An electrochemical impedance model for HTPEM fuel cells

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Abstract

Electrochemical impedance spectroscopy has become a popular characterisation method for PEM fuel cells. The method method is used for extracting information on the individual losses mechanisms in the fuel cell. There is however still some disagreement in the scientific community about how the data obtained from impedance measurements should be interpreted.

The models which are used to reproduce measured impedance spectra and quantify individual loss components are simple equivalent circuit models which provide no insight into the actual causes of the recorded impedance spectrum. This report treats the development of a novel electrochemical impedance model for HTPEM fuel cells. The model is based on a 2D finite volume approach and incorporates the effects of cathode mass transport, electrode kinetics and proton conduction.

In order to enable validation of the model a number of polarisation curves and impedance spectra have been recorded on a BASF Celtec 2100 MEA. The measurements are carried out in the laboratory using a single cell HTPEM test rig. An attempt has been made to fit the model to the data but no successful fit has been obtained. Instead the model is validated by comparing the effects of operating parameter variations on the data and the model results.

In order to improve the understanding of the phenomena which dominate individual parts of the impedance spectrum a parameter variation study is performed on the model. The study indicates that some of the interpretations of impedance spectra presented in the literature are based on incorrect assumptions.

It is concluded that the model developed has potential for becoming a useful tool in impedance spectroscopy studies providing that sufficient improvements can be made to enable fitting to experimental data.

Copies:3Pages total:60Appendix:A-BSupplements:CD-ROM

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Preface

This report has been written during the spring semester of 2010. It contains documentation of the project work which I have performed during the 10th semester of the Fuel Cell and Hydrogen Technology graduate programme at the Department of Energy Technology, Aalborg University.

The report is divided into a main part and an appendix. The main part contains the most vital documentation of the project work. The appendix contains additional non-vital details.

Figures, tables and equations are numbered using the number of the chapter and the number of the figure, table or equation. Example: Table 3.2 refers to the second table in chapter 3 and equation (2.5) refers to the fifth equation of chapter 2.

Sources are cited using a number enclosed in square brackets. The number corresponds to the number given to the source in the bibliographic record in the back of the report. Example: [4] refers to the fourth entry in the bibliography. Sources are are numbered in the order that they are cited.

An appendix CD is enclosed with the printed version of the report. The CD contains the Matlab Simulink code for different versions of the model developed in the project as well as data from the experiments conducted.

I would like to thank Mads Bang of Serenergy A/S for providing me with data on the Celtec P2100 MEA. I would also like to thank my supervisor Søren Juhl Andreasen for providing me with invaluable advice and assistance in the course of the project.

Finally I would like to thank the staff and students at the Department of Energy Technology for making my time at Aalborg University an enjoyable and rewarding experience.

Jakob Rabjerg Vang

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Nomenclature

A	Area $[m^2]$
a	Activity
A_0	Pre-exponential factor $\left[\frac{SK}{m}\right]$
BC	Boundary condition
AFC	Alkaline fuel cell
α	Charge transfer coefficient
LTPEM	Low temperature PEM
C	Molar concentration $\left[\text{mol}/\text{m}^3 \right]$
C_{dl}	Double layer capacitance [F]
CFD	Computational fluid dynamics
D_i	Mixture diffusion coefficient $\left[\mathrm{m}^2/\mathrm{s}\right]$
D_i^{eff}	Effective diffusion coefficient $[m^2/s]$
D_{ik}	Binary diffusion coefficient $\left[m^2/s\right]$
DMFC	Direct methanol fuel cell
E	Reversible cell potential [V]
E_a	Activation energy $[J/mol]$
EIS	Electrochemical impedance spectroscopy
ϵ	Electrode porosity
η	Local overpotential [V]
F	Faraday's constant (= $96487 \mathrm{C/mol}$)
γ	Concentration parameter
h	Geometry height [m]
HTPEM	High temperature PEM
Ι	Current

i	Current density $\left[A/cm^2\right]$
i^{ref}	Exchange current density A/m^3
j	Reaction rate $[A/m^3]$
κ_i	Ionic conductivity [V]
λ	Stoichiometric ratio
LHV	Lower heating value
MCFC	Molten carbonate fuel cell
MEA	Membrane electrode assembly
MFC	Mass flow controller
μCHP	Micro combined heat and power
\mathbf{n}_k	Outward facing normal vector
ORR	Oxygen reduction reaction
Р	Pressure [Pa]
PBI	Polybenzimidazole
PEM	Proton exchange membrane
φ	Phase shift
ϕ_e	Electrode potential [V]
ϕ_i	Ionic potential [V]
R	Universal gas constant $(= 8.31747 \frac{\text{J}}{\text{mol K}})$
8	Specific entropy $\left[\frac{J}{mol K}\right]$
S_i	Source term $\left[\frac{\text{mol}}{\text{m}^3 \text{s}}\right]$
SOFC	Solid oxide fuel cell
Т	Temperature [K]
au	Electrode tortuosity correction factor
U	Voltage [V]
u_{air}	Air velocity [m/s]
V	Volume $[m^3]$
w	Geometry width [m]
y_i	Mole fraction
Ζ	Impedance $\left[\Omega cm^2\right]$

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Chapter 1

Introduction

In recent years fuel cells have become an increasingly popular research topic. Researchers around the world believe that fuel cells will play an important part in the energy system of tomorrow due to the promise of clean and efficient energy conversion.

A fuel cell is an electrochemical device which converts chemical energy in a fuel to electrical energy through electrochemical oxidation. Fuel cells differ from heat engines in the sense that no combustion chamber or similar heat source is necessary for operation. Thus fuel cells can operate at much lower temperatures. Properly integrated fuel cells are capable of operating quietly, cleanly and efficiently compared to state of the art heat engines. On the other hand fuel cells have advantages compared to batteries. While batteries are discharged when a current is drawn fuel cells are (ideally) capable of supplying a constant current as long as a sufficient reactant flow is supplied. Even today fuel cells are replacing batteries as the technology of choice in some backup power applications.

In the long term the collective goal of fuel cell researchers is the general availability of fuel cells for applications as diverse as laptop computers, automobiles, micro combined heat and power (μ CHP) systems and MW scale power plants. This thesis is an attempt to make a small contribution towards the achievement of this goal.

1.1 Fuel cell history

Generation of electrical energy by electrochemical conversion of hydrogen and oxygen was first witnessed in 1839. The discoverer was the lawyer and part time scientist William Robert Grove. He called his discovery a *gas voltaic battery* and published a number of articles on the subject [1]. His cell design consisted of two platinum electrodes partially submerged in sulphuric acid. Two inverted glass tubes filled with hydrogen and oxygen respectively were placed over the electrodes. An example of one of his setups can be seen in figure 1.1. Other researchers followed in the footprints of Grove developing their own versions of the gas battery. While some progress was made none managed to develop a cell which could be used commercially.

In 1894 Friedrich Wilhelm Ostwald envisioned direct electrochemical conversion of coal as a way to replace the inefficient and polluting steam engines. Several attempts were made at producing a direct carbon fuel cell. This eventually lead to the development of the first solid oxide fuel cell (SOFC) by Baur and Preis in 1937. Their work also inspired the high temperature fuel cell developed by Davtyan in 1946



Figure 1.1: Illustration of one of William Grove's experimental setups in which a four cell gas voltaic battery is connected to a voltameter [2].

which lead to the development of the molten carbonate fuel cell (MCFC).

In the 1930s Francis T. Bacon worked on developing a hydrogen fuel cell. In 1939 he successfully developed a prototype alkaline fuel cell (AFC). During the 1950s Bacon and his research team developed several AFC systems but there was little commercial interest in the technology at the time. The technology however rose to glory when stacks based on Bacon's design were used for the 1965 Apollo missions.

In 1960 another important fuel cell type saw the light of day. The first proton exchange membrane (PEM) fuel cell was developed at General Electric by Grubb and Niedrach. The introduction of a solid polymer electrolyte enabled simpler system design improving the volumetric power density over that of AFC systems. A PEM fuel cell system was used to produce power and drinking water for the Gemini space missions. The first PEM fuel cells were based on polystyrene but in 1972 a new polymer was introduced by Grot of E.I. du Pont de Nemours & Company. The polymer became known as Nafion and greatly improved fuel cell durability. Nafion doped with sulphuric acid is still the material of choice for low temperature PEM (LTPEM) fuel cell membranes. [3]

Wainright et al. [4] introduced a new polymer membrane for fuel cells in 1995. The basis was polybenzimidazole (PBI) doped with phosphoric acid. Unlike the Nafion based fuel cells the new membrane operated above 100 °C. The new membrane was first considered for direct methanol fuel cell (DMFC) application since the methanol permeability of PBI is low. It was however soon established that the membrane performed well when fuelled with hydrogen [5]. This discovery laid the basis for development of the modern high temperature PEM (HTPEM) fuel cell.

1.2 HTPEM fuel cells

In the last 15 years much work has been done to improve the HTPEM fuel cell technology. In this section an attempt will be made to give an overview of the the technology as well as the work which has been done in the field. Though the HTPEM fuel cells are becoming increasingly popular LTPEM fuel cells are still a much bigger field of research. This means that in some areas most or all of the published research has been done on LTPEM fuel cells. Due to the similarities between HTPEM and LTPEM fuel cells this work may also be relevant and will be included whenever applicable.

1.2.1 HTPEM technology features

HTPEM fuel cells have a number of attractive features compared to LTPEM fuel cells. As previously mentioned operating temperature of HTPEM fuel cells is above 100 °C whereas LTPEM fuel cells are seldom operated above 80 °C. This means that all water within the HTPEM fuel cell electrode compartments is gaseous during fuel cell operation. Consequently there is no risk of flooding of the electrodes. This minimises the need for water management compared to LTPEM fuel cells. With no liquid water present the flow field can be simplified which in return allows for lower pressure loss and lower parasitic losses.

The increased temperature also means that both anode and cathode kinetics are faster. Since the oxygen reduction reaction (ORR) is usually a limiting factor in fuel cell performance this is a desirable feature. Ionic conductivity of the electrolyte is also improved by elevating the temperature. While sulphuric acid is a better proton conductor than phosphoric acid HTPEM fuel cells may still exhibit better proton conductivity because of the higher operating temperature [6]. Cooling of the fuel cell stack is also simplified by the high operating temperature. Some HTPEM stack designs use only the cathode air for cooling.

One of the perhaps most compelling features of the HTPEM fuel cell technology is the increased tolerance to CO in the fuel compared to LTPEM. In spite of extensive research in improving CO tolerance LTPEM fuel cells can only tolerate around 50 or 100 ppm CO [7, 8, 9, 10]. For HTPEM fuel cells the amount of CO in the fuel can be several orders of magnitude larger while still retaining acceptable performance. Das et al. [11] performed CO poisoning tests on BASF Celtec-P MEAs and concluded that an acceptable performance could be achieved at 180 °C with both 2% and 5% CO in the fuel. At 160 °C 2% CO was tolerated quite well, but increasing the CO fraction or lowering the temperature lead to large power losses above a current density of 0.2 A/cm^2 . To illustrate the rapid development within the field of HTPEM fuel cells it is worth noting that a similar study of a home made MEA only three years earlier showed that the temperature had to be raised to 210 °C to avoid serious performance losses at 1% CO [12].

As is illustrated in the next section the many attractive features of the HTPEM technology makes it well suited for system integration in a variety of applications.

