Low-temperature fuel cells operating with contaminated feedstock

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Low-temperature fuel cells operating with contaminated feedstock

Paul Wingelaar

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As an Electrical Engineer, he approaches the Fuel Cell from an electrical point of view. Traditionally, the approach to characterize fuel cells is by performing steady-state measurements. However, electrical engineers are more interested in the dynamic behavior of an electricity source. By keeping close to the electrochemistry, the “dynastatic” model, which is constructed from impedance spectroscopy, steady-state, and step response measurements, can be used in electrical and chemical modeling.

In order to contribute to a CO₂-neutral energy generation system, biomass gas is used as the feedstock for the fuel cells. Because biogas contains trace amounts of CO, which is a contaminant for low-temperature fuel cells, Paul searched for an electrical regeneration method for the polluted catalysts. The found and described regeneration method includes applying negative voltage pulses to the individual cells of the stack, and changing the electrical position of the cells in the stack. This regeneration method electro-oxidizes the adsorbed CO to CO₂, which will disconnect from the catalyst surface.
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Trefw.: brandstofcellen / impedantiespectroscopie / duurzame energie / elektrochemische analyse.
Subject headings: proton exchange membrane fuel cells / electrochemical impedance spectroscopy / renewable energy sources / electrochemical analysis.
Aan Marijke
en aan ons ongeboren kindje...
Summary

This work concerns the analysis and modeling of the dynamic and static behavior of Polymer Electrolyte Membrane Fuel Cells (PEMFC). Three fundamentally different measurement methods are used to determine the static, the large-signal, and the small-signal dynamic behavior of a fuel cell system. By combining the results of the three types of measurements, a joint dynamic and static (or dynastatic) model of the fuel cell is proposed. This model covers all three operational states of the fuel cell, while keeping close to the electrochemical aspects of the system. The dynastatic model describes the electrical behavior of the fuel cell to within 5%.

The remaining part of this study is concerned with the integration of biomass energy generation systems together with fuel cells with the aim to convert biogas to electricity. With the conversion of biomass to hydrogen rich gas, polluting gasses (from the viewpoint of the fuel cell) are released. One of the major pollutions for the PEM fuel cell platinum catalyst is carbon monoxide (CO). Trace amounts of this gas, as low as 30 ppm, are responsible for lower output voltages of PEM fuel cells. This phenomenon is called CO-poisoning, and is related to the adsorption of CO to the platinum catalysts. To cope with this pollution, this work introduces an electrical regeneration procedure. The regeneration is done by pulsing the CO-poisoned cells with negative voltage, in order to electro-oxidize the adsorbed CO to carbon dioxide (CO$_2$). In this way, carbon dioxide will disconnect itself from the platinum catalyst, making the occupied position free for the hydrogen reaction.

Measurements show that the electrical regeneration of the PEM fuel cell is effective for gas mixtures containing up to 100 ppm CO. Compared with the same fuel cell operating with pure hydrogen, the regeneration method consumes only 2% of the produced electrical energy. This kind of performance has
not been previously reported for fuel cell stacks with pure platinum catalysts. This study shows that the behavior of the individual cells in a fuel cell series stack differs as a consequence of a cell’s electrical position within the stack. It is demonstrated that the cells at the higher potential position in the stack can be electrically regenerated, while the cells in the lower potential position can not. It is also observed that the cell at the highest potential position in a four membrane stack can show “self-oxidizing” behavior in order to electro-oxidize the adsorbed CO to CO$_2$. This self-oxidizing behavior was not reported before in the literature for fuel cells with pure platinum catalysts.
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Chapter 1
Introduction

Introductions are expected to start with an eye-catcher, which is intended to illustrate, in a appetizing manner, some of the work to be explained in the following chapters. However, the cover is the part of a book which is first inspected, also for a Ph.D. thesis, and thus that would be the ideal place to put an eye-catcher on.

There are Ph.D. theses produced in the Department of Electrical Engineering of the Eindhoven University of Technology which have a plain colored cover with the title and name of the author in a sans-serif font. These kind of covers do not provide sufficient background of the subject described, and thus will not work as eye-catcher.

So, if a cover should replace the eye-catcher in the introduction, then it should fulfil the following criteria:

1. It must provide the title and the author name,
2. it should give an idea of what may be expected inside,
3. it must provide some background information,
4. the color must be chosen according to the subject,
5. it must challenge the potential reader to actually read the book.

According to these simple rules, I would like to explain the cover of this thesis. The first rule is clear, and thus at the top of the cover, the title and the author name are set. The use of the second and third rules are also clearly visible, that is, one finds information about fuel cells, about their modeling, and about their typical chemistry driven phenomena (thanks to ArgusLab [100]). It proved even possible to illustrate the construction of a fuel cell (background
information) using the covers: On the front cover the anode electrode of the fuel cell is shown, and together with the diffusion layer with platinum catalyst, it forms the anode. The membrane, which is the most important part of the fuel cell, can be imagined as the pages of the thesis, while the cathode diffusion layer and electrode are illustrated on the back cover. On the cathode side of the cover, some additional background information about the author is given. As this thesis is about green energy generation, the color of the thesis had to be a shade of green (fourth rule).

I did not mention rule number five yet. This is the most important rule for an author, but it is also the most difficult one. It is clear that it is very difficult to make a cover which is interesting for everyone, because one cannot dispute taste. For this reason I have shown the cover to a lot of people, and asked what they liked and disliked about it.

Since you are now reading this sentence, I may conclude that the cover of this work succeeds in being a good eye-catcher, and I hope that the content of this thesis will fulfil the expectations you got from the cover.

1.1 Motivation

Disturbing reports on climate change find their way to the daily news. Since the industrial revolution the average temperature on earth has risen with 0.7 °C and it is expected that this will go on with an increasing rate. In the best case, global warming is limited at the end of this century to 1.5 °C. However, if greenhouse gas emissions are not reduced with at least 15 to 30% in 2020, which is the European goal [79, 93, 105], then it is very unlikely that the rise in global temperature stays below 2 °C in 2100.

Higher global temperatures will contribute to more extreme weather. This will show up in the form of storms, flooding and dryness, longer grow seasons, higher sea levels, and more extreme temperature variations [105].

Since the pre-industrial time (1750), the CO₂ concentration has increased with 35% [79, 93, 105]. The effect of greenhouse gases is graphically shown in Fig. 1.1 [105]. The figure shows the sun radiation received on the Earth (a). A part of the radiation is reflected before it reaches the surface (b). Another part is reflected by the Earth surface (c). A part of the infrared radiation reflected on the Earth (d) is re-emitted back because of the greenhouse gases (e). A natural balance of greenhouse gases maintains the temperature of the earth at a level that supports life. However, if the concentration of greenhouse gases is raised in an artificial way (f), then the amount of radiation that is re-emitted (e)
1.1. Motivation

Figure 1.1: The greenhouse effect in the atmosphere.

becomes higher, and the temperature will rise [59, 74, 105, 96].

The Kyoto protocol is a good starting point to reduce greenhouse gas emissions like carbon dioxide (CO$_2$), methane (CH$_4$), and nitrous oxide (N$_2$O) [101]. To achieve the goals of the Kyoto protocol, or better, the aims of the European Union (EU), new techniques to reduce emissions are needed.

High expectations for reducing greenhouse gas emissions are there for Fuel Cell (FC) energy generation systems. Fuel cells work by reducing oxygen and oxidizing hydrogen to form water, and produce electricity. This is a very environmentally friendly technique when the hydrogen is produced in an environmentally friendly way.

One of the possible paths to generate hydrogen is biomass. Biomass is an environmentally friendly energy source when it is managed well, that is, by using sustainable biomass management. If wood is used as biomass source, then the term sustainable biomass management means that the forest is reforested.

One of the drawbacks of using biomass for hydrogen production is the creation of carbon monoxide (CO), which can reduce the performance of a particular, very popular fuel cell type, the low-temperature Polymer Electrolyte Membrane Fuel Cell (PEMFC). This is, to date, the only commercially available fuel cell type.

This thesis attempts to contribute to the implementation of a technical and economical feasible path for a biomass-fuel cell system, where low-temperature fuel cells can be operated with higher CO concentration in the hydrogen gas stream. Chapter 4 describes an electrical way of boosting the CO-tolerance of a low-temperature fuel cell.
1.2 Overview of fuel cell technology

Fuel cell technology is old. One of the first publications about fuel cells is from William Grove, a British scientist who worked on an electrochemical battery that used hydrogen and oxygen as fuel. Grove published his results in the *Philosophical Magazine and Journal of Science* in 1843 [54, 94, 110].

There are five known fuel cell types presented in Table 1.1. The name of the fuel cell type is based on the material of the electrolyte. So, a Phosphoric Acid Fuel Cell (PAFC) uses phosphoric acid as its electrolyte. An Alkali FC (AFC) uses an alkali such as potassium hydroxide as its electrolyte; a Polymer Electrolyte Membrane FC (PEMFC\(^1\)) has a polymer electrolyte, which can also be named as Polymer Electrolyte FC (PEFC); a Molten Carbonate FC (MCFC) has an electrolyte of molten carbonate melts (\(\text{Li}_2\text{CO}_3 / \text{Na}_2\text{CO}_3\)); and a Solid Oxide FC (SOFC) has a ceramic oxide as its electrolyte (\(\text{Y}_2\text{O}_3 / \text{ZrO}_2\)) [33, 94, 110].

Specific features of FC types can be used to categorize them, such as the state of the membrane, which can be a solid or a liquid, the temperature range, that is low, medium, or high, and the application orientation. Fuel cells with solid membranes, the PEMFC and SOFC, have the advantage over liquid membrane FC’s because the membrane cannot leak. The advantage of high temperature FC’s over low temperature FC’s is that the waste heat is of higher quality, however, the disadvantage is that they need more shielding in order to avoid perilous situations [94, 110].

The PEMFC is compact, operates with the lowest temperature, and has a short startup period. These advantages make this kind of fuel cell suitable for both mobile and stationary applications. Furthermore, the membrane is made from a polymer, which can leak nor crack. This is an advantage over the SOFC and the liquid based electrolyte types [33, 94, 110]. Last but not least, it is currently the only type that is commercially available.

