Nafion[®] membrane that causes an increase in its electric resistivity. This effect is very significant, especially when operating the fuel cell at higher electric current densities and leads thus to the need of having a balance of plant component that can either supply external water to the inlet hydrogen stream, or recover the water produced by the fuel cell. After simulations done with different relative humidities of the air stream, it was concluded that the model fails to predict variations of the voltage produced by the fuel cell. It was found that the assumptions done in the model, operation with air with 100% relative humidity and the water activity of the membrane at the interface membrane-cathode being equal to the unity, are coupled. This coupling lead to the model not being able to predict a decrease in the voltage of the fuel cell as it has experimentally found to occur.

4.3. Recommendations for future work

Modeling, as has been shown throughout this document, is an essential part of the design of a fuel cell system, because it brings understanding of the physical and chemical processes that occur in such a device. Modeling creates a link between the experimental results and the empirical choices made on the selection of balance of plant components and operating conditions in a fuel cell system; it can help prevent failures and ensure that the fuel cell system operates at its optimal conditions in terms of energy production and durability.

As was shown in the previous chapters, the modeling of the fuel cell is always accompanied by parameter and assumption choices that help develop an understanding of the nature of the fuel cell, and depict reality with mathematical equations. The first recommendation that can be given in this regard is that a model is as good as its parameters and equations and, as such, no model is accurate unless it can be deployed within a specific framework of assumptions that match the nature of the processes occurring both inside and around a fuel cell. In this work, it was found that there were some assumptions made in previous modeling exercises that did not match entirely the nature of the fuel cell and, thus, their removal was an essential part of this particular modeling exercise. Other assumptions were found to be coupled with each other, which calls out for further work on this model in order to understand the physical phenomena governing those assumptions.

The transport parameters are also prone to enhancement. The transport parameters in the membrane were found to be not entirely consistent with the model utilized, according to the Second Law of Thermodynamics. The work done here proved that the water diffusivity was underestimated, while the thermal conductivity and electro-osmotic drag coefficient were overestimated, in comparison to the base case values utilized in this work. The model was unable to show if these differences in the values are caused by the dependence on either the temperature or the water content of the membrane, which points out to the fact that new measurements should be done in the Nafion[®] membrane, in order to better correlate the transport parameters with the temperature and the water content. A new parameter was found, namely the electrode water diffusivity, whose value is unknown due to the fact that experiments have not focused on the interfaces electrode-membrane and electrode-porous transport layer. Further work should also consist on finding this transport parameter, which was proven to be of utmost importance for the modeling of the water transport across the electrodes; the model was able to pinpoint a range of values in which this parameter should be found, and experimentation could confirm what was found in this work.

The final recommendation of this work ought to regard the modeling of the fuel cell system, that is, with its balance of plant components. As was seen in this document, the results that spawned from the simulations done with the model lead to understand the effect of the water management and heat removal on the correct operation of a fuel cell. The next step has to be, naturally, the modeling of the whole fuel cell system, including the balance of plant components, so as to understand the effect of different design choices on the performance of a fuel cell stack. In the end, a model of such characteristics can be utilized for the prediction of the operation of the fuel cell system, and this would represent an advantage for both designers and operators.

List of symbols

Abbreviations

Abbreviation	Description
Α	Anode
AFC	Alkaline Fuel Cell
AL	Anode left hand side
AP	Anode-side porous transport layer
AR	Anode right hand side
С	Cathode
CL	Cathode left hand side
CP	Cathode-side porous transport layer
CR	Cathode right hand side
DMFC	Direct Methanol Fuel Cell
М	Membrane
MCFC	Molten Carbonate Fuel Cell
PAFC	Phosphoric Acid Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
PTL	Porous Transport Layer
SOFC	Solid Oxide Fuel Cell

Greek symbols

Symbol	Units	Description
ε	K	Lennard-Jones potential well depth
η	V	Overpotential
λ	$\frac{W}{mK}$, $\frac{W}{m^2K}$	Heat conductivity, Thermal conductivity
μ	$\frac{J}{mol}$	Chemical potential
π	$\frac{J}{mol}$	Peltier heat coefficient
ρ	$\frac{kg}{m^3}$	Density
Σ	Å	Hard sphere radius
σ	$\frac{W}{m^2K}$	Entropy production
ϕ	V	Electric potential
Ω_D	-	Collisional integral for diffusion

Latin symbols

Symbol	Units	Description
A _c	<u>eq</u> kg	Total membrane acid capacity
a_w	-	Water activity
Cp_{H_2}	$\frac{J}{molK}$	Hydrogen specific heat capacity
<i>Cp</i> _{<i>O</i>₂}	$\frac{J}{molK}$	Oxygen specific heat capacity
Cp_w	$\frac{J}{molK}$	Water specific heat capacity
C _W	$\frac{mol}{m^3}$	Water concentration
D_{O_2}	$\frac{m^2}{s}$	Diffusivity of oxygen in nitrogen
D_w	$\frac{m^2}{s}, \frac{m}{s}$	Diffusivity of water in hydrogen, diffusivity of water in the electrodes
F	$\frac{C}{mol}$	Faraday's constant (96485 C/mol)
G	$\frac{J}{mol}$	Gibbs free energy
H_{H_2}	$\frac{J}{mol}$	Hydrogen specific enthalpy
H_{O_2}	$\frac{J}{mol}$	Oxygen specific enthalpy
H_w	$\frac{J}{mol}$	Water specific enthalpy
H^0	$\frac{J}{mol}$	Reference enthalpy
J _D	$\frac{mol}{m^2s}$	Interdiffusional molar flux
J_{H_2}	$\frac{mol}{m^2s}$	Hydrogen molar flux
J_{O_2}	$\frac{mol}{m^2s}$	Oxygen molar flux
Js	$\frac{W}{m^2K}$	Entropy flux
J_w	$\frac{mol}{m^2s}$	Water molar flux
J'_q	$\frac{W}{m^2}$	Heat flux
j	$\frac{A}{m^2}$	Electric current density
j ₀	$\frac{A}{m^2}$	Cathode exchange current density
l_w	mol _{water} mol _{sulphonic} acid group	Membrane water content
$l_{\mu\mu}$	$\frac{mol^2}{lm^2s}$	Onsager mass transport coefficient
Μ	kg mol	Molar mass
p	atm	Total pressure
p_w	atm	Water saturation pressure
q^*	$\frac{J}{mol}$	Heat of transfer
R	$\frac{J}{molK}$	Universal gas constant (8.314 J/mol K)
r ^{ohm}	Ωm	Electric resistivity
S _{dev}	%	Entropy production departure
S _e	$\frac{J}{molK}$	Transported entropy of electrons
S_{H_2}	$\frac{J}{molK}$	Hydrogen specific entropy
<i>S</i> ₀₂	$\frac{J}{molK}$	Oxygen specific entropy
S _w	$\frac{J}{molK}$	Water specific entropy

Symbol	Units	Description
<i>S</i> ⁰	J molK	Reference entropy
Т	Κ	Temperature
T _{ad}	_	Dimensionless temperature
t _w	-	Transference coefficient, electro-osmotic drag coefficient
x	т, μт	Thickness of the fuel cell, Cartesian coordinate
x_{H_2}	_	Hydrogen mole fraction
<i>x</i> ₀₂	_	Oxygen mole fraction
x_w	_	Water mole fraction

Mathematical operators

Symbol	Description
$\frac{d}{dx}$	Spatial derivative (derivative with respect to the Cartesian coordinate x)
$\frac{d}{da_{w}}$	Derivative with respect to the variable a_w
Δ	Difference
II	Absolute value

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