1.2.2 HTPEM fuel cell systems

One of the many possible uses for HTPEM fuel cells is in automotive applications to extend the range of battery electric vehicles. Andreasen et al. demonstrated that HTPEM fuel cells could be integrated in both the small single person City-El vehicle [13] and the somewhat larger three person Buddy electrical vehicle [14].

While the systems proposed by Andreasen et al. were fuelled with compressed hydrogen Pfeifer et al. [15] investigated thermal integration of a metal hydride hydrogen storage tank with a HTPEM fuel cell stack. A system modelling study was conducted and results showed that from a 2 kg hydride tank a total of 0.8 kWh of electrical energy could be extracted. By comparison the lower heating value (LHV) of hydrogen is 7.45 kWh/kg¹ indicating that unless lighter and more efficient hydrides are developed this is probably not the best solution for automotive applications.

Systems utilising reformers for hydrogen production may on the other hand prove to be a viable solution. Pan et al. [16] demonstrated that by filling a small evaporator for a DMFC with catalyst a two cell HTPEM fuel cell stack could be operated on the reformate gas without the need for any CO removal. CO levels as low as low as 0.1% were achievable depending on the required mass flow. Andreasen et al. [17] made a proof of concept study of a plate heat exchanger methanol reformer. The study showed that the reformer design was feasible but due to a poor choice of catalyst material the CO levels measured were around 6.8%. It was concluded that a the system had to be fitted with a water-gas shift reactor if it was to be connected to a fuel cell stack.

The perhaps most promising application of HTPEM fuel cells is in residential μ CHP. The high CO tolerance enables easy reforming of natural gas and the high operating temperature means high quality waste heat which can be used for providing hot water and heating. Korsgaard et al. treated modelling and control of a μ CHP system in two papers [18, 19]. In this natural gas fuelled system the fuel cell stack was placed inside the thermal reservoir to keep the fuel cell stack at the operating temperature at all times. A transient model of the system capable of simulating the operation of the system during a whole year was developed in Matlab Simulink. Steady state results showed that $45\%_{LHV}$ electrical efficiency and $88\%_{LHV}$ total efficiency were achievable when only little heating was required. When high heating output was necessary total efficiencies as high as $101\%_{LHV}$ were achievable. When simulating the operation of the system during a whole year average efficiencies were up to $41\%_{LHV}$ electrical an $92\%_{LHV}$ total. Under the assumption applied the economy of the system was more than 25% better than for a natural gas boiler.

1.2.3 Challenges in HTPEM development

While the HTPEM fuel cell technology is a promising candidate for a number of applications some problems still persist. Generally the source of the problems is the high operating temperature. One problem relates to heating of the fuel cells stack. While LTPEM fuel cells can be started as soon as the temperature is above 0° C HTPEM fuel cells have to be heated to a minimum of 100° C to avoid the presence of liquid water which will cause the H_3PO_4 to leak from the membrane decreasing the membrane conductivity. Andreasen and Kær [20] conducted a study of HTPEM fuel cell stack heating strategies comparing heating using hot air with direct electrical heating using heaters attached to the fuel cell stack surface. The experiments conducted showed that when heating a 1 kW fuel cell stack using 240 W heating foil the time required to heat the entire fuel cell stack to a minimum of $100 \,^{\circ}\text{C}$ was just under an hour. When heating using hot air at $160 \,^{\circ}\text{C}$ the heating time varied from 35 minutes at 100 L/min to just 6 minutes at 500 L/min. It was concluded that using hot air is superior when start-up times are critical. However it was noted that electrical heating could also be a very fast and efficient solution if the heating elements were integrated within the bipolar plates.

The perhaps most severe problem in HTPEM fuel cell research is that of fuel cell life time. A large number fuel cell life time tests have been published. Most of

¹Calculated using the EES software package.

these have been made using single cells [21, 22, 23]. While these results are useful they cannot be readily applied to stack level degradation since uneven temperature distribution and differences in cell quality result in different degradation rates in different parts of the fuel cell stack.

A stack level degradation study was performed by Moçotéguy et al. [24]. Here simulated reformate gas was used to approximate real μ CHP operating conditions. The investigation revealed significant differences in the degradation rates of the individual cells. At the beginning of the test the cell voltages were all within 10% of each other but after 650 hours the voltage of the most degraded cell was less than half of that of the least degraded cell.

1.2.4 HTPEM fuel cell models

Several different models of HTPEM fuel cells have been developed. The detail level of the models varies greatly depending on the application to which they are developed.

A relatively simple semi empirical steady-state model was developed by Korsgaard et al. [25]. The model was in good agreement with experimental results with a deviation of no more than 5%. The model was later expanded to include the effects of CO poisoning on the performance of the fuel cell [26]. This model was used to simulate the fuel cell stack in the previously mentioned modelling study [18, 19].

Hu et al. [27] developed a more detailed two dimensional cathode model which took into account that the bipolar plate prevents direct access of oxygen to some of the electrode. The model showed good agreement with polarisation curves obtained from experiments.

A simple analytical HTPEM fuel cell was presented in [28]. The model focused on the effect of gas cross over. It was concluded that the over potential due to cross over was only significant at low stoichiometries. The model was fitted to experimental data and good agreement was achieved in all presented cases.

Computational fluid dynamics (CFD) was used by Peng et al. for modelling HTPEM fuel cells in two papers. In the first paper a steady state three dimensional model was presented. The model was capable of computing the distribution of temperature, potential, current density and chemical species in the fuel cell [29]. In the subsequent paper accumulation terms were added to the steady state model in order to capture transient phenomena. The transient model also included the effect of the double layer capacitance. The transient behaviour was illustrated by recording the response to a voltage step. When the double layer effect was disregarded there was a small overshoot in the current density when stepping. Including the double layer effect eliminated the overshoot [30].

Wang et al. [31] modelled the transient effects of CO poisoning in PBI based fuel cells. The model was one dimensional considering only the anode and cathode catalyst layers and the electrolyte. When comparing the development of the current density at constant voltage predicted by the model with experimental results some discrepancy was observed. This was attributed to the assumption of a linear relation between CO coverage and current density as well the fact that the gas diffusion layer and the flow channel was not included in the model.

1.2.5 Electrochemical impedance spectroscopy

In order to characterise HTPEM fuel cells and validate the results obtained from models a number of different diagnostic tools are used. These tools range from simple current and voltage measurements, which are the back bone of most characterisation methods, to advanced tools such as transmission electron microscopy which can be used to visually inspect the nano scale effects of degradation on the fuel cell membrane electrode assembly (MEA) [23]. Accounting for all the methods which are available is beyond the scope of this text but interested readers are referred to [32] and [33] which treat electrochemical methods and physical/chemical methods respectively.

The perhaps most important characterisation method is the polarisation curve. Polarisation curves show the dependence of the fuel cell voltage on the current density. This curve is extremely useful since it shows the actual performance of the fuel cell at the conditions at which it is recorded. The polarisation curve does however not provide very detailed information about the mechanisms that govern the performance. To obtain this information other methods must be applied. One of these methods which has become very popular in recent years is electrochemical impedance spectroscopy (EIS). EIS is performed by superimposing a sinusoidal signal upon either the current (galvanostatic mode) or the voltage (potentiostatic mode) and recording the response. The impedance at a given frequency is calculated from equation 1.1:

$$Z = \frac{U_0}{i_0} \left(\cos \varphi \pm j \sin \varphi \right) \tag{1.1}$$

Here $Z \ [\Omega \text{cm}^2]$ is the impedance. $U_0 \ [V]$ and $i_0 \ [A/\text{cm}^2]$ are the voltage and current density amplitudes respectively. φ is the phase shift. The \pm in the equation signifies that the last term is added when running in potentiostatic mode and subtracted when running in galvanostatic mode.

The impedance will change depending on the frequency of the signal since different phenomena have different time scales. In order to properly characterise the fuel cell the frequency of the signal is varied across a range. The feasible range varies between fuel cell types but for PEM fuel cells it is from above $10 \, kHz$ to below $1 \, Hz$.



Figure 1.2: Idealised Nyquist plot of the impedance spectrum of a HTPEM fuel cell.

Figure 1.2 shows an idealised impedance spectrum of a HTPEM fuel cell. The intersection of the curves with the real axis corresponds to the ohmic resistance in the fuel cell. The three arches that are visible in the curves correspond to different transient phenomena in the fuel cell. Different sources employ different interpretations of what causes the individual arches. As an aid in the interpretation of the impedance spectra equivalent circuit models are used. In these models serial and parallel connections of passive components are fitted to the actual impedance spectra obtained from the fuel cells. The values extracted from the models can then be used to quantify the individual impedances in the fuel cell.

EIS has been used extensively in PEM fuel cell research. Yuan et al. [34] conducted a literature review on the application of EIS in the field of LTPEM fuel cells. They noted that EIS can be used to characterise the effects of different modes of operation as well as the effects of differences in MEA design and manufacturing processes.

While the number of studies of HTPEM fuel cells using EIS is not as great as for LTPEM fuel cells the problems to which EIS has been applied are still diverse. A characterisation study was conducted by Zhang et al. [35] in order to investigate the effects of temperature, oxygen stoichiometry and current density on the impedance of a PEMEAS HTPEM MEA. It was observed that ohmic resistance and the charge transfer resistance both decreased with increasing temperature and current density. The gas transfer resistance however increased with both current density and temperature. When increasing the oxygen stoichiometry both charge transfer resistance and gas transfer resistance decreased. The effect on gas transfer resistance was however only significant at high current densities. A similar study investigated a BASF Celtec P-1000 MEA [36]. Similar results were obtained for the dependence of gas transfer resistance on temperature and of charge transfer resistance on temperature and current density. The ohmic resistance also decreased with increasing current density. When increasing the temperature the ohmic resistance decreased up to $140^{\circ}C$, remained almost constant from $140^{\circ}C$ to $170^{\circ}C$ and then increased sharply above $170 \,^{\circ}C$. No explanation was proposed for the discrepancy.

In a study by Andreasen et al. [37] a LabView program for fuel cell impedance measurements was presented. The results obtained were validated against results from a Gamry FC350 fuel cell monitor and good agreement was obtained. In the same paper impedance spectra obtained at different temperatures were fitted to an equivalent circuit model. Linear regression was performed of the temperature dependence of the individual circuit elements. These dependencies were then used to simulate the impedance profile of a fuel cell stack at different temperature profiles.

Hu et al. [22] conducted a 500 hour degradation study of a home made H_3PO_4 -PBI based HTPEM MEA. They used EIS to monitor the ohmic resistance and the charge transfer resistance during the test. It was observed that the ohmic resistance was almost constant but the charge transfer resistance increased linearly after an initial 100 hours of break in. Modestov et al. [38] also performed a life test during which EIS was used to monitor the membrane resistance. The membrane resistance decreased 20% during the test. This was attributed to membrane thinning since the hydrogen crossover increase by 1400% during the same period.

In a previous project the author of this report investigated CO poisoning of HT-PEM fuel cells using EIS. It was observed that CO affected the whole impedance spectrum when the fuel cell was operated at low temperatures. This was assumed to indicate that the individual features of the Nyquist plot are dominated by different phenomena at different operating points. The data obtained was fitted to an equivalent circuit model but much scatter in the extracted resistances was observed in spite of excellent fits to the data. Based on these observation it was concluded that an impedance model based on actual electrochemistry would be a useful tool in HTPEM fuel cell research [39]. The development of such a model is treated in this report.