Unfortunately, the PEMFC has also its drawbacks, which are the high catalytic loadings of noble metals and its CO intolerance. High temperature FC’s suffer less from polluting gases, except for the AFC, which suffers from CO\(_2\) poisoning [33]. The catalytic loading of platinum on the electrodes of PEMFC’s did reduce from 0.80 mg/cm\(^2\) in 2000 to 0.30 mg/cm\(^2\) in 2004 [26], which shows the positive development in tackling the first drawback. Solutions for the second drawback will be described in this thesis in Chapters 4 and 5.

\(^1\)The abbreviation PEMFC is also used for proton exchange membrane fuel cell. There is no difference between both fuel cells, except for the name. A Direct Methanol Fuel Cell (DMFC) is a special type of PEMFC, which converts methanol directly into electricity.
1.3 Definitions of basic fuel cell terms

“A fuel cell is a device that converts chemical energy of a fuel directly into electricity. Fuel cells are intrinsically more efficient than most other energy-conversion devices. Electrolytic chemical reactions cause electrons to be released on one electrode and flow through an external circuit to a second electrode. Whereas in batteries the electrodes are the source of the active ingredients, which are altered and depleted during the reaction, in fuel cells the gas or liquid fuel (often hydrogen, methyl alcohol, hydrazine, or a simple hydrocarbon) is supplied continuously to one electrode and oxygen or air to the other from an external source. So, as long as fuel and oxidant are supplied, the fuel cell will not run down or require recharging. Fuel cells can be used in virtually all places where nowadays another source of electricity is used. They are especially being developed for use in electric automobiles, in the hope of achieving enormous reductions in pollution” [39].

In this section, basic definitions of fuel cell characteristics are formulated. These definitions are used throughout this thesis.

Fuel cell

A fuel cell is a device that converts hydrogen and oxygen into electricity. The noun “fuel cell” is used as a collective term for a single cell or a series stack of single cells.

<table>
<thead>
<tr>
<th>FC type</th>
<th>Electrolyte material</th>
<th>Temperature</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>Potassium hydroxide</td>
<td>± 200 °C</td>
<td>Space, transport</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Polymer</td>
<td>± 60 °C</td>
<td>Transport, stationary and portable</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid</td>
<td>± 200 °C</td>
<td>Small power</td>
</tr>
<tr>
<td>MCFC</td>
<td>Molten carbonate</td>
<td>± 650 °C</td>
<td>Stationary</td>
</tr>
<tr>
<td>SOFC</td>
<td>Ceramic oxide</td>
<td>± 1000 °C</td>
<td>Stationary</td>
</tr>
</tbody>
</table>
A single cell is a fuel cell containing one membrane, as is shown in Fig. 1.2. A cell contains the anode electrode (a), the anode diffusion layer including the platinum catalyst (b), the polymer membrane (c), the cathode diffusion layer with platinum catalyst (d), and the cathode electrode (e).

At the anode side of the cell, hydrogen ($\text{H}_2$) is supplied. At the catalyst, the hydrogen splits in protons ($\text{H}^+$), which can travel through the polymer membrane, and in electrons ($\text{e}^-$), which have to travel through the metal electrodes. At the cathode side, oxygen ($\text{O}_2$) reacts under the influence of the catalyst with the protons and electrons to form water ($\text{H}_2\text{O}$). The electrons traveling in an external circuit are doing “electrical work”.

Stack

A stack is a series connection of various single cells in order to increase the output voltage. There is no limitation in the number of single cells placed in series. However, it is also possible to stack single cells in parallel, in order to increase the output current. When in this thesis a parallel stack is discussed, it will be explicitly mentioned.
1.4 Overview of the thesis

A cartridge is a stack of four single cells, bundled in one casing, as is shown in Fig. 1.3 [48, 49, 50]. It is, of course, possible to stack multiple cartridges, which means that the stack increases per cartridge with four additional single cells.

Figure 1.3 shows an artist impression of the construction of a cartridge, based on [48, 49, 50]. The major parts of the cartridge from Fig. 1.3 are: a) half of the cartridge, b) in the top the anode electrode, in the bottom a packed electrode, diffusion layer and membrane, c) a single anode diffusion layer, d) a single membrane, e) a double cathode diffusion layer, f) a double cathode electrode, g) spring array for a single membrane, and h) the outer casing.

1.4 Overview of the thesis

The thesis is divided in three major parts, and the appendices. The first part describes the Polymer Electrolyte Membrane fuel cell with pure hydrogen feedstock. Chapter 2 describes the characteristics of a PEM fuel cell. The characteristics of the steady-state, step, and small-signal response are discussed. A thorough theoretical basis supports the descriptions. In Chapter 3 the three characteristic models, namely steady state, small signal, and large signal, are combined into a single “dynastatic” model. This model does not only describe the fuel cell in its response to load changes, but it can also be used to determine aging and concentration failure of oxygen.
Chapter 1. Introduction

The second part describes the Polymer Electrolyte Membrane fuel cell with contaminated feedstock. Chapter 4 describes the effects of carbon monoxide as contaminant in the feedstock of a polymer electrolyte membrane fuel cell. Electrical regeneration of CO from the platinum catalysts is demonstrated. In Chapter 5, the technical description of the fuel cell system is completed with the energetic balance, the environmental impact, and some economical issues of the system.

The third part contains the conclusions that can be drawn from the described work in parts I and II.
Part I

Polymer Electrolyte Membrane fuel cells
Chapter 2
Characterization of PEM fuel cells

The principles of fuel cells are very old. One of the first references to a fuel cell is dated in 1843, when Sir William Grove described his “gas voltaic battery” [54]. Although several attempts were made to use the fuel cell concept in state-of-the-art applications, such as the “Apollo space program” [94], the use of these green power generators stayed rather modest.

The basic principle of the fuel cell is the reduction of oxygen at the cathode and oxidation of hydrogen at the anode side. Because the anode is defined as the electrical connection of a device where the current enters, the anode of the fuel cell is its negative terminal [6].

A Polymer Electrolyte Membrane Fuel Cell (PEMFC or PEM fuel cell) uses a polymer membrane to separate anode and cathode. Sometimes, this fuel cell is also called Proton Exchange Membrane (PEM) fuel cell or Proton Exchange (PE) fuel cell, because the membrane only conducts positively charged particles, which are, in the case of hydrogen conversion, protons.

The chemical half-cell reaction of the anode is given by

\[ H_2 \rightarrow 2H^+ + 2e^- , \]  \hspace{1cm} (2.1)

the cathode reaction is given by

\[ \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O . \]  \hspace{1cm} (2.2)
As a consequence, the overall chemical reaction of the PEM fuel cell is found to be

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O.$$  \hfill (2.3)

This reaction is exothermic, which means that the fuel cell produces heat. The composition of the polymer membrane is made in a way that it only allows protons to pass. Therefore, the electrons involved in the reaction have to flow in a circuit external to the fuel cell, doing electrical work.

An exploded view of the mechanical construction of a fuel cell is shown in Fig. 2.1, where point “a” shows the anode conducting plate, “b” is the anode and “d” is the cathode, which are made of a platinum catalyst on a carbon based diffusion layers, “c” shows the polymer membrane, which is often made from Nafion, and finally “e” represents the cathode conducting plate.

In this chapter the basic characteristics of PEM fuel cells are explained, that is, the steady-state characteristic, the step-response characteristic and the small-signal behavior, together with some basic electrochemical theory.

### 2.1 Experimental test-setup

The fuel cell characteristics are presented on the basis of measurements using a commercial available “SR-12” fuel cell system from Avista-Labs [5]. The
stack contains 48 membranes, divided over 12 cartridges (4 membranes per cartridge). The advantage of using cartridges is that if one sub-stack fails, the cartridge can be replaced during operation. Furthermore, the system is capable of delivering 500 W continuous electrical output power, with a maximum hydrogen consumption of 7 l/min. Hydrogen has an energy density of 119.96 MJ/kg (LHV) [84], and a mass density of 0.090 kg/m$^3$ [84], resulting in an energy density of 10.80 MJ/m$^3$. So, this fuel cell system consumes per hour

$$
E_{ch,LHV} = 10.80 \text{MJ/m}^3 \cdot 0.420 \text{m}^3 = 4.535 \text{MJ},
$$

(2.4)

while the fuel cell system produces an electrical energy of

$$
E_{el} = 500W \cdot 3600s = 1.80 \text{MJ}.
$$

(2.5)

Hence, the fuel cell system efficiency at full load, where the efficiency is defined as the electrical output energy divided by the input energy, is 39%.

Steady-state and step-response measurements have shown that this fuel cell system uses electrical regeneration of the cartridge in order to humidify the membranes [50, 110, 111]. Because it was impossible to get rid of this electrical switching behavior, this work focuses on a test-setup which contains just one of the 12 cartridges. The measurement setup is shown in Fig. 2.2.

The hydrogen is supplied from a hydrogen cylinder via a double reducing valve and, occasionally, a flow meter to the cartridge. The oxygen is supplied
from the ambient air with a fan. The fan is uncontrolled, and therefore, the oxygen supply to the cartridge is also not controlled. The hydrogen channel of the cartridge has a purge opening, which can be used to "clean" the channel by opening the purge valve. The electromechanical purge valve can be controlled by a digital signal processor (DSP) measuring system. Furthermore, a needle valve and flow meter (F) are also put into the purge line.

The electrical part of the test-setup is a linear regulator using MOSFET’s to control the output current of the fuel cell stack [111]. The linear regulator is shown with dashed lines in Fig. 2.2. The regulator is controlled by the same DSP-system. The control circuit ensures that the standard voltages of the fuel cell stack and other connected devices are amplified to match the voltages required by the DSP-system, in order to minimize the bit error.

The DSP-system used is a “dSpace DS1104” system with four multiplexed 16-bit AD converters, four parallel 12-bit AD converters, eight 16-bit DA converters, a slave DSP with PWM output, some multi-programmable IO bits and the possibility to connect other devices through a RS232 or RS488 serial bus [37]. The on-board DSP is controlled from Matlab-Simulink, so that it is possible to change variables in real time using the Controldesk software.