1.3 Project focus

As has been documented in the previous section HTPEM fuel cells is an active area of research. In this report an attempt is made to construct an impedance model based on fuel cell electrochemistry. This issue seems to have been neglected by fuel cell researchers until now. The absence of an electrochemically founded impedance model limits the usability of EIS since the equivalent circuit models used do not give any explanation of which mechanisms actually cause the different features of the impedance spectra. Also the impedance models based on equivalent circuits are not necessarily physically meaningful even though a good fit to the data can be obtained.

As fuel cell modelling has been studied extensively the theoretical basis for a more advanced impedance model already exists. The main challenge for this project is to make a model which is sufficiently detailed to reproduce the fuel cell impedance spectrum while being sufficiently computationally inexpensive to be of practical use.

Chapter 2

Impedance model

In this section the fuel cell impedance model developed in the course of the project is presented. The model is developed in Matlab Simulink using the 2D finite volume approach taking into account transient and spatial variations along the flow channel and through the GDL. The novelty of the model consist in the application. To the best of the author's knowledge this work the first attempt to model fuel cell impedance spectra using electrochemistry rather than equivalent circuits.

2.1 Assumptions

The main assumptions applied in the model are listed in this section.

- Constant pressure
 - Since HTPEM fuel cells are normally operated at atmospheric pressure with only little pressure loss in the flow channels it is deemed feasible to assume constant operating pressure. In the simulations a constant pressure of P = 101325 Pa is assumed.
- Ideal gas behaviour
 - All gaseous species are assumed to obey the ideal gas law. This is feasible since all species are far from the critical point.
- Infinite electrical conductivity
 - In order to simplify calculations no gradients in electrical potential are assumed to exist in the CL, the GDL and the bipolar plates. This is a reasonable assumption since the majority of the ohmic losses are due to proton conduction.
- Isothermal operation
 - The temperature is assumed to be constant throughout the computational region.
- Impermeable membrane

- The electrolyte membrane is assumed impermeable to all gasses.
- No mass transport losses on the anode side
 - The mole fraction of hydrogen on the anode side is assumed to be 1 at all times. This is deemed feasible since diffusion of hydrogen is very fast. Mass transport losses on the anode side are usually negligible when running on pure hydrogen.
- Plug flow in flow channel
 - The flow in the cathode flow channel is assumed to be perfect plug flow with no gradients normal to the flow direction. While disregarding concentration gradients normal to the flow direction does introduce an error the effect of the gradient along the flow direction is assumed to be more important.
- Inductive behaviour is neglected
 - The inductive behaviour of wires and other components in an actual fuel cell are neglected. This means that the Nyquist curve produced by the model will not actually intersect the real axis. Instead the imaginary component of the impedance will approach 0 as the frequency goes towards ∞ or 0.

2.2 Model overview

The degree of detail in the modelling is different in the different parts of the fuel cell. Table 2.1 gives an overview of the parameters which are calculated in each part of the fuel cell. Time dependent variables have their time derivative calculated and integrated at each time step. Quasi-steady variables are solved for directly at each time step.

Variable types	Anode gas channel	Anode GDL	Anode CL	Membrane	Cathode CL	Cathode GDL	Cathode gas channel
Time dependent	None	None	Over potential	None	Over potential O_2 mole fraction H_2O mole fraction	${ m O}_2$ mole fraction ${ m H}_2{ m O}$ mole fraction	O_2 mole fraction H_2O mole fraction
Quasi-steady	None	None	Ionic potential Reaction rate	Ionic potential	Ionic potential Reaction rate N_2 mole fraction	${\rm N_2}$ mole fraction	N_2 mole fraction

Table 2.1: Parameters solved for in the different parts of the computational domain.

A schematic drawing of the computational domain is shown in figure 2.1. The anode gas channel and GDL are omitted since no equations are solved here. The grid in the figure illustrates the discretisation used. The grid points are evenly spaced in the *y*-direction. In the *x*-direction the grid points are evenly spaced within each layer but the spacing varies between layers. The cathode flow channel is not discretised in the *x*-direction due to the assumption of plug flow.

The control volumes in each layer are numbered from 1 to m in the x-direction and 1 to n in the y-direction where m and n are the total number of grid points in the x and y-directions in the given layer.



Figure 2.1: Illustration of the discretisation of the computational domain.

2.3 Dimensions

The dimensions used in the model are derived from the actual dimensions of the fuel cell MEA and the experimental setup described in chapter 3. The porosity of the fuel cell GDL and CL is assumed to be 0.5 since the necessary data was unavailable. Dimensions of the individual fuel cell layers have not been printed here due to confidentiality issues. Table 2.2 summarises the dimensions which are important for the model.

Dimension	Variable	Value	Comment
Fuel cell area	A_{FC}	$45{ m cm}^2$	
Cathode gas channel height	h_{ch}	$2\mathrm{mm}$	
Cathode gas channel width	w_{ch}	$1\mathrm{mm}$	
Cathode land width	w_{land}	$1\mathrm{mm}$	
Fuel cell GDL porosity	ϵ_{GDL}	0.5	Assumed
Fuel cell CL porosity	ϵ_{CL}	0.5	Assumed

Table 2.2: Dimensions used in the model.

2.4 Electrochemical model

The electrochemical model describes the dynamics in relation to the electrochemical reactions and proton transport. Electron transport is neglected to simplify the calculations. This is deemed feasible since proton transport accounts for the majority of the of ohmic loss in a HTPEM fuel cell.

The time rate of change of the over potentials at the anode and cathode catalyst layers are calculated using equations (2.1) and (2.2)[30]:

$$\frac{\partial \eta_A}{\partial t} = -\frac{\nabla \cdot (\kappa_{i,A} \nabla \phi_{i,A}) + j_A}{C_{dl,A}}$$
(2.1)

$$\frac{\partial \eta_C}{\partial t} = -\frac{\nabla \cdot (\kappa_{i,C} \nabla \phi_{i,C}) - j_C}{C_{dl,C}}$$
(2.2)

Here subscripts A and C refer to anode and cathode respectively. η [V] is the local over potential which determines the local reaction rate. C_{dl} [F] is the capacitance of the charge double layer. ϕ_i [V] is the local ionic potential and κ_i [S/m] is the ionic conductivity of the electrolyte. j [A/m³] is the local reaction rate. Equation (2.1) is only valid in the catalyst layer. Within the membrane the transient term and the source term are zero. Equation (2.1) then reduces to:

$$\nabla \cdot (\kappa_{i,MEM} \nabla \phi_{i,MEM}) = 0 \tag{2.3}$$

Equation (2.3) is solved iteratively for $\phi_{i,MEM}$ at each time step. The discrete formulations of equations (2.1), (2.2) and (2.3) are derived in appendix A.

In the anode and cathode catalyst layers the ionic potential is calculated using equations (2.4) and (2.5) [30].

$$\phi_{i,A} = \phi_{e,A} - \eta_A \tag{2.4}$$

$$\phi_{i,C} = \phi_{e,C} - \eta_C - E \tag{2.5}$$

 ϕ_e [V] is the electrode potential. Since electron transport is neglected the electrode potential is constant throughout both electrodes. At the anode the electrode potential is 0. The cathode electrode potential is set equal to the applied voltage U_{DC} [V]. E [V] is the reversible cell potential which is calculated using the Nernst equation in equation (2.6). This version of the Nernst equation is modified to include temperature effects[40].

$$E = E_0 + \frac{\Delta s}{2F}(T - T_0) - \frac{RT}{2F} \ln\left(\frac{a_{H_2O}}{a_{H_2}a_{O_2}^{1/2}}\right)$$
(2.6)

Here $E_0 = 1.229 \text{ V}$ is the reversible cell potential at standard temperature and pressure ($T_0 = 298 \text{ K}$ and $P_0 = 101325 \text{ Pa}$). $\Delta s = 44.34 \frac{\text{J}}{\text{mol K}}$ is the entropy change during the fuel cell reaction. F = 96487 C/mol is Faraday's constant. $R = 8.31747 \frac{\text{J}}{\text{mol K}}$ is the universal gas constant. a_{H_2O} , a_{H_2} and a_{O_2} are the activities of the individual species. Since the fuel cell is assumed to operate at a constant pressure of $P = P_0$ the activities are equal to the partial pressures of the individual species. Since the reversible cell potential is used on the cathode side local values of a_{H_2O} and a_{O_2} are used to evaluate equation (2.6). For a_{H_2} the value at the interface between the anode GDL and the anode CL is used.

The local reaction rate is calculated using the Butler-Volmer equation. The formulation used here is modified from [30].

$$j_A = i_A^{ref} a_{H_2}^{\gamma_{H_2}} \left(\exp\left(\frac{\alpha_A F}{RT} \eta_A\right) - \exp\left(-\frac{\alpha_A F}{RT} \eta_A\right) \right)$$
(2.7)

$$j_C = i_C^{ref} a_{O_2}^{\gamma_{O_2}} \left(\exp\left(-\frac{\alpha_C F}{RT} \eta_C\right) - \exp\left(\frac{\alpha_C F}{RT} \eta_C\right) \right)$$
(2.8)

Here $\gamma_{H_2} = 0.25$ and $\gamma_{O_2} = 0.5$ are empirical concentration parameters. $\alpha_A = \alpha_C = 1$ are the charge transfer coefficients. i^{ref} [A/m³] are the exchange current densities. No relations for HTPEM exchange current densities applicable to this model were found in the literature.

The ionic conductivity of the electrolyte and the catalyst layers are calculated using the Arrhenius relation of equation (2.9) [41]. Here E_a [J/mol] is the activation energy and A_0 [$\frac{SK}{m}$] is the pre-exponential factor. The relation determining the conductivity is assumed to be equal in both catalyst layers and membrane disregarding the effect of the catalyst layer porosity.

$$\kappa_i = \frac{A_0}{T} exp\left(\frac{E_a}{RT}\right) \tag{2.9}$$

In order to calculate the impedance of the fuel cell the net current through the membrane must be calculated. This is done by integrating the current across the fuel cell membrane as shown in equation (2.10).

$$I = \int_{A_{FC}} -\kappa_{i,MEM} \nabla \phi_{i,MEM} \, dA \tag{2.10}$$

Here A_{FC} $[m^2]$ is the fuel cell area.

2.5 Mass transport model

Another important contribution to the fuel cell impedance is the transport of reactants through the GDL and CL. It is assumed that species transportation in the GDL and the CL takes place only by diffusion. Equation (2.11) governs species transport.

$$\frac{\partial y_i}{\partial t} = \frac{\nabla \left(-CD_i^{eff} \nabla y_i\right)}{C} + S_i \tag{2.11}$$

In equation (2.11) y_i is the mole fraction of species *i*. D_i^{eff} [m²/s] is the effective diffusion coefficient of species *i* in the mixture. C [mol/m³] is the total gas concentration. S_i [$\frac{\text{mol}}{\text{m}^3\text{s}}$] is the source term representing the consumption or generation of the species in question. The source terms for the individual species are shown in table 2.3. The discretised formulation of equation 2.11 is derived in appendix A.

Equation (2.11) is not applied for all species. Due to the assumption of constant pressure the mole fraction of one species must be calculated directly to satisfy continuity. For the cathode side this species is nitrogen.

$$y_{\rm N_2} = 1 - y_{\rm O_2} - y_{\rm H_2O} \tag{2.12}$$

	Source terms					
Species	Anode GDL	Anode CL	Cathode CL	Cathode GDL		
H_2O	-	-	$rac{j_C}{2F}$	-		
O_2	-	-	$-rac{j_C}{4F}$	-		
\mathbf{N}_2	-	-	-	-		
${\rm H}_2$	-	-	-	-		

Table 2.3: Source terms for use in equation 2.11. No source terms are given for H_2 since the model fraction of H_2 in the anode compartment is assumed to be 1 at all times.