The controller for the test-setup is implemented in Simulink. The linear regulator input current, which is the same as the fuel cell stack output current, is controlled with a PI controller. Because the maximum sample frequency of the DSP-system is 10 kHz, the control circuit from Fig. 2.2 is equipped with anti-aliasing filters with cut-off frequencies of 1 kHz and an attenuation of -80 dB above 5 kHz.

### 2.2 Steady-state operation

The steady-state characteristics of a PEM fuel cell are well described in the literature, especially by chemists and electrochemists. Much research has been done by Amphlett et al in developing very detailed steady-state models for PEM fuel cells [2, 3, 44, 76]. Although the models describe very well all electrochemical and physicochemical aspects of the internal working principles of the fuel cell, not all the parameters described can be found with electrical measurements. Therefore, a more empirical approach as introduced by Lee et al is also described in this section [70, 71, 72].
2.2. Steady-state operation

2.2.1 The open circuit voltage

To start the electrochemical discussion of a fuel cell, first the boundary conditions of the thermodynamic functions have to be set. In this discussion, the temperature \( T \) and pressure \( p \) of the reactants are assumed to be constant. The best understood thermodynamic functions under these conditions are the Gibbs energy \( (G) \) (2.6) and the enthalpy \( (H) \) (2.7) \[6\]

\[
G = U + pV - TS,
\]

(2.6)

\[
H = U + pV,
\]

(2.7)

where \( U \) is the internal energy, \( V \) is the volume, and \( S \) is the entropy.

The change of the Gibbs energy \( (\Delta G) \) by one of its reaction components can be expressed as

\[
\Delta G = \mu_k \Delta n_k,
\]

(2.8)

\[
\mu_k = \mu_k^0 + RT \ln p_k,
\]

(2.10)

in which \( \mu_k \) is called the chemical potential of component \( k \), and \( n_k \) is the number of moles of component \( k \). The chemical potential of a gaseous component is dependent on the partial pressure of the gas \( (p_k) \), which can be written as

\[
\mu_k = \mu_k^0 + RT \ln p_k,
\]

(2.10)

The fuel cell is a galvanic cell, which means that the overall current producing reaction (2.3) occurs spontaneously without external supply of energy. In battery operation, the Gibbs energy will be negative and can be separated into two electrode parts with subscript 1 and 2, as \[6\]

\[
\pm \Delta G = \sum_{1} \nu_j \mu_j - \sum_{2} \nu_j \mu_j,
\]

(2.11)

where \( \nu_j \) is the stoichiometric coefficient. Because the maximum value of electrical work that can be done by \( n \) moles of charge carriers is equal to \( E \cdot n \cdot F \), the standard reversible voltage \( E_{rev}^0 \) may be written as

\[
E_{rev}^0 = \frac{\Delta G}{nF} = \frac{\Delta G}{nF},
\]

(2.12)
where $F$ is Faraday’s constant.

If the pressure effects of (2.10) are introduced in (2.12), the electromotive force (EMF) of the electrochemical reaction becomes

$$E_{rev} = E_{rev}^0 + \frac{RT}{nF} \left( \nu_j \ln p_j - \sum \nu_j \ln p_j \right).$$  

(2.13)

This equation is called the Nernst equation.

Equation (2.10) gives a rather simplified connection between chemical potentials and the partial pressure of the reactants. In a real system, this connection gets lost [6]. By introducing the thermodynamic activity, $a_k$, (2.10) is often rewritten as

$$\mu_k \equiv \mu_k^0 + RT \ln a_k.$$  

(2.14)

When the reactant gasses act as ideal gasses, the activity of a reactive gas can be obtained with a very simple relationship

$$a_k = \frac{p_k}{P_0},$$  

(2.15)

in which $P_0$ is the standard gas pressure [70]. The standard chemical potential $\mu_k^0$ is chosen such that when the activity of the species goes to 1 (an ideal situation), $\mu_k = \mu_k^0$. For single component liquids, the activity is always one. Therefore, the activity of water in reaction (2.3), which is assumed to be produced as a liquid, is equal to unity ($a_{H_2O} = 1$) [70].

If the Nernst equation (2.13) is rewritten for practical systems, it follows that

$$E_{rev} = E_{rev}^0 + \frac{RT}{nF} \left( \nu_j \ln a_j - \sum \nu_j \ln a_j \right).$$  

(2.16)

For reaction (2.3), the Nernst equation is represented by

$$E_{rev} = E_{rev}^0 + \frac{RT}{nF} \ln \left( \frac{a_{H_2} \sqrt{a_{O_2}}}{a_{H_2O}} \right).$$  

(2.17)

This EMF is sometimes called the “Nernst voltage”, and is the reversible cell voltage for a certain pressure and temperature.

### 2.2.2 Polarization of the electrodes

A PEM fuel cell has different kinds of electrode polarizations. The term polarization is defined as a shift in potential away from the equilibrium. Two
polarizations will be mentioned. The first polarization is caused by a shifts of the equilibrium potential of the cell, which trigger some very specific features of an electrochemical reaction. The potential shift can occur in low, medium or high current densities, but all are combined in the term activation polarization. The second polarization type deals with the balance of the surface concentrations of the reactant species. This balance is a relationship between the rate of the electrode reaction and the supply of the reactants to the electrode, or the elimination of the species from the electrode due to diffusion. Therefore, this polarization is called the concentration polarization [6, 70].

When the former polarization is the only one operative, the cell is working in kinetic mode. If the cell is working only in the latter polarization type, then the cell works in diffusion mode [6]. In most of the cases the electrochemical cell works in a combined mode, or mixed mode. This is assumed to be the case for PEM fuel cells.

The electrochemical reaction rate is defined as the amount of reactants converted in a certain time, and is proportional to the current density. However, not only the current density is of influence on the magnitude of polarization, but also the nature of the reaction. High polarization occurs normally with slow reactions, that is, it occurs at (very) low current densities [6].

**Activation polarization**

Not only the electrode polarization influences the specific rate of an electrode reaction, but also the concentration of the reactants. If the reaction rate is assumed to be proportional to the concentration of the reacting species $c_j$, then the first-order reaction rate equation is given as [6, 28]

$$ j = \pm nF k_m c_j e^{\pm \frac{nF}{RT}(E - E^0)}. $$

(2.18)

in which $k_m$ is the reaction rate constant, $\alpha$ is the transfer coefficient, which is often taken to be 0.5, $E$ is the electrode potential, and $E^0$ is the standard potential of the electrochemical reaction. A plus sign is used to indicate the anode reaction and the minus sign for the cathode reaction. An electrochemical reaction is mainly driven by the difference between the electrode potential and the standard potential $(E - E^0)$, which is called the overpotential\(^1\) [28].

\(^1\)The term overvoltage or overpotential comes originally from an electrostatic cell, in which a rise in voltage over the equilibrium potential of the cell is needed in order to start an electrochemical reaction, hence, overvoltage [6].
The general reaction rate equation (2.18) can be rewritten to an anodic (subscript \(a\), or \(ox\) because the oxidation takes always place at the anode), and a cathodic (subscript \(c\), or \(red\) because the reduction takes always place at the cathode) current density equation as follows

\[
\begin{align*}
    j_a &= nFk_\alpha c_\alpha e^{\frac{\alpha nF}{RT}(E - E^0)}, \\
    j_c &= -nFk_\gamma c_\gamma e^{-(1-\alpha)\frac{nF}{RT}(E - E^0)}.
\end{align*}
\] (2.19)

(2.20)

The total current density of a reaction is presented as a combination of (2.19) and (2.20) being

\[
    j = j_a + j_c = nF \left\{k_\alpha c_\alpha e^{\frac{\alpha nF}{RT}(E - E^0)} - k_\gamma c_\gamma e^{-(1-\alpha)\frac{nF}{RT}(E - E^0)}\right\}.
\] (2.21)

In this expression, the concentration of reactant species (c) and the electrode potential (E) appear explicitly \([2, 6, 44, 76]\).

If it is assumed that for the equilibrium potential\(^2\), the cathodic and anodic terms are equal, the exchange current density \(j_0 = j_a = -j_c\) becomes

\[
    j^0 = nFk_\alpha c_\alpha e^{\frac{\alpha nF}{RT}E^0} = nFk_\gamma c_\gamma e^{-(1-\alpha)\frac{nF}{RT}E^0}.
\] (2.22)

Equation (2.19) and (2.20) are called the kinetic equations and are valid for all current densities. It is possible to include the exchange current density \(j_0\) in (2.19) and (2.20) for high anodic and cathodic polarizations. These equations become \([6, 70]\)

\[
\begin{align*}
    j_a &= j^0 e^{\frac{\alpha nF}{RT}\eta_{act}}, \\
    j_c &= -j^0 e^{-(1-\alpha)\frac{nF}{RT}\eta_{act}},
\end{align*}
\] (2.23)
(2.24)

where \(\eta_{act} = (E - E^0)\) is the activation overpotential.

Combining these equations results in

\[
    j = j^0 \left\{e^{\frac{\alpha nF}{RT}\eta_{act}} - e^{-(1-\alpha)\frac{nF}{RT}\eta_{act}}\right\},
\] (2.25)

which is known as the Butler-Volmer equation. In contrast to (2.21), the polarization equation (2.25) does not explicitly show the electrode potentials and the concentration of the reactant species.

\(^2\) The equilibrium potential for the half cell reaction (2.1) is \(E^0 = 0\) V, and for (2.2) is \(E^0 = 1.229\) V \([28]\).
To the purpose of the research, there can be chosen which equations are convenient to be used. If a complete polarization curve can be measured at both high and low polarization, then one can best choose the polarization equations (2.23), (2.24) and (2.25). However, if non-invertible reactions or the influence of the component concentrations on reaction kinetics is of interest, then it can be more beneficial to use the kinetic equations (2.19), (2.20) and (2.21) [6].

The Butler-Volmer expression (2.25) can be rewritten as a relationship between the activation polarization $\eta_{\text{act}}$ and the current density $j$ as

$$\eta_{\text{act}} = a + b \ln j,$$

in which $a$ and $b$ are constants in volts. This expression is known as the so-called Tafel equation[6, 15, 70].