For the anode side the only species present is hydrogen. This means that the mole fraction of hydrogen must always be 1. For the cathode side the assumption introduces an error since equation (2.11) neglects the effect of convection in the CL and GDL. In a real fuel cell the generation of two mole of water vapour for each mole of oxygen consumed in the cathode CL would generate a diffusive flux of all species. The model just assumes that nitrogen in the CL is replaced by water vapour.

The concentration used in equation (2.11) is calculated as in equation (2.13) using the ideal gas relation.

$$C = \frac{P}{RT} \tag{2.13}$$

The diffusion coefficients are calculated by correcting experimentally obtained binary diffusion coefficients. The corrections account for the presence of other species as well as the porous and tortuous nature of the GDL and CL. Binary diffusion coefficients are calculated from experimental data using equation (2.14) [42].

$$D_{ik} = D_{ik,ref} \frac{P_{ref}}{P} \left(\frac{T}{T_{ref}}\right)^{\gamma}$$
(2.14)

Here D_{ik} [m²/s] denotes the binary diffusion coefficient of species *i* with respect to species *k*. $D_{ik,ref}$ [m²/s] is the binary diffusion coefficient at the reference temperature (T_{ref} [K]) and pressure ($P_{ref} = 101325$ Pa). The exponent γ is experimentally determined for each binary mixture. The relevant values for calculating the necessary diffusion coefficients for diffusion on the cathode side are given in table 2.4.

Equation (2.15) calculates the diffusion coefficient of species i in a multicomponent mixture.

$$D_i = \frac{1 - y_i}{\sum_k \frac{y_k}{D_{ik}}} \tag{2.15}$$

Equation (2.15) assumes that the mole fraction of species i is much smaller than one. This assumption is violated to some extend in the cathode compartment since the mole fractions of water vapour and oxygen reach values well beyond 10%.

The effective diffusion coefficient D_i^{eff} for use in equation (2.11) is obtained by applying the Brüggeman correction of equation ??.

$$D_i^{eff} = D_i \epsilon^{\tau} \tag{2.16}$$

Here ϵ is the electrode porosity and τ is the tortuosity correction factor. Normally a value of 1.5 is used for τ but a value of 2 has been shown to give more accurate results Bang [42].

293.15 293.15	1.728 1.967
	$293.15 \\ 293.15 \\ 293.15$

Table 2.4: Reference binary diffusion coefficients, temperatures and exponents for use in equation (2.14) [42].

2.5.1 Flow channel model

In order to properly account for the effect of mass transport on the fuel cell impedance the variation in gas composition along the cathode gas channel must be included in the model. The flow in the channel is assumed to be perfectly mixed in the xdirection. Also it is assumed that the effect of the of diffusion in the y-direction is negligible compared to the effect of convection. The time rate of change of the mass fraction of species i in a given section of the cathode gas channel is thus determined by the convective flux in the y-direction and the diffusive flux in the x-direction.

$$\frac{\partial y_i}{\partial t} = \frac{\frac{\partial}{\partial x} \left(-CD_i^{eff} \frac{\partial y_i}{\partial x} \right)}{C} - \frac{\frac{\partial}{\partial y} (Cy_i u_{air})}{C}$$
(2.17)

Here u_{air} [m/s] is the gas flow velocity. The velocity in the channel is calculated using the stoichiometric ratio and the current drawn from the fuel cell. The velocity is assumed to be constant throughout the channel.

$$u_{air} = \frac{\lambda I}{4 F y_{\mathcal{O}_{2},0} C A_{ch}} \tag{2.18}$$

Here λ is the stoichiometric ratio, I [A] is the DC current drawn from the fuel cell, $y_{O_2,0} = 0.21$ is the mole fraction of oxygen at the inlet and A_{ch} [m²] is the channel cross sectional area. Since the model only considers two dimensions some simplifications of the flow channel geometry are necessary. The bipolar plate used for the measurements described in chapter 3 have three flow channels which follow a serpentine pattern. In the model it is assumed that all the channels including the land between them can be approximated as one straight channel of width $w_{tot} = 3(w_{ch} + w_{land})$. This is illustrated in figure 2.2.

2.6 Boundary conditions

In order to enable solution of the formulated equations boundary conditions (BCs) must be formulated for the ionic potential and the mole fractions.



Figure 2.2: Simplification of the flow geometry used in the model.

2.6.1 Mole fractions

Mole fraction BCs are specified at the following interfaces:

- *x*-direction
 - Membrane Cathode CL
 - * No flux of reactants through the membrane. $\frac{\partial y_i}{\partial x} = 0$
 - Cathode gas channel bipolar plate
 - * The bipolar plate is assumed impermeable to gasses. $\frac{\partial y_i}{\partial x} = 0$
- *y*-direction
 - Cathode flow channel inlet

* Moist air. $y_{{\rm O}_2,0}=0.21,\,y_{{\rm H}_2{\rm O},0}=0.015$

- Cathode CL and GDL end faces
 - * No flux of reactants through the end faces. $\frac{\partial y_i}{\partial y} = 0$

2.6.2 Ionic potential

The following BCs are specified for the ionic potential:

- *x*-direction
 - Anode GDL Anode CL
 - * No proton transport in the GDL. $\frac{\partial \phi_{i,A}}{\partial x}=0$
 - Cathode CL Cathode GDL
 - * No proton transport in the GDL. $\frac{\partial \phi_{i,C}}{\partial x} = 0$
- y-direction
 - CL and membrane end faces
 - * No proton conduction through the end faces. $\frac{\partial \phi_i}{\partial y} = 0$

2.7 Simulation

The model is capable of generating both impedance spectra and polarisation curves. The approaches used are outlined in this section.

2.7.1 Impedance calculations

In order to calculate the impedance of the fuel cell the the model is first simulated at the selected DC voltage for 10 seconds to obtain steady state. Using the steady state values as initial condition the model is simulated repeatedly with sinusoidal signals superimposed on the voltage. After each run the AC part of the current signal is fitted to a phase shifted sinusoid of the same frequency as the voltage signal. The first period of the AC signal is neglected since it may not be perfectly sinusoidal.

$$i_{AC} = i_0 \sin\left(\omega t - \varphi\right)$$

Here i_{AC} [A/cm²] is the AC current density, i_0 [A/cm²] is the amplitude, ω [1/s] is the angular frequency of the signal and φ is the phase shift.

The impedance of the fuel cell is then calculated using equation 2.19. The reason for adding π to the phase shift is to compensate for the fact that the current and voltage signals are phase shifted by π by default.

$$Z = \frac{U_0}{i_0} \left(\cos(\varphi + \pi) + j \sin(\varphi + \pi) \right)$$
(2.19)

After sweeping across a suitable range of frequencies the calculated impedances are presented in a Nyquist plot.

2.7.2 Polarisation curve

In order to record a polarisation curve of the model the model is run with a simulation time of 10 seconds at 15 equally spaced voltages between U = 0.95 V and U = 0.2 V. Voltage and steady state current density are recorded at each point.

2.8 Summary

In this chapter the governing equations of the transient HTPEM fuel cell model for impedance calculation have been presented. The governing equations have been formulated taking into account the influence of 2D cathode mass transport, double layer effects and protonic conductivity. The model is capable of calculating the transient response in the current produced by the fuel cell to an applied potential signal. This response is used for calculating the fuel cell impedance. In order to verify the model it must be compared to experimental data. This data basis is generated as described in the following section.

Chapter 3

Experimental work

In order to verify the model developed a number of impedance measurements have been performed. This chapter describes the experimental work performed in the course of the project work. The experimental part of this project consists of a number of impedance measurements performed on the commercially available Celtec P-2100 MEA from BASF. The experiments have been performed on a single cell test rig constructed in the laboratory. The test rig was designed for use in a previous project by the author [39].

3.1 Test setup

A schematic drawing and a photo of the test setup can be seen in figures 3.1 and 3.2 respectively. The setup can perform a fully automated sequence of impedance measurements in galvanostatic mode. In the following sections the individual parts of the setup are described.



Figure 3.1: The test setup for the impedance measurements

3.1.1 Real-time systems

The setup is controlled by two LabVIEW real time systems labelled 'EIS computer' and 'FC control computer'. The FC control computer takes care of the operation of the fuel cell. It monitors and controls the flows of fuel and oxidant to the fuel cell as well as the temperature. When not performing impedance measurements the FC control computer also controls the load current drawn from the fuel cell. When performing impedance measurements the EIS computer takes control of the load



Figure 3.2: Photo of the test setup for the impedance measurements

current. It imposes a sinusoidal signal on the current and records the response in the cell voltage. The amplitude of the sinusoidal signal is adjusted to achieve a specified amplitude in the voltage. Keeping a constant voltage amplitude enables comparison of the results to the simulation results which are obtained in potentiostatic mode. A detailed description of the LabVIEW programs running on the two systems is given in [39].

3.1.2 Fuel cell MEA

The fuel cell used is a Celtec P-2100 MEA from BASF. Break in of the MEA has been performed by running at a constant current density of $0.2 \,\text{A/cm}^2$ for 96 hours.

3.1.3 Single cell test unit

The single cell test unit used in the setup is a standard BASF design for testing HTPEM MEAs. The individual components of the unit can be seen in figure 3.3. The end plates provide mechanical stability and have fittings for gas inlets and outlets. Two cartridge heaters of 300 W rated power each are inserted into each end plate. Electrical insulation of the end plates is ensured by a coating of dielectric material. The current collector enables connection of the fuel cell to the electronic load. The contact resistance between the current collector and the bipolar plate is reduced by a film of conduction enhancing material. Serpentine channels in the bipolar plates supply reactants to the MEA. In the anode bipolar plate two type T thermocouples are mounted. Gas leakage is prevented by gaskets between the bipolar plates and the MEA.

3.1.4 Mass flow controllers

The reactants are supplied to the fuel cell using mass flow controllers (MFCs). The specifications are given in table 3.1. The accuracy of the MFCs are $\pm 0.3\%$ of the maximum flow rate. The settling time is 300 ms.



Figure 3.3: Components of the single cell test unit. A: End plate. B: Current collector. C: Conduction enhancer. D: Bipolar plate. E: Gasket. F: MEA.

Gas	Model	Max flow $[L/min]$	Min flow $[L/min]$
Air	Bürkert 8712	2	0.04
H_2	Bürkert 8711	1	0.02
CO	Bürkert 8711	0.05	0.001
CO_2	Bürkert 8711	0.5	0.01

Table 3.1: Mass flow controller specifications

3.1.5 Electronic load

The electronic load used for the setup is a RBL488 50-150-800 from TDI Power. The rated maximum frequency of the load is 20kHz. This is sufficient to capture the region of interest for the impedance measurements which is 10 kHz to 0.01 Hz. The load can be operated in the current rages 0 - 2 A, 0 - 20 A and 0 - 150 A. The accuracy is 0.5% in the range 0 - 2 A and 0.25% in the range 0 - 20 A and 0 - 150 A. Since the measurements are conducted below 20 A the range 0 - 20 A is used to improve accuracy.

3.2 Operating conditions

The range of measurements conducted for this study is intended for testing whether the model developed is capable of reproducing actual impedance data. The operating condition varied in the measurement range is thus chosen to reflect the parameters considered in the model. The operating conditions chosen are summed up in table 3.2.