Because the hydrogen reaction of the fuel cell (2.1) is only described with the anodic part of the Butler-Volmer equation, and the oxygen reaction (2.2) by the cathodic part, the activation polarization (2.26) is expressed by

$$\eta_{\text{act}} = b_a \ln \left( \frac{j}{j^0_a} \right) + b_c \ln \left( \frac{j}{j^0_c} \right),$$

where the anode part and the cathode part are separated. By assuming that $b = b_a + b_c$ and $j^0 = j^0_a \frac{b_a}{b} + j^0_c \frac{b_c}{b}$ the simple Tafel relation is found

$$\eta_{\text{act}} = b \ln \left( \frac{j}{j^0} \right).$$

If the Tafel slope $b$ is defined as

$$b = \frac{RT}{\alpha n F},$$

then the Tafel constant $a$ will become

$$a = -\frac{RT}{\alpha n F} \left( \ln j^0 \right).$$

This kind of relationship is often found in regions of high polarization. In the region of low polarization, the activation polarization is usually proportional to the current density

$$\eta_{\text{ohmic}} = \rho j,$$
in which \( \rho \) is the reaction resistance in \( \Omega \text{cm}^2 \). In this case, the activation polarization is denoted as \( \eta_{\text{ohmic}} \) (ohmic polarization) because it acts as an ohmic loss [6].

The activation overvoltage described in (2.28) is widely used, and is known as the “more empirical” model of activation polarization [2, 6, 16, 20, 21, 22, 44, 70, 71, 72, 76, 112, 113, 114].

Besides the “more empirical” activation polarization model there is also a “more theoretical” model known in literature [2, 44, 55, 76, 97, 120], which is based on the kinetic equations (2.19), (2.20), (2.21), and the theory of chemisorption [15]. However, because the “more empirical” model is more suitable for the aim of the presented work, there will be no thorough description of the “more theoretical” model in this thesis.

**Concentration polarization**

In the PEM fuel cell, diffusion is marked as the main proton transport mechanism [70, 102]. The diffusion flux of one of the reactants in a fuel cell can be described by Fick’s law [6, 102]

\[
J_{d,j} = D_j \nabla c_j, \tag{2.32}
\]

in which \( D_j \) is the diffusion coefficient of the species involved and \( \nabla c_j \) the spatial gradient of the concentration of reactant \( j \). If the diffusion layer thickness of the fuel cell is assumed to be constant with a value of \( \delta \), then (2.32) can be written as

\[
J_{d,j} = D_j \frac{\Delta c_j}{\delta} = \kappa_j \Delta c_j, \tag{2.33}
\]

\[
\kappa_j \equiv \frac{D_j}{\delta}, \tag{2.34}
\]

where \( \kappa_j \) is the diffusion-flux constant and \( \Delta c_j \) is the difference in concentration of reactant \( j \) over the thickness of the diffusion layer.

The current density is related to (2.33) and is given by

\[
j = \frac{n_j F}{n_j} \kappa_j \Delta c_j, \tag{2.35}
\]

where \( n_j \) denotes the number of particles \( j \). If the difference in concentration is defined as the bulk concentration of species \( j \) minus the surface concentration,
\[ \Delta c_j = c_{v,j} - c_{s,j}, \] which is correct for reactant species, then the relationship between the surface concentration and the current density becomes

\[ c_{s,j} = c_{v,j} - \frac{n_j}{nF\kappa_j} j. \] (2.36)

Relationship (2.36) shows that with an increasing current density, the surface concentration decreases. This means that at a certain value of the current density the surface concentration of reactant \( j \) becomes zero. In this case, we can define a limiting diffusion current density \( j_{\text{lim},j} \) as [6, 70]

\[ j_{\text{lim},j} = \frac{nF}{n_j}\kappa_j c_{v,j}. \] (2.37)

Using (2.37), (2.36) can be rewritten to

\[ c_{s,j} = c_{v,j}\left(1 - \frac{j}{j_{\text{lim},j}}\right). \] (2.38)

For reaction products, the diffusion direction is in the opposite way. In the case of limiting diffusion current densities related to products of the electrochemical reaction, (2.38) becomes [6]

\[ c_{s,j} = c_{v,j}\left(1 + \frac{j}{j_{\text{lim},\text{prod}}}\right). \] (2.39)

If the electrode potential only suffers from concentration polarization, then this potential is defined as a potential with a part whose value is related to non-equilibrium values of the surface concentrations, being given by

\[ E = E^0 + \frac{RT}{nF}\ln c_{s,j}, \] (2.40)

like in the Nernst equation (2.13). The definition for concentration polarization is then expressed as

\[ \eta_{\text{lim}} \equiv E - E^0 = \frac{RT}{nF}\ln c_{s,j}. \] (2.41)

By replacing the surface concentration term in (2.41) by (2.38) and (2.39) for reactants resp. products, the concentration polarization equation becomes

\[ \eta_{\text{lim}} = \frac{RT}{nF}\ln \left(\frac{1 + \frac{j}{j_{\text{lim,prod}}}}{1 - \frac{j}{j_{\text{lim,react}}}}\right). \] (2.42)
The PEM fuel cell with a pure hydrogen and an air supply will most probably only suffer from a limiting current density of oxygen, which reduces (2.42) to the concentration overvoltage [70]

\[ \eta_{lim} = -\frac{RT}{nF} \ln \left( 1 - \frac{j}{j_{lim}} \right). \]  

(2.43)

### 2.2.3 Steady-state model

The steady-state model is a combination of reversible (open circuit voltage) and irreversible mechanisms (activation and concentration overvoltages). There is another irreversibility, sometimes described as the internal losses due to fuel crossover [70]. Although most electrochemical cells suffer from this loss, it will not be taken into account for the steady-state model used in this chapter, because it is not possible to measure the internal current at the output terminals of the fuel cell without knowing the internal resistance characteristics in detail. A description of the fuel crossover loss can be found in Appendix B.

The steady-state model gives the output voltage of the fuel cell \( v_{cell} \) as a function of the current density \( j \). From (2.17), (2.31), (2.28), and (2.43) follows

\[ v_{cell} = E_{rev} - \eta_{act} - \eta_{ohmic} - \eta_{lim}, \]  

(2.44)

and the relationship in (2.44) is graphically represented in Fig. 2.3. In the figure, the dominant regions of polarization are indicated.

### Steady-state model of a fuel cell stack

As mentioned in section 2.1, the fuel cell that is used in the experiments is a small stack of four membranes in series. With one cell represented as a voltage source, a series of \( N \) cells results in \( N \) times higher output voltage. Literature review indicates that the equations for a single cell may be used for a stack of cells in series [68, 110, 112, 113]. However, it is not proven that the parameters of the model may be scaled linearly with the number of cells stacked.

It can be assumed that the open circuit voltages (\( E_{ocv} \)) is the superpositions of the reversible cell voltages (\( E_{rev} \)) of the single cells. Therefore, the open circuit voltage term of the steady-state equation for a \( N \) cells stack is in accor-
2.2. Steady-state operation

Figure 2.3: Fuel cell voltage as function of the fuel cell current density.

dance with (2.17)

\[ E_{ocv} = NE_{rev} \]
\[ = NE_{rev}^0 + N \frac{RT}{nF} \ln \left( \frac{a_{H_2} \sqrt{a_{O_2}}}{a_{H_2O}} \right), \] (2.45)

\[ E_{rev}^0 = -\Delta G \frac{nF}{n}. \] (2.46)

The operating temperature of a PEM fuel cell ranges between 60°C and 80°C [70]. The temperature influences the Gibbs energy of the reaction, which means that the standard electrode potential of the fuel cell reaction at room temperature, \( E_{rev}^0 = 1.23 \) V, cannot be used. Therefore, the change in Gibbs energy for a temperature of 60°C, \( \Delta G = -228.2 \text{ kJ/mole} \) is used, resulting in a standard reversible cell voltage of \( E_{rev} = 1.18 \text{ V} \) [70, 113, 114]. Furthermore, the activity of water may be expected to approach unity \((a_{H_2O} = 1)\), because the standard chemical potential \( \mu_{H_2O}^0 \) in a single component liquid approaches the ideal state [6]. Also, unity can be applied for the activity of hydrogen \((a_{H_2} = 1)\), because the system will work on pure hydrogen supply. For the supply of oxygen, open air is used. Following (2.15), the activity of oxygen is \( a_{O_2} = 0.21 \). When the activities are incorporated in (2.45), the reversible cell voltage is \( E_{rev} = 1.17 \text{ V} \) and the stack reversible voltage is

\[ E_{ocv} = NE_{rev} = 4 \cdot 1.17 = 4.68 \text{ V}. \] (2.47)
Chapter 2. Characterization of PEM fuel cells

The stack model will be characterized by measuring voltages and current, not current densities. The active area of a single cell used in this research is approximately \( A_e = 60 \text{ cm}^2 \). Unfortunately, this value can not be exactly determined. Therefore, the stack model is dependent on the output fuel cell current \( I_{FC} \) instead of the current density. This conversion will only affect the irreversible parts of the model.

The activation overvoltage for the stack is based on (2.28). Because it is not known whether all parameters linearly scale with a series stack, the Tafel coefficient \( b \) is replaced with an activation coefficient \( A \) as is given in

\[
\eta_{act} = A \ln \left( \frac{I_{FC}}{I_0} \right),
\]

(2.48)

where the exchange current density is replaced by an exchange current \( I_0 \). The value of \( A \) will be determined by measurements.

The concentration polarization influences the value of the activation polarization [6, 20, 21, 70]. When the fuel cell works in mixed mode, the activation polarization and the concentration polarization can not simply be superimposed [6]. A practical solutions is to increase the value concentration coefficient \( (B) \) [20, 21, 70]. The equation for the concentration polarization for stacks takes the form

\[
\eta_{lim} = -B \ln \left( 1 - \frac{I_{FC}}{I_{lim}} \right),
\]

(2.49)

where \( I_{lim} \) is the limiting (diffusion) current.

The ohmic polarization from (2.31) is easily rewritten for the stack model. When the reaction resistance is purely ohmic, the expression for the ohmic polarization becomes

\[
\eta_{ohmic} = R_{int} I_{FC},
\]

(2.50)

where \( R_{int} \) represents the internal ohmic resistance of the fuel cell stack.