3.2.1 Temperature

The temperature is an important variable for fuel cell impedance since it affects both reaction kinetics, diffusion coefficients and ohmic losses. However no relation for the temperature dependence of the exchange current densities for the Celtec P2100 MEA are available in the literature. Manual fitting of the exchange current densities must thus be performed at each temperature. Since the benefit of repeating this exercise

is deemed small it is chosen to perform measurements at 160 °C only.

3.2.2 Current density

The current density affects the fuel cell impedance since the slope of the polarisation curve varies with current density. The importance of individual loss mechanisms also vary with current density. Mass transport effects are expected to be more important at high current densities while activation losses are more important at low current densities. Measurements are conducted at $0.11 \,\text{A/cm}^2$, $0.22 \,\text{A/cm}^2$ and $0.33 \,\text{A/cm}^2$.

3.2.3 Stoichiometries

The stoichiometries at which the measurements are performed also affect the impedance of the fuel cell. Higher stoichiometries are expected to lead to smaller mass transport losses due to more uniform reactant concentration throughout the fuel cell. Reports in the literature suggest that oxygen stoichiometry has an important effect on fuel cell impedance [35, 36] while hydrogen stoichiometry is relatively unimportant as long as it is kept above 1 [36, 43]. Jespersen et al. [36] reported that the effects of air stoichiometry on the impedance of a Celtec P1000 MEA operated at 160 °C and 0.33 A/cm² became increasingly important when decreasing the stoichiometry. Above $\lambda_{air} = 4$ no significant effects were observed, at $\lambda_{air} = 2$ the effects were significant and at $\lambda_{air} = 1.1$ the response was totally dominated by mass transport effects. The measurements are carried out at $\lambda_{air} = 2$ and $\lambda_{air} = 5$. Hydrogen stoichiometry is kept constant at $\lambda_{H_2} = 2$.

Temperature	Current density	Air stoichiometry	Hydrogen stoichiometry
$160^{\circ}\mathrm{C}$	$0.11 \mathrm{A/cm^2}$	2	2
	$0.22 \mathrm{A/cm^2}$	5	
	$0.33 \mathrm{A/cm^2}$		

Table 3.2:	Operating	parameters	for the	measurements
	1 0	1		

3.3 Sweep parameters

In order to get measurements of sufficient quality a number of important sweep parameters must be chosen. These are the frequency range, the desired voltage amplitude, the number of periods sampled per frequency and the number of frequencies measured per decade.

3.3.1 Frequency range

The frequency range must be sufficiently wide to capture both intercepts of the real axis at either end of the impedance spectrum. Sweeping from 10 kHz to 0.01 Hz is deemed sufficient to capture the entire region of interest.

3.3.2 Voltage amplitude

The desired voltage amplitude (U_0) is chosen as a compromise between linearity and signal to noise ratio. Setting a low value will improve the assumption of linear
dependence of current and voltage. A high value is expected to improve the signal to noise ratio. In a previous study by the author [39] measurements were carried out a $U_0 = 0.01$ V. At this value the signal-to-noise ratio was too low in the area around 100 Hz resulting in obscuring of the results by electrical noise. In an attempt to reduce this undesired effect the measurements are conducted at $U_0 = 0.02$ V.

3.3.3 Periods per frequency

The number of periods sampled per frequency (n_{samp}) should be as high as possible to even out variations during the measurement. On the other hand the time required to conduct the measurement sets an upper limit. This is especially the case for the lower frequencies where one period takes several seconds to complete. For the high frequencies $n_{samp} = 10$. Below 10 Hz $n_{samp} = 4$. This is deemed a feasible trade off between accuracy and measurement time.

3.3.4 Frequencies per decade

The number of frequencies sampled per decade (n_{dec}) is a trade off between accuracy and measurement time in much the same way as the number of periods sampled per frequency. The value chosen is $n_{dec} = 35$.

3.4 Measurement sequence

When performing the measurements the fuel cell is first run at the desired operating point until steady state is achieved. Then a polarisation curve is recorded by ramping the current up from 0 A to 20 A at a rate of 4 A/min. This is assumed sufficiently slow for the fuel cell to be in near-steady state. After recording the polarisation curve the fuel cell is returned to the operating point. When steady state is achieved an EIS sweep is performed. When the EIS sweep is complete the operating point is changed and the process is repeated. The sequence in which the measurements are performed is showed in table 3.3.

Measurement number	Current density	Air stoichiometry
1	$0.11 ~\rm{A/cm^2}$	5
2	0.22 A/cm^2	5
3	$0.33 ~\rm{A/cm^2}$	5
4	$0.11 ~ {\rm A/cm^2}$	2
5	0.22 A/cm^2	2
6	$0.33 ~\rm{A/cm^2}$	2

Table 3.3: Operating parameters for the measurements

3.5 Uncertainty factors

The test setup has a number of inherent uncertainty factors which influence the accuracy of the results. An account of these are given below.

3.5.1 Temperature measurement

Since it is not possible to measure the temperature inside the MEA the temperature measured by the thermocouples may not be equal to the actual MEA temperature. Temperature gradients in the MEA itself further reduce the validity of the the measured temperature.

3.5.2 Temperature control

The duty cycle of the resistance heaters is controlled by the a PI controller implemented in the LabVIEW program which runs on the 'FC control computer'. Due to the placing of the heaters and the relatively large thermal mass of the system temperature control of the system is not a trivial task. Care has been taken to reduce the temperature transients during the measurements by carefully tuning controller parameters and waiting for the system to achieve steady state before performing sweeps. It is however impossible to completely eliminate temperature variation during the measurement sequence. This is not a serious problem at high frequencies since the temperature cannot vary much during the relatively short sweep times. At low frequencies there is more time for the temperature to change during the measurement which may lead to increased inaccuracy.

3.5.3 Linearity problems

In order for the impedance measurements to be accurate the relationship between the current and the voltage must be approximately linear around the operating point at which the impedance is measured. In this case the response to a superimposed sinusoidal on the current should be a near-perfect phase shifted sinusoidal response in the voltage. As can be seen from the polarisation curve in figure 3.4 this is not the case for a fuel cell. It can however be approximated by choosing a sufficiently small amplitude for the AC signal.



Figure 3.4: Polarisation curve recorded at 160 °C and $\lambda_{air} = 5$.

When running the measurements it was however observed that the AC signals were not perfectly sinusoidal at frequencies in the range of 10 kHz. This was observed

to be the case for both the current and the voltage signals. It is assumed to stem from one of two possible causes. Either the load may be unable to properly generate sine waves at this frequency thus causing distortion of the signal or the current amplitude necessary to achieve the desired voltage amplitude is too high for the response to be linear at high frequencies. The phenomenon is assumed to be of little importance to the results since the linearity problems have only been observed in a narrow frequency band before the Nyquist plot intersects the real axis.

3.5.4 Electrical noise

Electrical noise manifests itself in two ways in the data. The effect of electrical noise is the oscillation of the measured values about a mean value. An example of this can be seen in the the polarisation curve (figure 3.4). While the noise is no serious problem for the recording of a polarisation curve it becomes more important when performing impedance measurements. As can be seen from the Nyquist plots in figure 3.5 the noise produces consistent patterns around 100 Hz. While the distortion of the data is serious in the region around 100 Hz the effect of the on the rest of the impedance spectrum is assumed to be negligible



Figure 3.5: Two Nyquist plots of the fuel cell impedance at different operating points. Notice the effects of electrical noise around 100 Hz.

3.6 Summary

In this section an account has been given of the experimental work performed in this project. Sets of polarisation curves and impedance spectra have been been recorded at 6 different operating points. This data is deemed sufficient to enable validation of the impedance model.

Chapter 4

Results and discussion

In this section the model developed is used for three separate analyses. The first analysis treats grid independence of the solution by comparing solutions obtained using different grid resolutions. The second analysis seeks to validate the model by comparing the simulation results to experimental data obtained as described in chapter 3. The third analysis seeks to clarify which phenomena actually cause the individual arches that are evident in the impedance spectrum. This is done by evaluating the effects of varying a parameter or disabling a transient effect. Finally a number of improvements are suggested to enable fitting of the model to experimental data.

4.1 Base case

As a starting point for the investigation a base case is defined. The parameter values chosen for the base case are shown in table 4.1. The values are chosen arbitrarily to give a performance which seems reasonable for a HTPEM fuel cell. Also a grid must be chosen for the calculations. The grid chosen for the base case has 5x10 grid points in each fuel cell layer and 1x10 grid points in the cathode flow channel.

Parameters	Values	Comments
Exchange current densities	$i_{0,A} = 10^7 {\rm A/m^3}$	Cathode kinetics are much
	$i_{0,C} = 50 {\rm A/m^3}$	slower than anode kinetics.
Double layer capacitances	$C_{dl,A} = 10^7 \mathrm{F/m^3}$	The assumption that both double layer
	$C_{dl,C}=10^7\mathrm{F/m^3}$	capacitances are equal is used in [30].
Cathode stoichiometry	$\lambda_{air} = 5$	
Operating temperature	$T_{FC} = 160 ^{\circ}\mathrm{C}$	
Cell voltage	$U_{DC}=0.4\mathrm{V}$	
Ionic conductivity pre-exponential factor	$A_0 = 100e^{9.8} \frac{\text{S K}}{\text{m}}$	[41]
Ionic conductivity activation energy	$E_a = 24000 \mathrm{J/mol}$	[41]

Table 4.1: Base case simulation parameters.

Figures 4.1 and 4.2 show a simulated polarisation curve and a simulated impedance spectrum using the base case model parameters. As can be seen from the polarisation curve the impedance spectrum is recorded at a current density of approximately

 $0.6 \,\mathrm{A/cm^2}$. The impedance spectrum has three visible arches. This is consistent with impedance spectra presented in the literature [36, 35].



Figure 4.1: Simulated polarisation curve for the base case.



Figure 4.2: Simulated impedance spectrum for the base case.

4.2 Grid independence

In order to assess the grid independence of the solution the base case has been solved on two grids with improved resolution. In the first grid the resolution is doubled in the x-direction giving 10x10 grid points per fuel cell layer. In the second grid the y-direction resolution is doubled giving 5x20 cells per layer.

As can be seen from figures 4.3 and 4.3 the solution is not completely independent of the grid resolution. Also it can be seen that the most prominent effect is derived from increasing the resolution in the x-direction even though the step size in the y-direction is several orders of magnitude larger than in the x-direction. Considering that the number of cells is doubled in both cases the change in the solution is assumed to be sufficiently small to justify using the coarser grid for the rest of the simulations.



Figure 4.3: Effect of using double grid resolution in the x-direction.



Figure 4.3: Effect of using double grid resolution in the y-direction.

4.3 Model validation

In order to validate the model the behaviour of the model is compared to the experimental data. An attempt has been made to fit the model to the data but no successful fit was obtained. Consequently the simulated impedance spectra and polarisation curves are not compared directly to their experimental counterparts. The validation thus consists of ensuring that variations in the operating parameters have similar effects on the simulations as on the experimental results .

4.3.1 Polarisation curves

Figure 4.4 shows four polarisation curves. Two have been recorded at an operating temperature of 160 °C and air stoichiometries of 5 and 2 respectively. The other two are simulated using the base case parameters at the same stoichiometries. As can be seen from the recorded polarisation curves the performance of the fuel cell is more or less independent of stoichiometry in this range with only a slight reduction in performance at $\lambda_{air} = 2$. While the noise does obscure the data to some extend it seems that the voltage loss is approximately constant above a current density of $0.1 \,\text{A/cm}^2$.