From (2.44) combined with (2.47), (2.48), (2.49) and (2.50) follows, according to the notations in section 2.2.2, a mixed mode (2.51) and a kinetic mode (2.52) stack model

\[
V_{FC} = E_{ocv} - A \ln \left( \frac{I_{FC}}{I_0} \right) - R_{int} I_{FC} + B \ln \left( 1 - \frac{I_{FC}}{I_{lim}} \right),
\]

(2.51)

\[
V_{FC} = E_{ocv} - A \ln \left( \frac{I_{FC}}{I_0} \right) - R_{int} I_{FC}.
\]

(2.52)
2.2.4 Steady-state characteristics

Measurements on the fuel cell can either be performed under galvanostatic or potentiostatic conditions. In the former case, the current is set and the electrode potential changes from its initial value to its new (steady-state) value. In the latter case, the value of the electrode potential is set and the current changes from its initial value to its new (steady-state) value. Steady-state measurement focuses on the new steady-state value of voltage and current after a change in conditions. The time between the initial values of voltage and current and their new values is called the transition time, and depends on various reactions in the fuel cell [6].

The construction of the test-setup as described in section 2.1 restricts the measurement method to galvanostatic conditions. If the polarization curve ($V_{FC}$ vs. $I_{FC}$) is monotonically falling or rising, the difference between galvanostatic and potentiostatic measurements has no influence on the result [6].

Steady-state measurements can be made discrete or continuously. In the latter case, the current variation must be executed so slowly that the change in current does not affect the system’s steady-state behavior. In the former case, the measurement can only be taken after the transition time has passed.

Finally, all the polarization characteristics are recorded at room temperature. The hydrogen pressure was set to 0.5 $P_0$, and the humidification of the membranes was performed by the humidification pulsing technique as is described in appendix C.

Steady state of individual cells and stack

To prove that the steady-state equation (2.44) may be used as a basis for the stack equation (2.51), the polarization curves of the individual cells are given in Fig. 2.4(a). These curves are fitted on the basis of the method of least squares on the steady-state equation for the individual cells

$$v_{cell} = E_{rev} - b \ln \left( \frac{I_{FC}}{i_0} \right) - r^{int} I_{FC} + b' \ln \left( 1 - \frac{I_{FC}}{i_{lim}} \right).$$

(2.53)

For $b$, the definition of (2.29) is taken, where the transfer coefficient $\alpha$ is set to $1/2$ [6, 70, 102], and the hydrogen reaction uses two electrons, giving the value of $n$. The results of the fit are presented in Table 2.1.

The total stack polarization curve, Fig. 2.4(b), shows the same regions of polarization as can be seen in the individual cells characteristics. Therefore,
Chapter 2. Characterization of PEM fuel cells

Figure 2.4: Polarization curves of (a) the single cells (○ = cell 1, ▽ = cell 2, □ = cell 3 and ◇ = cell 4) and (b) the stack.

The curve can be fitted to the mixed mode steady-state model of (2.51) where

\[
A = N \frac{RT}{\alpha F}, \quad (2.54)
\]

\[
B = N \frac{RT}{n F}. \quad (2.55)
\]

\( N = 4 \) is the number of cells in the stack, \( \alpha = 1/2 \) and \( n = 2 \) are equal to the values used in the equations of the individual cells.

However, the value for the transfer coefficient \( \alpha \) is not verified in practice and the voltage drop as a result of concentration polarization cannot be determined with the performed tests. Therefore, it is possible that the fuel cell

<table>
<thead>
<tr>
<th>cell</th>
<th>( E_{rev}[V] )</th>
<th>( b[V] )</th>
<th>( i_0[\mu A] )</th>
<th>( r_{int}[m\Omega] )</th>
<th>( b'[V] )</th>
<th>( i_{lim}[A] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.17</td>
<td>( \frac{RT}{\alpha F} = 0.0574 )</td>
<td>268</td>
<td>76.2</td>
<td>( -\frac{RT}{n F} = 0.0143 )</td>
<td>7.03</td>
</tr>
<tr>
<td>2</td>
<td>1.17</td>
<td>( \frac{RT}{\alpha F} )</td>
<td>210</td>
<td>47.6</td>
<td>( -\frac{RT}{n F} )</td>
<td>8.29</td>
</tr>
<tr>
<td>3</td>
<td>1.17</td>
<td>( \frac{RT}{\alpha F} )</td>
<td>300</td>
<td>42.9</td>
<td>( -\frac{RT}{n F} )</td>
<td>7.33</td>
</tr>
<tr>
<td>4</td>
<td>1.17</td>
<td>( \frac{RT}{\alpha F} )</td>
<td>460</td>
<td>51.5</td>
<td>( -\frac{RT}{n F} )</td>
<td>7.16</td>
</tr>
</tbody>
</table>
2.2. Steady-state operation

does not work in mixed mode, but in kinetic mode. To check that, the model of a mixed mode fuel cell stack is fitted with restrictions ($A \approx 0.230 V$ and $B \approx 57.4 mV$) and without restrictions on parameters $A$ and $B$, resulting in the fit results presented in Table 2.2.

If the transfer coefficient $\alpha$ is not fixed during the fitting procedure, then it follows from Table 2.2, that the concentration coefficient $B$ of the fuel cell stack approaches zero. Therefore, the model of the stack can be reduced to the kinetic mode representation (2.52). From the results in Table 2.2, the transfer coefficient for this type of fuel cell can be determined as

$$\alpha = \frac{RTN}{AF} = 0.552,$$

(2.56)

which is a value between the limits of zero and one, and close to the initial value chosen for it.

Influence of air flow

The test-setup from section 2.1 is equipped with a fixed air supply. However, to verify the influence of the air flow, two air supplies can be chosen, labeled as "high" and "low", where high means at least twice more air flow than low. Most of the characteristics presented in this chapter are recorded with the low air flow supply. Nevertheless, it is interesting to show the influence of air flow on the output voltage $V_{FC}$ and current $I_{FC}$.

In Fig. 2.5 the single stack voltage vs. current characteristic for different air flows is presented. It is clear from the figure that the influence of the air flow is significant. The high air flow characteristic (⋄-mark) delivers almost double the current of the low air flow characteristic (◦-mark).

Both characteristics are fitted on the kinetic mode steady-state equation (2.52). Because the high polarization part of the high air flow characteristic differed too much from the kinetic mode equation, Table 2.3 shows also the fitted parameters for the mixed mode steady-state equation (2.51).

<table>
<thead>
<tr>
<th>Model</th>
<th>$E_{ocv}[V]$</th>
<th>$A[V]$</th>
<th>$I_0[\mu A]$</th>
<th>$R_{int}[\Omega]$</th>
<th>$B[V]$</th>
<th>$I_{lim}[A]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Restricted</td>
<td>4.68 $N\frac{R_T}{\alpha F}$ 298 0.218 $-N\frac{R_T}{n F}$</td>
<td>7.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unrestricted</td>
<td>4.68 0.208 157 0.249 $4.44 \cdot 10^{-14}$</td>
<td>8.61</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The activation coefficient $A$ was not expected to change very much, because this coefficient is mainly dependent on the temperature. To reduce dispersion of the parameters, the activation coefficient is fixed to $A = 0.229 V$. The parameters that change significantly in the fits are the exchange current $I_0$, the limiting current $I_{lim}$ and the concentration coefficient $B$. Because the exchange current is directly dependent on the concentration of the reactants at the electrolyte surface (2.22), the largest change was expected in that coefficient. The concentration polarization part of the fuel cell is characterized by $B$ en $I_{lim}$. It was, of course, expected that more energy could be drawn from the fuel cell due to the higher air flow, resulting in a higher limiting current ($I_{lim}$). As a consequence of a higher maximum current, the slope of the V-I characteristic was also expected to be less steep, resulting in a lower internal resistance $R_{int}$.

The limiting current for the low air flow supply was found by the impossibility to measure above the found limiting current of $I_{lim} = 8.47 \, A$. The concentration coefficient was found to be close to the theoretical value of $B = 0.057 \, V$. However, there is too little information in the measured data to verify this value properly. The measured data of the high air flow supply do provide that information. The result is that the concentration coefficient for the high air flow supply is much higher than the theoretical value. This higher value was also reported in literature [70].
2.2. Steady-state operation

Figure 2.6: Steady-state characteristics measured with cathodic (◦) and anodic (⋄) scan direction.

**Direction dependency of the steady-state characteristic**

Normally, while measuring steady-state characteristics, increasing or decreasing the test current leads to the same results. However, in our case the shape of the curve is dependent on the scan direction, creating some sort of hysteresis curve. This means that during the measurements the properties of the electrode surface change, which produce differences in the kinetic parameters [6].

The figures shown up till now were recorded in the cathodic scan direction, that is, the direction in which the potential decreases in value. If the scan is changed to the anodic direction, the steady-state characteristic changes as shown in Fig 2.6.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>4.68</td>
<td>0.229</td>
<td>208</td>
<td>0.126</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High</td>
<td>4.68</td>
<td>0.229</td>
<td>1040</td>
<td>0.105</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>4.68</td>
<td>0.229</td>
<td>175</td>
<td>0.107</td>
<td>0.062</td>
<td>8.47</td>
</tr>
<tr>
<td>High</td>
<td>4.68</td>
<td>0.229</td>
<td>942</td>
<td>0.083</td>
<td>0.170</td>
<td>15.6</td>
</tr>
</tbody>
</table>
If both steady-state measurements are fitted on the kinetic mode equation (2.52), the results\(^3\) are

\[
V_{FC,\text{cathodic}} = E_{ocv} - 0.223 \ln \left( \frac{I_{FC}}{187 \cdot 10^{-6}} \right) - 0.138 I_{FC}, \quad (2.57)
\]

\[
V_{FC,\text{anodic}} = E_{ocv} - 0.170 \ln \left( \frac{I_{FC}}{27.4 \cdot 10^{-6}} \right) - 0.162 I_{FC}. \quad (2.58)
\]

The difference in voltage between the anodic and cathodic scan direction is at most 7\%, and can be decreased by extending the transition time of the measurement. This phenomenon was observed earlier while measuring the complete SR-12 fuel cell system [110].