Comparing the recorded polarisation curves to their simulated counterparts it seems that reducing the stoichiometry has a similar effect on the model as on the actual fuel cell. In this case the voltage loss is also more or less constant above $0.1 \,\mathrm{A/cm^2}$. The performance of the model is however much different from the performance of the fuel cell. The exchange current densities chosen for the model seem to be too low since the activation losses at low current density are clearly too large compared to the recorded polarisation curves. On the other hand the slope of the recorded polarisation curves are steeper at high current densities. In the absence



Figure 4.4: Comparison of simulated and recorded polarisation curves at 160 °C.

of any other data for comparison the logical assumption would be that the ionic conductivity used in the model is too high. As is shown in the following section the explanation is probably not as simple as that.

4.3.2 Impedance spectra

As described in section 3.2 EIS sweeps have been performed at current densities 0.11 A/cm^2 , 0.22 A/cm^2 and 0.33 A/cm^2 . As can be seen from figure 4.4 these points correspond approximately to voltages of 0.69 V, 0.60 V and 0.52 V. Figure 4.5 shows an impedance spectrum recorded at $i_{DC} = 0.22 \text{ A/cm}^2$ and $\lambda_{air} = 5$. A large inductive arch is visible in the figure spanning the region from 10 kHz to a little below 1 kHz. This is assumed to mainly originate from the inductance of wires and the end plates of the single cell setup. The intersection with the real axis occurs around $0.2 \Omega \text{cm}^2$. No clear distinction can be made between between the high frequency arch and the intermediate frequency arch due to the significant scatter in the data around 100 Hz. The low frequency arch is however clearly visible in the region around 1 Hz. All the impedance spectra recorded can be seen in appendix B.



Figure 4.5: Impedance spectrum for $T = 160 \,^{\circ}\text{C}$, $i_{DC} = 0.22 \,\text{A/cm}^2$ and $\lambda_{air} = 5$.

Since the inductive behaviour is assumed to be unrelated to the fuel cell MEA itself this analysis focuses on the range of frequencies from 1 kHz to 0.1 Hz. In figure 4.6 the effects of stoichiometry on the impedance spectrum is presented. The most prominent effect observed is the increase of the low frequency arch at $\lambda_{air} = 2$. The intermediate frequency arch is also slightly larger at low stoichiometry. It is also worthy noting that the scatter of the data in the high and intermediate frequency regions follows the exact same pattern down to around 10 Hz. At lower frequencies the scatter seems to become more random indicating that noise of a more random nature becomes important here.



Figure 4.6: Comparison of recorded impedance spectra at $\lambda_{air} = 5$ and $\lambda_{air} = 2$.

The effect of the air stoichiometry on the simulated impedance spectra can be seen in figure 4.7. In order to get a DC current density of approximately 0.22 A/cm^2 for both impedance spectra the DC voltage is specified manually. As can be seen the effects produced by varying the stoichiometry in the model are similar to those observed in the recorded impedance spectra: The size of the low frequency arch increases notably. The intermediate frequency arch becomes a bit smaller however. It is assumed that this is because the DC current densities differ slightly. Considering that the model reproduces the effects of stoichiometry variations on both impedance and polarisation rather well it is assumed that the mass transport part of the model is physically meaningful.

The effect of varying the DC current is shown in figure 4.8. As can be seen the size of the intermediate frequency arch is reduced as the current is increased. This behaviour is consistent with several observations presented in the literature [37, 36, 35]. In the high frequency region above 100 Hz the curves are almost identical except for the curve for $i_{DC} = 0.33 \text{ A/cm}^2$ which is translated slightly to the right. This indicates that the ohmic losses have increased a little before this spectrum was recorded. In the low frequency region the curves also look similar. The size seems to increase slightly with decreasing current but the scatter of the data makes it difficult to confirm whether this is the case.

In the model the specified DC voltage controls the operating point at which the impedance spectrum is calculated. As can be seen from figure 4.9 the effect of varying the DC voltage by 0.1 V is significant. All simulations are made using base case parameters.

The trend observed is increasing impedance with increasing voltage. The effects



Figure 4.7: Comparison of simulated impedance spectra at $\lambda_{air} = 5$ and $\lambda_{air} = 2$.



Figure 4.8: Comparison of recorded impedance spectra at different DC current densities.

on the intermediate and low frequency arches are most significant while the high frequency region is largely unaffected. Also it should be noted that the shape of the impedance spectra are similar in the low and intermediate frequency regions. The trends agree with those observed for the experimentally obtained impedance spectra.

As documented the effects of stoichiometry variations and DC current on the impedance spectrum are reproduced quite well by the model. When it comes to reproducing the curves themselves the model is less successful however. The individual arches are much more pronounced in the simulated impedance spectra than in the recorded spectra. This is deemed a significant deviation though this effect can to some degree be attributed to the obscuring of the individual features by noise in the recorded spectra. Also the low frequency intersection of the simulated impedance spectra at a similar operating point. This is probably due to the larger size of the intermediate frequency arch. This difference is best illustrated by comparing the spectra of figures 4.6 and 4.7. As mentioned in section 4.3.1 the comparison between the recorded and the simulated polarisation curves indicate that the ohmic losses in the



Figure 4.9: Simulated impedance spectra for various values of U_{DC} .

fuel cell are under predicted by the model. The high frequency intersection between the impedance spectrum and the real axis however occurs at a higher value of Z_{real} in the simulated impedance spectra. This means that the ohmic losses are actually exaggerated in the simulations. This indicates that there must be some other reason than ohmic losses for the steep slope of the measured polarisation curve.

In order to investigate which parameters should be tweaked to make the model fit the data and to investigate the sources of the individual features of the impedance spectrum a parameter variation analysis has been performed in the following section.

4.4 Parameter variation

The reason for the individual arches in the impedance spectrum is a matter of some controversy in the literature. This is especially true for the high frequency arch. Some sources [35, 36] either do not observe it in the data or disregard it. Others [44, 37] assume that it stems from the charge transfer losses in the anode CL. Yet another explanation is that it is caused by ohmic losses within the catalyst layer [45]. The intermediate frequency loop is generally assumed to be a result of cathode charge transfer impedance or a combination of cathode and anode impedance [43, 37, 35]. Finally the low frequency arch is attributed to mass transfer losses [36]. Here the controversy is whether diffusion through the porous electrode or transient variations along the flow channel [45] is the reason.

To find out which of these interpretations are actually plausible a number of different cases are simulated to investigate individual effects. The cases used in the analysis are listed in table 4.2.

4.4.1 Double layer capacitance

Looking at the effects of double layer capacitance on the simulated impedance spectrum should shed some light on which arches can be attributed to the electrode kinetics. Both anode and cathode have the same double layer capacitance in the

Case	Change compared to base case
1	Increased cathode double layer capacitance. $C_{dl,C} = 10^8$
2	Increased anode double layer capacitance. $C_{dl,A} = 10^8$
3	Increased cathode double layer capacitance. $C_{dl,C} = 7 \cdot 10^7$
4	Reduce exchange current densities by 10%
5	Increase exchange current densities by 10%
6	Use steady state values for cathode gas channel gas composition.
7	Use steady state values for gas composition on entire cathode side.
8	Case 5 with increased cathode double layer capacitance. $C_{dl,C} = 10^8$
9	Case 5 with increased anode double layer capacitance. $C_{dl,A} = 10^8$
10	Reduce CL ionic conductivity by 50%
11	Double CL ionic conductivity

Table 4.2: Cases investigated in the parameter variation analysis.

base case. Thus it can be assumed that they contribute to the same arch since their time constants should be equal. The effect of increasing cathode double layer capacitance by an order of magnitude can be seen in figure 4.10. As can be seen the low frequency loop grows considerably in size while the intermediate frequency arch shrinks. It seems that the time constant of the cathode capacitive effects now coincides with the effects that dominated the low frequency arch in the base case. The remaining intermediate frequency arch must thus be caused by the anode kinetics. The individual importance of anode and cathode contributions are illustrated in figure 4.11. Increasing the anode double layer capacitance causes a more modest increase in the low frequency loop while the intermediate frequency arch remains the largest. This is expected since the losses on the cathode side are much more significant than on the anode side.



Figure 4.10: Simulated impedance spectra for case 1 and the base case.

The simulated impedance spectrum for case 3 is shown in figure 4.12. Looking closely at the figure four individual arches can be identified. Since the two intermedi-



Figure 4.11: Simulated impedance spectra for cases 1 and 2.

ate frequency arches must be dominated by anode and cathode kinetics respectively some other phenomena must be dominating the high frequency arch and the low frequency arch.



Figure 4.12: Simulated impedance spectrum for case 3.

4.4.2 Exchange current density

Varying the exchange current density of anode and cathode by 10% has quite modest effects on the polarisation curve as shown in figure 4.13. The performance is increased with increasing exchange current density as should be expected. Looking at the impedance spectra in figure 4.14 the size of the intermediate frequency arch is reduced with increasing i_0 . This is also be expected since the current density at $V_{DC} = 0.4$ V increases with fuel cell performance. Essentially what is shown in figure 4.14 is similar to the effect of varying U_{DC} as shown in figure 4.9.



Figure 4.13: Simulated polarisation curves for cases 4 and 5 compared to the base case.



Figure 4.14: Simulated impedance spectra for cases 4 and 5 compared to the base case.

4.4.3 Mass transfer

The effect of mass transfer on the impedance spectrum is investigated using cases 6 and 7. In case 6 transient variations in the cathode flow channel gas composition are eliminated by setting $y_{O_2,ch}$ and $y_{H_2O,ch}$ equal to the steady state values. From figure 4.15 it is clear that the low frequency arch vanishes completely when the transient variations in the gas channel are neglected. Consequently the low frequency arch must be a caused solely by oscillations in the gas channel. This is in agreement with the results of a localised impedance study by Schneider et al. [45].

The effect of disregarding all concentration transients in the cathode can be seen in figure 4.16. The size of the intermediate frequency arch is reduced significantly compared to case 6. This indicates that diffusion effects in the cathode GDL and CL contribute significantly to the cathode impedance. This suggests that the effects of mass transport through the electrode cannot be distinguished from the effects of



Figure 4.15: Simulated impedance spectra for case 6 and the base case.

electrode kinetics in a real fuel cell. Also it should be noted that the high frequency arch is completely unaffected.



Figure 4.16: Simulated impedance spectra for cases 6 and 7.

Since it is clear that transient variations of concentrations in the cathode GDL and CL increase the cathode contribution to the impedance spectrum it could be interesting to investigate how the anode and cathode contributions compare when both have been stripped of diffusion effects. As can be seen from figure 4.17 the curves for cases 8 and 9 are almost completely coincident. This strongly suggests that the contributions from anode and cathode polarisation are coupled in a way that causes them to contribute equally to the impedance even though the actual losses occurring at the cathode are much more significant than those occurring at the anode.



Figure 4.17: Simulated impedance spectra for cases 7, 8 and 9.

4.4.4 Catalyst layer ionic conductivity

Since the high frequency impedance can be attributed to neither electrode kinetics nor mass transport phenomena it is likely to assume that it is related to ionic conductivity of the catalyst layers as suggested by Schneider et al. [45]. This is investigated by subsequently halving and doubling the ionic conductivity of the catalyst layers as in cases 10 and 11 (see table 4.2). The conductivity of the membrane is kept constant. In figure 4.18 it can be seen that the performance is increased with increasing CL conductivity as should be expected.



Figure 4.18: Simulated impedance polarisation curves for cases 6 and 7 compared to the base case.

As can be seen from figure 4.19 the effects of varying the CL conductivity are not confined to the high frequency arch. While the high frequency arch does become smaller when increasing the CL ionic conductivity the high frequency intersection with the real axis is also affected. The same is true for the intermediate frequency arch and the low frequency real axis intersection. The fact that varying the CL conductivity affects the whole impedance spectrum makes it difficult to draw any clear conclusions. This is a clear indication of the degree to which the the individual contributions to the impedance are coupled. In spite of this there does however seem to be an important connection between the shape of the high frequency arch and the catalyst layer conductivity. Comparing figures 4.19 and 4.5 it seems that the shape the high frequency loop best resembles the experimental data when the CL conductivity is reduced. This indicates that the effective ionic conductivity of the catalyst layer in a real fuel cell is indeed reduced compared to the membrane.



Figure 4.19: Simulated impedance spectra various CL ionic conductivities.

4.4.5 Parameter variation conclusion

The conclusions drawn from this parametric study clearly demonstrates the power of detailed modelling in impedance spectroscopy studies. The detail level to which the individual effects can be investigated by using the model would only be achievable by experimental means through the applications of exceedingly complex experimental setups. The author believes that the full potential of the model can be harnessed if a good fit to the data can be achieved.

4.5 Fitting considerations

In order for the model developed to be useful beyond the capability of explaining the interaction of different phenomena in a fuel cell it must also be capable of predicting the performance of an actual fuel cell. As is shown in this chapter the model developed in the course of this project has not yet reached this level. Attempts have been made to fit the model to the experimental data but no satisfactory fit was obtained. The attempts however hinted at some adjustments which are assumed necessary to enable the model to fit the data. An account of these is given below.

4.5.1 Adjustments to improve fitting

• Increase exchange current densities.

- As was discussed in section 4.3.1 the exchange current densities assumed in the simulation base case are too small. Increasing i_0 reduces activation losses and may help reduce the size of the intermediate frequency arch. Ideally reliable data for the temperature dependence of anode and cathode exchange current densities should be included in the model.
- Decrease catalyst layer ionic conductivity
 - As discussed in section 4.4.4 reducing the catalyst layer conductivity both increases the slope of the polarisation curve and affects the shape of the high frequency arch. Reducing the catalyst layer conductivity may be achieved by applying the Brüggeman correction to the conductivity. This is assumed feasible since the H⁺- ions conducted through the catalyst layer must follow a tortuous path in the same way that diffusing species must.
- Reduce OCV
 - The open circuit voltage calculated using the Nernst equation (2.6) is higher than the open circuit voltage which can actually be measured in the laboratory. Part of this discrepancy could be caused by fuel cross-over through the membrane. Implementing the effects of fuel crossover may help improve the fitting of the model. Alternatively the measured OCV could be used directly and the model parameters adjusted accordingly. This approach has been used previously for semi empirical steady state modelling [25].
- Adjust double layer capacitances
 - As pointed out in section 4.3.2 the shape of the individual arches in the simulated impedance spectra deviate from those in the measured ones. One way to remedy this is by adjusting the double layer capacitances of the catalyst layers to better reflect real values. Implementing some form of spatial variation in C_{dl} may also be necessary.

By implementing the adjustments proposed in this section and carefully tweaking the model parameters it is assumed that a good fit to the experimental data can be obtained. This must however be confined to future work since the time frame of the current project is insufficient for the purpose.

4.6 Summary

In this section the capabilities of the finite volume based impedance model have been demonstrated. A grid independence analysis has been carried out to verify that the solutions obtained are not too dependent on grid resolution. When comparing the model results to experimentally obtained data it was concluded that the model was unable to properly reproduce measured impedance spectra and polarisation curves. The trends observed in the solution when varying the operating parameters of the model however agreed with those observed in the data as well as in the literature. In conducting a parameter variation analysis a number of interesting discoveries were made. It was established that the intermediate frequency arch is most likely caused by the combined impedance of the anode and cathode assuming that anode and cathode double layer capacitance are the same order of magnitude. It was further concluded that diffusion through the porous electrode contributes to this impedance. The magnitude of anode and cathode contributions were unexpectedly discovered to be equal in spite of the greater importance of the cathode losses.

The low frequency arch was concluded to originate in transient variation in gas composition in the cathode flow channel. This agrees with the results obtained by Schneider et al. [45] on LTPEM fuel cells.

The high frequency arch proved to be independent of electrode kinetics but sensitive to catalyst layer conductivity.

As has been shown the model developed is a potentially useful tool in studies using electrochemical impedance spectroscopy. Much work however remains before faithful reproduction of actual impedance spectra can be performed by the model.

Chapter 5

Conclusion

In this report the development of a novel HTPEM fuel cell impedance model based on the finite volume approach has been presented. The model considers transient species transport on the cathode side and effects of double layer capacitance on the transient variations in anode and cathode over potentials. Spatial variations are considered along the channel and through the MEA.

In order to validate the model a small set of impedance spectra and polarisation curves have been recorded in the laboratory using a single cell test setup. The MEA used for the experiments is a BASF Celtec P2100. The impedance spectra have been recorded at 160 °C at various stoichiometries and current densities.

In order to validate the model it has been attempted to fit the model to the recorded data. The attempt was unsuccessful due to the highly nonlinear coupling of the governing equations and the limited time available for the task. Instead validation has been carried out by comparing the effects of the operating parameters on the model and the recorded impedance spectra and polarisation curves. It can be concluded that the behaviour of the model is physically sensible even if the experimental data is not accurately reproduced.

Using the model the origins of the individual features of the impedance spectrum have been investigated. A number of remarkable results have been obtained: The low frequency arch is concluded to be a result of oscillations in the cathode flow channel gas composition. This has previously been confirmed by sectioned electrode studies of LTPEM fuel cells. The intermediate frequency arch stems from the combined effects of anode and cathode activation impedance and diffusion through the electrode. When disabling the transient diffusion effects in the cathode compartment it can be concluded that the anode and cathode activation contributions are equal in magnitude. This is remarkable since the majority of the activation losses occur at the cathode. No distinct reason for the high frequency arch have been determined but the shape is clearly affected when varying the catalyst layer conductivity.

Carrying out similar investigations using an experimental approach would require very complex and expensive experimental setups. The ability to study the individual contributions to the impedance spectrum makes the model a powerful tool in impedance spectroscopy studies. The inability to accurately reproduce the recorded impedance spectra is however a drawback of the model. Remedying this by improving the modelling detail and tweaking the model parameters should be the first priority in future investigations.

On the long term a possible development of the model could be simulation of

localised impedance spectra along the channel. This would enable investigation of the spatial variations of the of importance different phenomena. Another very interesting possibility is the improvement of the anode model to incorporate the effects of CO poisoning.

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Appendix A Discretised equations

In this appendix the discretised versions of the governing differential equations in the model are derived. The discretisation is based on a rectangular grid with nonuniform spacing. The notation for the neighboring cells used in the derivation is shown in figure A.1.



Figure A.1: Notation used for neighboring cells and cell faces

A.1 Charge transport

The equations governing charge transport (equations (2.1), (2.2) and (2.3)) are discretised as shown in this section. The discretisation of equation (2.1) is presented in detail to show the approach. In order to obtain the discrete formulation the differential equation is first integrated over the control volume.

$$\int_{CV} \frac{\partial \eta_A}{\partial t} dV = -\int_{CV} \frac{\nabla \left(\kappa_{i,A} \nabla \phi_{i,A}\right) + j_A}{C_{dl,A}} dV$$
(A.1)

Applying the Gauss divergence theorem and noting that the double layer capacitance is assumed constant in the catalyst layer the equation becomes:

$$\int_{CV} \frac{\partial \eta_A}{\partial t} dV = -\frac{\sum_k \int_{A_k} \mathbf{n}_k \left(\kappa_{i,A} \nabla \phi_{i,A}\right) dA + \int_{CV} j_A dV}{C_{dl,A}}$$
(A.2)

Here \mathbf{n}_k is the outward facing normal vector at the control volume boundary. Assuming that $\frac{\partial \eta_A}{\partial t}$ and j_A are constant inside the control volume and $\frac{(\kappa_{i,A} \nabla \phi_{i,A})}{C_{dl,A}}$ is constant across each face the equation formulation becomes:

$$\frac{\partial \eta_A}{\partial t} V_{CV} = -\frac{\sum_k \left(\mathbf{n}_k \left(\kappa_{i,A} \nabla \phi_{i,A} \right) \right)_k \cdot A_k + j_A V_{CV}}{C_{dl,A}} \tag{A.3}$$

Denoting the control volume faces as shown in figure A.1 we can rewrite equation A.3 as:

$$\frac{\partial \eta_A}{\partial t} V_{CV} = -\frac{\left(\kappa_{i,A} \frac{\partial \phi_{i,A}}{\partial x}\right)_e A_e - \left(\kappa_{i,A} \frac{\partial \phi_{i,A}}{\partial x}\right)_w A_w + \left(\kappa_{i,A} \frac{\partial \phi_{i,A}}{\partial y}\right)_n A_n - \left(\kappa_{i,A} \frac{\partial \phi_{i,A}}{\partial y}\right)_s \cdot A_s + j_A V_{CV}}{C_{dl,A}}$$
(A.4)

The values of the gradient and the conductivity at the control volume faces are calculated using central differencing. The values in adjacent control volumes are designated by an additional subscript denoting the position relative to the control volume in question as shown in figure A.1 (e.g. N, S, E, W). Values at the control volume in question have no extra subscripts. This leads to:

$$\frac{\partial \eta_A}{\partial t} V_{CV} = -\frac{\left(\frac{\kappa_{i,A,E}\Delta x_E + \kappa_{i,A}\Delta x}{\Delta x_E + \Delta x} \cdot \frac{\phi_{i,A,E} - \phi_{i,A}}{(\Delta x_E + \Delta x)/2}\right) A_e}{C_{dl,A}} + \frac{\left(\frac{\kappa_{i,A,W}\Delta x_W + \kappa_{i,A,W}\Delta x}{\Delta x_W + \Delta x} \cdot \frac{\phi_{i,A} - \phi_{i,A,W}}{(\Delta x_W + \Delta x)/2}\right) A_w}{C_{dl,A}} - \frac{\left(\frac{\kappa_{i,A,N}\Delta y_N + \kappa_{i,A}\Delta y}{\Delta y_N + \Delta y} \cdot \frac{\phi_{i,A,N} - \phi_{i,A}}{(\Delta y_N + \Delta y)/2}\right) A_n}{C_{dl,A}} + \frac{\left(\frac{\kappa_{i,A,S}\Delta y_S + \kappa_{i,A}\Delta y}{\Delta y_S + \Delta y} \cdot \frac{\phi_{i,A} - \phi_{i,A,S}}{(\Delta y_S + \Delta y)/2}\right) A_s}{C_{dl,A}} - \frac{j_A V_{CV}}{C_{dl,A}}$$