The differences found in the fitted parameters in (2.57) with respect to the values from Tables 2.2 and 2.3 are caused by using different stacks for the different measurements.

**Quasi steady-state characteristics**

A fuel cell is an electricity generation system which is normally used in steady-state operation. However, not all applications require a fixed operation mode. One can imagine that the load of a fuel cell is switched cyclically from one state to another and back within a certain time interval. The state in which the fuel cell operates just before it is forced to another load condition can be seen as a quasi or a relative steady-state operation.

The quasi steady-state characteristics for different transition times are presented in Fig. 2.7. It is clear from this figure that the quasi steady-state parameters in (2.52) change as a function of transition time.

The fitting results for the curves to the kinetic mode model (2.52) are shown in Table 2.4. The trend that can be seen here is that the internal resistance is decreasing with increasing transition time duration, while the exchange current and the activation coefficient are increasing slightly.

If the transitory processes associated with the changes in current and potential have ended, the fuel cell does not have to be in steady state, because very slow changes within the fuel cell can prohibit the fuel cell from reaching that point. This effect is sometimes described in literature as electrochemical drift [92]. Therefore, to use the steady-state model, it is necessary to know the time-base on which variations in current or voltage can be expected.

\(^3\)The results presented here cannot be compared to the earlier results, because a different cartridge was used. More on the used cartridges can be found in Table 2.5.
Aging effect

The effect of using PEM fuel cells for long time-spans is not studied well. Literature indicates that aging effects can be destructive [14, 61] but also sometimes partly regenerable [61]. Therefore, the measurements for this research work are done with one cartridge, #0377, over three years of intensive use. Afterwards, many measurements were verified with two “fresh” cartridge stacks, #0183 and #1472.

To compare the aged cartridge with the unaged cartridges, Table 2.5 gives the different parameters for the kinetic mode steady-state equation (2.52). The figure numbers of the steady-state measurements on a specific cartridge stack are also in the table.

<table>
<thead>
<tr>
<th>$\tau$ (s)</th>
<th>$E_{ocv}$ [V]</th>
<th>$A$ [V]</th>
<th>$I_0$ [$\mu$A]</th>
<th>$R_{int}$ [Ω]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.68</td>
<td>0.190</td>
<td>92</td>
<td>0.158</td>
</tr>
<tr>
<td>60</td>
<td>4.68</td>
<td>0.194</td>
<td>95</td>
<td>0.153</td>
</tr>
<tr>
<td>180</td>
<td>4.68</td>
<td>0.197</td>
<td>96</td>
<td>0.149</td>
</tr>
<tr>
<td>300</td>
<td>4.68</td>
<td>0.200</td>
<td>103</td>
<td>0.146</td>
</tr>
</tbody>
</table>
From Table 2.5, it can be concluded that the activation coefficient is not changing significantly due to aging. The internal resistance, however, increases dramatically.

When the results of aging are plotted graphically, Fig. 2.8 shows the result. It is clear that the new stacks are producing substantially higher output powers than the aged stack.

### 2.3 Dynamics of fuel cells

The dynamics of a fuel cell are heavily dependent on a phenomenon called the electric double layer. The electric double layer is an interfacial region near
the boundary between two different phases of a substance, in which physical properties vary markedly (in contrast with those in the bulk phases). For electrically conducting media, charge distribution occurs in this interfacial region, and it may be approximated as two differently charged parallel sheets. The name “electric double layer” is retained even if the interfacial region is more complex. Double layers arise from an excess of charge in the interfacial region. This charge may be electrons, ions, or oriented dipoles. Because of the charge distribution at the interfaces, the electric double layer is sometimes called the charge double layer [56].

To explain the charge double layer effect, this section will discuss the interfacial potentials between two metals and between metal electrolyte contacts. Adsorption (or chemisorption) effects can influence the dynamics of fuel cells as well.

Finally, temperature variations of the membrane do also influence the dynamics of the stack. However, because this subject is not investigated in this work, it will not be included in this chapter. A well described model of PEM fuel cells on temperature variations can be found in [3, 68].

### 2.3.1 Electric double layer

#### Galvani potentials between metal-metal interfaces

Two metals which are insulated from each other most likely have a certain potential difference between them. The potential is caused by charges accidentally created on the surface of the metal. If the two pieces of metal are brought in close contact with each other a charge redistribution will occur. When two identical metals are used the potential difference will completely disappear, but when the metals differ from each other a defined potential difference is set up over the interface as

\[
\varphi_G^{(2,1)} = \psi^{(2)} - \psi^{(1)}.
\]  

(2.59)

In (2.59), \( \varphi_G^{(2,1)} \) is called the Galvani potential, which is a potential difference between an arbitrary point in metal one where the inner potential is presented as \( \psi^{(1)} \), and an arbitrary point in metal two with inner potential \( \psi^{(2)} \) [6].

Galvani potentials are a result of chemical forces on the electrons in a surface layer of a metal. The chemical forces on the electrons cause the electrons to migrate from one metal to the other, creating an electric field in the interfacial region which is called the electric double layer. The electric field will eventually stop the migration of electrons because it produces an electrical force on
the electrons opposing the chemical force [6].

The chemical potential difference ($\Delta \mu_j$) for particles in two media can be defined as

$$\Delta \mu_j = \frac{w_{ch}}{n_j},$$  \hspace{2cm} (2.60)

where $w_{ch}$ is the work done by the chemical forces in transferring $n_j$ moles of particles involved.

The electrochemical potential $\mu_j$, which is the total potential energy of the charged particles, is the sum of the chemical and the electrostatic components, which can be expressed as

$$\mu_j = \mu_j + z_j F \psi,$$  \hspace{2cm} (2.61)

where $z_j$ is the charge number of (in this case) the electrons involved and $F$ is Faraday’s constant. When the interface has reached steady state, which means that the electrical work $w_e$ is equal to the chemical work $w_{ch}$, the electrochemical potentials of metal one and two are $\mu_j^{(1)} = \mu_j^{(2)}$, and the Galvani potential follows from (2.61) as being

$$\varphi_G = \Delta \psi = -\frac{\Delta \mu_j}{z_j F}.$$  \hspace{2cm} (2.62)

The equilibrium of the Galvani potential only depends on the bulk properties of the two materials and not on the state of the interface [6].

**Galvani potentials between metal-electrolyte interfaces**

Galvani potentials not only exist between metals, but also between metal and electrolyte materials. Therefore, (2.59) can be rewritten as

$$\varphi_G^{(M,E)} = \psi^{(M)} - \psi^{(E)}.$$  \hspace{2cm} (2.63)

which gives the relationship between the inner potential of the electrode ($M$) and the electrolyte ($E$).

In contrast to the Galvani potential between two metals, the charge transfer between an electrode and electrolyte can only occur with an electrode reaction. This reaction may involve other species, which means that the equilibrium equation $\mu_j^{(1)} = \mu_j^{(2)}$ is written as an equilibrium of the overall reaction involving all reaction components. These components will also appear in (2.62) [6].
Because other species may be involved in the electrode reaction setting up the Galvani potential, different equilibria can be established at an interface. This will result in different electrode potentials [6].

The fact that Galvani potentials exist between two different conducting materials results in the formation of an electric double layer at the interface. A double layer can be seen as two parallel sheets of opposite charge with a very small distance in between. This distance is in the order of molecules, resulting in very large capacitances [6, 70, 102].

It is impossible to measure Galvani potentials, because if measurement equipment is attached to a cell, at least one additional Galvani potential is created (metal-metal contact). Additionally, methods for measuring charges are distorting the chemical forces on the particles in the material responsible for Galvani potentials, changing the equilibrium of the Galvani potential [6].

### 2.3.2 Adsorption (chemisorption) effects

Adsorption is, like the electric double layer, a surface effect and can be defined as a process in which liquids, gases, or suspended matter (adsorbate) adhere to a particular surface (adsorbent). The result is the formation of a liquid or gas film on that surface. One adsorption effect is the adsorption of ions from solutions onto electrode surfaces. This effect can be divided into two types, namely electrostatic adsorption, which is caused by the charge on the metal surface, and specific adsorption, that is adsorption due to chemical forces. The latter type of adsorption is also called chemisorption and is a much stronger bond to the surface than the electrostatic bond (Van Der Waals forces) [6].

In case of monolayer adsorption, that is, all adsorbed particles directly interact to the adsorbent surface, the degree of the surface coverage can be expressed as

\[
\theta = \frac{A_j}{A_j^0},
\]

where \( A_j^0 \) is the limiting adsorption value, which depends on the surface area \( S_j \) used for one particle, and \( A_j \) is the amount of species of the adsorbate \( j \) per surface area. It is clear from (2.64) that \( \theta \) lays between zero and one.

Adsorption in an interfacial area will always lead to a change in Gibbs free energy, in the enthalpy of the system, and heat. Adsorption energy is the sum of all energy effects associated with the reorganization of the system by means of formation and breaking of adsorbent-adsorbate bonds, dehydration and other effects [6].
Adsorption due to electrostatic forces are weak bonds. These Van der Waals forces decrease slowly with increasing distance, which makes this type of adsorption suitable for the multi-layer adsorption effect. However, chemical forces on adsorbate particles are strong, up to 20 times stronger than electrostatic forces. Hence, chemisorption is mostly mono-layer adsorption, and is often resulting in chemical changes such as adsorbate dissociation (breaking or splitting a molecule). For instance, the chemisorption of hydrogen to platinum can be presented as

\[ 2Pt + H_2 \rightleftharpoons 2Pt - H_{ads}. \]  

(2.65)

The dash in \( Pt - H_{ads} \) does not represent a minus-sign, but a chemical bond.

If an adsorption equilibrium exists between adsorbed particles on the adsorbent surface and the particles in the other phase (e.g. the electrolyte), and if the particles in the electrolyte are removed and the adsorbed particles leave the adsorbent surface to enter the electrolyte, then the adsorption effect is reversible. If, on the other hand, after removing the particles from the electrolyte, the adsorbates do not leave the adsorbent surface, then the process is irreversible. For the irreversible case, the adsorbed particles can only be removed from the surface by means of a chemical reaction, or by displacement processes during the adsorption of other substances. Adsorptive displacement is the phenomenon that positive adsorption of one component is always attended by negative adsorption, or desorption, of another component [6].