Dividing by V_{CV} yields:

$$\frac{\partial \eta_A}{\partial t} = -\frac{\left(\frac{\kappa_{i,A,E}\Delta x_E + \kappa_{i,A}\Delta x}{\Delta x_E + \Delta x} \cdot \frac{\phi_{i,A,E} - \phi_{i,A}}{(\Delta x_E + \Delta x)/2}\right)}{C_{dl,A}\Delta x} + \frac{\left(\frac{\kappa_{i,A,W}\Delta x_W + \kappa_{i,A,W}\Delta x}{\Delta x_W + \Delta x} \cdot \frac{\phi_{i,A} - \phi_{i,A,W}}{(\Delta x_W + \Delta x)/2}\right)}{C_{dl,A}\Delta x} - \frac{\left(\frac{\kappa_{i,A,N}\Delta y_N + \kappa_{i,A}\Delta y}{\Delta y_N + \Delta y} \cdot \frac{\phi_{i,A,N} - \phi_{i,A}}{(\Delta y_N + \Delta y)/2}\right)}{C_{dl,A}\Delta y} + \frac{\left(\frac{\kappa_{i,A,S}\Delta y_S + \kappa_{i,A}\Delta y}{\Delta y_S + \Delta y} \cdot \frac{\phi_{i,A} - \phi_{i,A,S}}{(\Delta y_S + \Delta y)/2}\right)}{C_{dl,A}\Delta y} - \frac{j_A}{C_{dl,A}}$$
(A.6)

For the cathode catalyst layer and the membrane similar derivations yield equations (A.7) and (A.8).

$$\frac{\partial \eta_{C}}{\partial t} = -\frac{\frac{\kappa_{i,C,E}\Delta x_{E} + \kappa_{i,C}\Delta x}{\Delta x_{E} + \Delta x} \cdot \frac{\phi_{i,C,E} - \phi_{i,A}}{(\Delta x_{E} + \Delta x)/2}}{C_{dl,A}\Delta x} \\
+ \frac{\frac{\kappa_{i,C,W}\Delta x_{W} + \kappa_{i,C,W}\Delta x}{\Delta x_{W} + \Delta x} \cdot \frac{\phi_{i,C} - \phi_{i,C,W}}{(\Delta x_{W} + \Delta x)/2}}{C_{dl,C}\Delta x} \\
- \frac{\frac{\kappa_{i,C,N}\Delta y_{N} + \kappa_{i,C}\Delta y}{\Delta y_{N} + \Delta y} \cdot \frac{\phi_{i,C,N} - \phi_{i,C}}{(\Delta y_{N} + \Delta y)/2}}{C_{dl,C}\Delta y} \\
+ \frac{\frac{\kappa_{i,C,S}\Delta y_{S} + \kappa_{i,C}\Delta y}{\Delta y_{S} + \Delta y} \cdot \frac{\phi_{i,C} - \phi_{i,C,S}}{(\Delta y_{S} + \Delta y)/2}}{C_{dl,C}\Delta y} + \frac{\frac{j_{C}}{C_{dl,C}}}{\Delta x_{E} + \Delta x} \cdot \frac{\phi_{i,C,N} - \phi_{i,C}}{(\Delta x_{E} + \Delta x)/2}}{\Delta x} \\
0 = -\frac{\frac{\kappa_{i,C,E}\Delta x_{E} + \kappa_{i,C}\Delta x}{\Delta x_{E} + \Delta x} \cdot \frac{\phi_{i,C} - \phi_{i,C,W}}{(\Delta x_{E} + \Delta x)/2}}{\Delta x} \\
- \frac{\frac{\kappa_{i,C,W}\Delta x_{W} + \kappa_{i,C,W}\Delta x}{\Delta x_{W} + \Delta x} \cdot \frac{\phi_{i,C,N} - \phi_{i,C}}{(\Delta x_{W} + \Delta x)/2}}{\Delta x} \\
- \frac{\frac{\kappa_{i,C,N}\Delta y_{N} + \kappa_{i,C}\Delta y}{\Delta y} \cdot \frac{\phi_{i,C} - \phi_{i,C,S}}{(\Delta y_{N} + \Delta y)/2}}{\Delta y} \\
+ \frac{\frac{\kappa_{i,C,S}\Delta y_{S} + \kappa_{i,C}\Delta y}{\Delta y} \cdot \frac{\phi_{i,C} - \phi_{i,C,S}}{(\Delta y_{S} + \Delta y)/2}}{\Delta y} \\$$
(A.8)

A.2 Mass transport

The discretisation of the equations governing mass transport is shown in this section. Equation (2.11) governs mass transport in the cathode GDL and CL and equation (2.17) governs mass transport in the air flow channel. In this derivation D_i^{eff} has been replaced by D_i to simplify the notation.

Integrating the diffusion equation for the cathode CL and GDL yields:

$$\int_{CV} \frac{\partial y_i}{\partial t} dV = \int_{CV} \frac{\nabla \left(-CD_i \nabla y_i\right)}{C} dV + \int_{CV} S_i dV$$
(A.9)

Applying the Gauss divergence theorem and assuming that C is constant inside a CV:

$$\int_{CV} \frac{\partial y_i}{\partial t} dV = \frac{\sum_k \int_{A_k} \mathbf{n}_k \left(-CD_i \nabla y_i\right) dA}{C} + \int_{CV} S_i dV$$
(A.10)

The integral signs are removed by assuming that the cell face value is equal to the midpoint value and that the transient terms and source terms are constant across the CV:

$$\frac{\partial y_i}{\partial t} V_{CV} = \frac{\sum_k \mathbf{n}_k \left(-CD_i \nabla y_i\right)_k A_k}{C} + S_i V_{CV} \tag{A.11}$$

Writing out the summation:

$$\frac{\partial y_i}{\partial t} V_{CV} = \frac{\left(CD_i \frac{\partial y_i}{\partial x}\right)_w A_w - \left(CD_i \frac{\partial y_i}{\partial x}\right)_e A_e + \left(CD_i \frac{\partial y_i}{\partial y}\right)_s A_s - \left(CD_i \frac{\partial y_i}{\partial y}\right)_n A_n}{C} + S_i V_{CV}$$
(A.12)

Applying central difference approximation to face values:

$$\frac{\partial y_{i}}{\partial t}V_{CV} = \frac{\left(\frac{CD_{i}\Delta x + C_{W}D_{i,W}\Delta x_{W}}{\Delta x + \Delta x_{W}} \cdot \frac{y_{i} - y_{i,W}}{(\Delta x + \Delta x_{W})/2}\right)A_{w}}{C} \\
- \frac{\left(\frac{CED_{i,E}\Delta x_{E} + CD_{i}\Delta x}{\Delta x_{E} + \Delta x} \cdot \frac{y_{i,E} - y_{i}}{(\Delta x_{E} + \Delta x)/2}\right)A_{e}}{C} \\
+ \frac{\left(\frac{CD_{i}\Delta x + C_{S}D_{i,S}\Delta x_{S}}{\Delta x + \Delta x_{S}} \cdot \frac{y_{i} - y_{i,S}}{(\Delta x + \Delta x_{S})/2}\right)A_{s}}{C} \\
- \frac{\left(\frac{CND_{i,N}\Delta x_{N} + CD_{i}\Delta x}{\Delta x_{N} + \Delta x} \cdot \frac{y_{i,N} - y_{i}}{(\Delta x_{N} + \Delta x)/2}\right)A_{n}}{C} + S_{i}V_{CV}$$
(A.13)

Dividing by V_{CV} the final discretised form of the discrete diffusion equation is obtained:

$$\frac{\partial y_{i}}{\partial t} = \frac{\left(\frac{CD_{i}\Delta x + C_{W}D_{i,W}\Delta x_{W}}{\Delta x + \Delta x_{W}} \cdot \frac{y_{i} - y_{i,W}}{(\Delta x + \Delta x_{W})/2}\right)}{C\Delta x} \\
- \frac{\left(\frac{C_{E}D_{i,E}\Delta x_{E} + CD_{i}\Delta x}{\Delta x_{E} + \Delta x} \cdot \frac{y_{i,E} - y_{i}}{(\Delta x_{E} + \Delta x)/2}\right)}{C\Delta x} \\
+ \frac{\left(\frac{CD_{i}\Delta x + C_{S}D_{i,S}\Delta x_{S}}{\Delta x + \Delta x_{S}} \cdot \frac{y_{i} - y_{i,S}}{(\Delta x + \Delta x_{S})/2}\right)A_{s}}{C\Delta y} \\
- \frac{\left(\frac{C_{N}D_{i,N}\Delta x_{N} + CD_{i}\Delta x}{\Delta x_{N} + \Delta x} \cdot \frac{y_{i,N} - y_{i}}{(\Delta x_{N} + \Delta x)/2}\right)A_{n}}{C\Delta y} + S_{i}$$
(A.14)

We now look at the mass transport in the flow channel. As mentioned in section 2.5.1 we assume no flow in the x-direction and neglect the effect of diffusion in the y-direction since it is not significant compared to the effect of convection. Integrating equation (2.17) we get:

$$\int_{CV} \frac{\partial y_i}{\partial t} dV = \frac{\int_{CV} \frac{\partial}{\partial x} \left(-CD_i \frac{\partial y_i}{\partial x} \right) dV}{C} - \frac{\int_{CV} \frac{\partial}{\partial y} (Cy_i u_{air}) dV}{C}$$
$$= \frac{\int_{A_e} \left(-CD_i \frac{\partial y_i}{\partial x} \right)_e dA}{C} - \frac{\int_{A_w} \left(-CD_i \frac{\partial y_i}{\partial x} \right)_w dA}{C}$$
$$= -\left(\frac{\int_{A_n} (Cy_i u_{air})_n dA}{C} - \frac{\int_{A_s} (Cy_i u_{air})_s dA}{C} \right)$$
(A.15)

Assuming that the value at the face centroid is equal to the mean across the face we remove the integral sign and rearrange.

$$\frac{\partial y_i}{\partial t} V_{CV} = \frac{\left(CD_i \frac{\partial y_i}{\partial x}\right)_w A_w}{C} - \frac{\left(CD_i \frac{\partial y_i}{\partial x}\right)_e A_e}{C} + \frac{\left(Cy_i u_{air}\right)_s A_s}{C} - \frac{\left(Cy_i u_{air}\right)_n A_n}{C}$$
(A.16)

We assume that there is no concentration gradient in the x-direction in the channel. This means that the diffusion rate across face w is only controlled by the mole fraction difference between the channel and the cathode GDL and the properties inside the GDL. Also there is no diffusion across face e since there is no diffusion through the bipolar plate. For the convective term the upwind values are used to calculate face values. This gives:

This concludes the derivation of the discretised versions of the governing equations for the model.

Appendix B Impedance spectra

In this appendix all the impedance spectra recorded in the lab are displayed.



Figure B.1: EIS spectrum recorded at $T=160\,^{\circ}\mathrm{C},\,i=0.11\,\mathrm{A/cm^2}$ and $\lambda_{air}=5$



Figure B.2: EIS spectrum recorded at $T=160\,{\rm ^{\circ}C},\,i=0.22\,{\rm A/cm^2}$ and $\lambda_{air}=5$



Figure B.3: EIS spectrum recorded at $T=160\,{\rm ^{\circ}C},\,i=0.33\,{\rm A/cm^2}$ and $\lambda_{air}=5$



Figure B.4: EIS spectrum recorded at $T=160\,^{\circ}\mathrm{C},\,i=0.11\,\mathrm{A/cm^2}$ and $\lambda_{air}=2$


Figure B.5: EIS spectrum recorded at $T=160\,{\rm ^{\circ}C},\,i=0.22\,{\rm A/cm^2}$ and $\lambda_{air}=2$



Figure B.6: EIS spectrum recorded at $T=160\,{\rm ^{\circ}C},\,i=0.33\,{\rm A/cm^2}$ and $\lambda_{air}=2$