### 2.3.3 Step response characteristics

In this section, the dynamics of fuel cells are expressed in electrical circuits. This is done by modeling the fuel cell as a Thévenin source⁴. Therefore a voltage source, \( E_{FC} \), is introduced with the following properties

\[
E_{FC} = E_{ocv} - A \ln \left( \frac{I_{FC}}{I_0} \right),
\]

(2.66)

\[
E_{FC} = E_{ocv} - A \ln \left( \frac{I_{FC}}{I_0} \right) + B \ln \left( 1 - \frac{I_{FC}}{I_{lim}} \right).
\]

(2.67)

This voltage source includes the non-linearities of the steady-state characteristic for kinetic mode (2.66) based on (2.52) or the mixed mode (2.67) based on (2.51).

⁴A Thévenin source is an ideal voltage source with an impedance in series.
Interrupted current method

This measurement method for determining large signal dynamics of the fuel cell is very popular in fuel cell research [32, 46, 53, 68, 95, 113] because the measurement equipment can be kept very simple [70]. By connecting the fuel cell to an (adjustable) resistive load via a switch and monitoring the voltage with an oscilloscope, the interrupted current measurement can take place. When the fuel cell delivers the right amount of current, the switch is turned off and the voltage response of the fuel cell is seen on the oscilloscope. From the measurement data a simple, electric equivalent circuit can be determined, as is shown in Fig. 2.9.

One can see from Fig. 2.9 that immediately after the current interruption, the voltage of the fuel cell \( V_{FC} \) will increase with a value of

\[
V_{\infty} = R_{\infty} \Delta I_{\text{step}},
\]

(2.68) \[
\Delta I_{\text{step}} = I_{FC}(t < 0) - I_{FC}(t \geq 0).
\]

(2.69)

In case of the interrupted current method, the fuel cell current after \( t = 0 \) is \( I_{FC}(t \geq 0) = 0 \). After the immediate voltage step across \( R_{\infty} \) the fuel cell voltage will exponentially increase across the parallel circuit of \( R_R \) and \( C_R \) with time constant \( \tau_R \) to its final value \( V_{FC} = E_{FC} \). This can be described by

\[
V_R(t) = V_R^0 e^{-\frac{1}{\tau_R}} t = \frac{1}{\tau_R} t,
\]

(2.70) \[
V_R^0 = R_R I_{FC}(t < 0).
\]

(2.71)

Besides the advantage of the very simple measurement equipment, there is also a big disadvantage to the interrupted current method. Because the step performed on the system is always monitored in one direction, that is, the current is always interrupted, one can not determine if this behavior is equal to
Step characteristics

The large signal behavior of the fuel cell can be examined with the step response measurements. For the experiments, the current from cartridge 0377 was stepped from a low value (1 A) to a high value (5 A), Fig. 2.10(a), and back, Fig. 2.10(b). It is clear from Fig. 2.10 that the step change in voltage lasts less than a second. The voltage change shows the predicted behavior modeled by Fig. 2.9. However, when the characteristics are fitted on the first order model, the value of the capacitor \( C_R \) for the low to the high current step is not equal to the capacitor value for the high to the low current step, which is not according to the theory [75]. The results of the fit are shown in Table 2.6.

From the values of Table 2.6, it is clear that the simple first order equivalent circuit presented in Fig. 2.9 is not sufficient for modeling the step response of the fuel cell. Although the step current \( \Delta I_{\text{step}} = 4 \) for both step directions is constant, which is also true for the bulk resistor \( R_\infty \), the time constant of the
model \( (\tau_R) \) differs significantly. Because the step direction is reversed while the current flows in the same direction, it is not feasible to describe this behavior with the presented equivalent circuit model.

### Settling response after the step

Electrochemical phenomena responsible for the transient behavior of the fuel cell are “relatively” fast in contrast to, for instance, temperature changes [3]. Therefore, it would be useful to show the long-term response of the fuel cell after a step has occurred. Figure 2.11 shows the same steps as in Fig. 2.10. However, the monitored duration of the step is 15 seconds.

From Fig. 2.11(b) it can be seen that the voltage first reaches a peak value and then slowly settles to its final “steady-state” value. Amphlett et al. mention that the temperature settlement of the tested fuel cell is in the order of

<table>
<thead>
<tr>
<th>Step</th>
<th>( R_\infty ) (Ω)</th>
<th>( C_R ) (F)</th>
<th>( R_R ) (mΩ)</th>
<th>( \tau_R ) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 A → 5 A</td>
<td>0.299</td>
<td>0.357</td>
<td>92.8</td>
<td>33.2</td>
</tr>
<tr>
<td>5 A → 1 A</td>
<td>0.296</td>
<td>0.687</td>
<td>103</td>
<td>70.5</td>
</tr>
</tbody>
</table>
minutes, not seconds [3], which means that this phenomenon should not be caused by temperature variations. However, the fuel cell system described in [3] was much larger (in power, volume and weight) than the cartridge used in this work. Therefore, this exponential settlement behavior could be related to temperature changes in the cell itself. Moreover, the "quasi" steady-state measurements presented in Fig. 2.7 show no large changes over several minutes, which could indicate that the cartridge heats up quickly.

2.3.4 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS), or in short impedance spectroscopy (IS) is a powerful method to characterize electrical and electrochemical properties of materials and interfaces with electrical conducting electrodes. Electrochemical impedance spectroscopy can be used to study the dynamics of mobile charge carriers in bulk material or at interfacial regions of solids or liquid materials [75].

In order to study the electrochemical behavior of electrode, electrolyte or a combination of both, electrical measurements are performed by applying an electrical stimulus to the electrodes and observing the response. For example, a known current is forced to the terminals of a fuel cell and the resulting voltage is monitored. From this data the impedance of the fuel cell can be calculated. If this is done for multiple frequencies, an electrochemical impedance spectrum is found, containing information on the electrochemical properties of the bulk materials and the electrode reactions [75].

Types of information that can be found from the spectrum of impedances are the transport of electrons through electrical conductors, the transport of electrons over the electrode-electrolyte interface, the flow of atoms (charged or uncharged) through the membrane, and the flow rate of charged particles through the membrane or across the electrode-electrolyte interfaces. For a wide range of materials, impedance spectroscopy can be used for evaluating their properties. This ranges from materials with ionic, semiconducting, mixed ionic-electronic properties and dielectrical materials [19, 75, 119].

There are three different types of electrical stimuli used in electrochemical impedance spectroscopy. The first method is already discussed in the previous section, i.e. a transient measurement of a step in voltage or current. The ratio

$$Z_{ind} = \frac{\Delta V_{step}}{i(t)}, \quad (2.72)$$

is called the indicial impedance, or the time-varying resistance, and represents
the impedance change of the voltage step at the electrochemical interface. Although this value is easily obtained, it does not represent the impedance which impedance spectroscopy refers to. When $Z_{ind}$ is transferred to the frequency domain it becomes a frequency dependent impedance. The Fourier transformation is only valid when $\Delta V_{step}$ is sufficiently small, so that the system response can be assumed linear[75].

The second measurement method applies a time-varying signal $v_{noise}(t)$ to the object. The signal is composed of “white” noise, and the resulting $i(t)$ is measured. By transforming the signals to the frequency domain using a Fourier transform, one obtains the frequency information of the impedance [75].

The last measurement method, and the most commonly used one, is measuring the impedance directly in the frequency domain by applying a known signal $v(t)$ of a single amplitude and frequency to the electrodes, and measuring the phase shift and amplitude of $i(t)$ at that specific frequency [19, 75, 119].

All voltages used up to now may be replaced with currents and vice versa. That is, if a voltage stimulus is used, it may also be a current. In the latter case the time-varying voltage is monitored. Furthermore, in this work the name (electrochemical) impedance spectroscopy is used for the last method. If the first method is used, then it is referred to as step response.

For non-linear systems, such as most electrode-electrolyte material systems, the results of impedance spectroscopy are only meaningful when the data is obtained from signals with amplitudes not exceeding the electrically linear overall electrode response [75].

The time-varying voltage and current are defined as

$$v(t) = V \sin(\omega t),$$  \hspace{1cm} (2.73)
$$i(t) = I \sin(\omega t + \theta),$$  \hspace{1cm} (2.74)

and thus the real ($Z'$) and imaginary ($Z''$) part of the impedance will be

$$Re(Z) \equiv Z' = |Z| \cos(\theta),$$  \hspace{1cm} (2.75)
$$Im(Z) \equiv Z'' = |Z| \sin(\theta).$$  \hspace{1cm} (2.76)

Figure 2.12(a) shows how a single impedance measurement point is presented graphically. The imaginary axis of the complex impedance plot is reversed from what is common in electrical engineering, because most electrochemical systems show capacitive behavior. Figure 2.12(b) shows the output when a complete spectrum of frequencies is plotted graphically. In this plot, the lowest
Chapter 2. Characterization of PEM fuel cells

Figure 2.12: Impedance data (a) for a single frequency and (b) for a spectrum of frequencies.

frequency is located closest to $R_0$, while the highest frequency is located near zero.

**Equivalent circuit elements**

To help interpreting experimental impedance data, as for instance shown in Fig. 2.12, it is possible to introduce an equivalent circuit made from ideal electrical components like resistors, capacitors and inductors. A resistor in such an equivalent circuit represents a conductive path, which can be related to the bulk conductivity of the material, but also to a chemical electrode reaction. Capacitances and inductances are usually associated with polarization regions and with specific adsorption processes at electrodes [75].

The interpretation of Fig. 2.12(b) to an equivalent circuit model starts with the small semi-circle between $Z' = 0$ and $Z' = R_\infty$. The frequencies corresponding to this semi-circle are high, which means that the responsible time constant is small. The second semi-circle, $R_\infty < Z' < R_0$ is recorded at much lower frequencies, indicating a larger time constant. Both semi-circles have negative imaginary impedances, which correspond to capacitative behavior. A possible equivalent circuit model for this complex impedance can be found in Fig. 2.13.
Every electrode material system contains a geometric capacitance $C_\infty$ and a bulk resistance $R_\infty$ in parallel to it. These elements represent the basic material, which is characterized with a dielectric relaxation time $\tau_D = R_\infty C_\infty$. The time constant $\tau_D$ is usually very small, and can only be measured at very high frequencies, which makes it a very difficult to measure this parameter [75]. That is, to measure the small semi-circle, the angular frequency $\omega$ must fulfill $\omega\tau_D \gg 1$. The top of the semi-circle can be found at a frequency equal to $\omega\tau_D = 1$ [75]. Therefore, the geometric capacitor in Fig. 2.13 is presented as a dashed line, because it is unlikely that the effect of this capacitance is measurable at all.

The second semi-circle, situated between $R_\infty$ and $R_0$, is often identified to be a heterogeneous electrode reaction. The semi-circle is characterized with a reaction resistance $R_1$ and a diffusion double layer capacitance $C_1$ leading to the reaction relaxation time $\tau_R = C_1 R_1$, representing the polarization region near the electrode. In the case that the dielectric relaxation time and the reaction relaxation time are well separated, $\tau_D \ll \tau_R$, the two semi-circles are also well separated, as is shown in Fig. 2.12(b) [75].

With respect to the analysis of the second semi-circle, it is easy to see that the reaction resistance $R_1$ of Fig. 2.13 can be defined as

$$ R_1 = R_0 - R_\infty, \quad (2.77) $$

where the values of $R_\infty$ and $R_0$ can be read in Fig. 2.12(b) as the points where the large semi-circle hits the real impedance axis $Z'$. The impedance arc $Z_{arc}$ is found to be

$$ Z_{arc} = R_\infty + \frac{R_1}{1 + j\omega\tau_R}. \quad (2.78) $$

From (2.78), one can conclude that the maximum imaginary value is reached
when
\[ \omega_n = \omega \tau_R = 1, \] (2.79)
where \( \omega_n \) is the normalized frequency. The value of the diffusion double layer capacitance \( C_1 \) follows from the values found in Fig. 2.12(b) and (2.79) [75].

The analysis of a single impedance arc becomes more complicated in case the center of the semi-circle is not situated at \( Z'' = 0 \), but shifted over the imaginary axis. In this case, the capacitance does not have a phase shift of 90°. The capacitance is then replaced by a “constant phase element”. The constant phase elements CPE are modeled by
\[ CPE = A_{cpe} (j \omega)^{\psi_{zc}} = (j \omega \tau_R)^{\psi_{zc}}, \] (2.80)
where \( A_{cpe} \) is the value of the admittance of the constant phase element and \( \psi_{zc} \) is the fractional exponent which is bounded by \( 0 \ll \psi_{zc} \ll 1 \). From (2.80) the complex arc impedance (2.78) can be rewritten to
\[ Z_{arc} = R_\infty + \frac{R_1}{1 + (j \omega \tau_R)^{\psi_{zc}}}. \] (2.81)

In the limiting case that \( \psi_{zc} = 1 \), a true capacitance is found [75, 91].

A very special case of a constant phase element is the so called Warburg impedance \( W \). The Warburg element represents a diffusion contribution to the impedance, and can be expressed as
\[ W = \sigma_w \omega^{-\frac{1}{2}} - j \sigma_w \omega^{-\frac{1}{2}}, \] (2.82)
where \( \sigma_w \) is the Warburg constant, which can be expressed as
\[ \sigma_w = \frac{RT}{n^2 F^2 \sqrt{2}} \left[ \frac{1}{c_{red} \sqrt{D_{red}}} + \frac{1}{c_{ox} \sqrt{D_{ox}}} \right], \] (2.83)
where \( n \) is the number of electrons transferred, \( F \) is Faraday’s constant, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( c_{ox} \) and \( c_{red} \) are the bulk concentration of the oxidized resp. reduced species, and \( D_{ox} \) and \( D_{red} \) are the diffusion coefficients of the oxidized resp. reduced species [10, 75].

Electrochemical impedance data can be expressed in an equivalent circuit model. Macdonald [75] presents three different circuit models that can be used to fit the data to, as shown in Fig. 2.14. These circuits are interchangeable when their elements are properly related. The different models have different advantages related to the order of the system, the simplicity of the model related to
2.3. Dynamics of fuel cells

Figure 2.14: Three different circuits with possibly identical impedances; (a) ladder circuit, (b) Voigt circuit, and (c) Maxwell circuit.

Parameter change or the knowledge of physical phenomena and the prediction of them. However, with increasing computational power of a PC, the difficulty in fitting higher order models to obtained data does not make a difference in the choice of a model anymore.

It was decided to use the ladder network in the analysis of the electrochemical impedance spectroscopy data, because the properties of this model allow for easy expanding. More on the theory of the ladder network can be found in Appendix D.

EIS characteristics

Because the fuel cell current changes more rapidly than the fuel cell voltage, the fuel cell current $i_{FC}(t)$ is used as the stimulus and the voltage $v_{FC}(V)$ is measured. The measurement setup in Fig. 2.2 is only capable of sinking current, not to excite the fuel cell. Therefore, it is necessary to let the stack deliver a certain amount of DC current (it is not possible to measure the impedance at $I_{DC} = 0$), and superimpose a small sinusoidal signal on it

$$i_{FC}(t) = I_{DC} + I_{AC} \sin(\omega t). \quad (2.84)$$

The resulting voltage has the general form of

$$v_{FC}(t) = V_{DC} + V_{AC} \sin(\omega t + \theta). \quad (2.85)$$

The DC values of the voltage and the current are related to the steady-state resistance value of the linear regulator and are not of interest to the impedance spectroscopy results. The interesting impedance, that is the impedance of the
fuel cell, can be calculated to be

\[
Z(j\omega) = \frac{V_{AC}}{I_{AC}} e^{j\theta},
\]

\[
= |Z|e^{j\theta},
\]

\[
= Z' + jZ''.
\]  \hspace{1cm} (2.86)

In (2.86), the real part \(Z'\) and the imaginary part \(Z''\) of the complex impedance are

\[
Z' = |Z|\cos(\theta),
\]  \hspace{1cm} (2.87)

\[
Z'' = |Z|\sin(\theta).
\]  \hspace{1cm} (2.88)

The amplitude of the stimulus has to be so small that the system responds linearly. Therefore, the amplitude of the current is set to \(I_{AC} = 0.1A\). The response voltage is then \(0.01 \leq V_{AC} \leq 0.06V\), which is within the linear response of the fuel cell.

**Measurements results**

The results obtained from the electrochemical impedance spectroscopy are plotted in Fig. 2.15. The fuel cell stack used for the measurement is the “aged” 0377 stack. Impedance data is acquired for different DC current settings \((I_{DC})\) from (2.84). The measurement of the 1 A DC set point, Fig. 2.15(a), ranges in frequency from 10 mHz to 22 Hz. For the other measurements the highest frequency is 45 Hz.

The measurements are all performed from low to high frequencies. The data set is at least ten times acquired, and the frequency information is found by using Fast Fourier Transform. The window of the FFT is rectangular and exactly as wide as the base harmonic of the signal. The signals monitored are pre-filtered with anti-aliasing filters with a cut-off frequency of approximately 1 kHz. The sampling frequency of the DSP is 10 kHz. The number of evaluated points of the FFT is variable, and matches the Nyquist rate [31, 45], that is, all higher order harmonics are analyzed up to \(f = f_s/2\).

The gray lines shown in Fig. 2.15 are the error bands of the fit. All measurements lie within this band.
Figure 2.15: Results of EIS measurements (frequency values in the figures are in Hertz) for different DC currents.
Figure 2.16: Equivalent second order impedance of the fuel cell stack. This impedance is placed in series with the non-linear voltage source $E_{FC}$.

2.3.5 Equivalent circuit model

The results of the electrochemical impedance spectroscopy, Fig. 2.15, show a large capacitive semi-circle between 200 mHz and the maximum frequency measured. Furthermore, the low frequencies show inductive behavior. This inductive behavior cannot be related to wiring of the fuel cell, because wires get inductive at high frequencies. Therefore, the behavior must be an electro-chemical effect, most likely adsorption [7, 8, 51, 57, 80, 89].

Second order model

The results can be fitted to an equivalent circuit model. The electrochemical impedance plots of Fig. 2.15 show a large capacitive semi-circle and a small inductive semi-circle in the low frequency range. The first choice of fitting circuit is a second order circuit as is shown in Fig. 2.16. In this figure, the variables are indicated with a superscript *, in order to distinguish them as "second order variables". The results of a least squares fit of the data to the model are given in Table 2.7.

From Table 2.7 it can be seen that the bulk resistance $R_{\infty}^*$ of the 1 A and 3 A

<table>
<thead>
<tr>
<th>$I_{DC}$[A]</th>
<th>$R_{\infty}^*$[Ω]</th>
<th>$C_{DL}^*$[F]</th>
<th>$R_{DL}^*$[mΩ]</th>
<th>$L_A^*$[mH]</th>
<th>$R_A^*$[mΩ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.292</td>
<td>0.283</td>
<td>275</td>
<td>48.6</td>
<td>23.2</td>
</tr>
<tr>
<td>2</td>
<td>0.274</td>
<td>0.334</td>
<td>157</td>
<td>48.7</td>
<td>19.2</td>
</tr>
<tr>
<td>3</td>
<td>0.293</td>
<td>0.319</td>
<td>123</td>
<td>42.3</td>
<td>13.5</td>
</tr>
<tr>
<td>4</td>
<td>0.262</td>
<td>0.323</td>
<td>99.4</td>
<td>42.7</td>
<td>9.8</td>
</tr>
<tr>
<td>5</td>
<td>0.270</td>
<td>0.323</td>
<td>83.6</td>
<td>42.9</td>
<td>8.6</td>
</tr>
<tr>
<td>6</td>
<td>0.270</td>
<td>0.337</td>
<td>76.5</td>
<td>48.1</td>
<td>6.0</td>
</tr>
</tbody>
</table>
measurement is shifted 0.02Ω along the $Z'$ axis in contrast to the other measured values. Furthermore, the double layer capacitor $C_{DL}^*$ and the adsorption inductor $L_{A}^*$ are more or less constant, while the double layer and adsorption resistor $R_{DL}^*$ resp. $R_{A}^*$ are decreasing in value.

**Third order model**

Although the second order model shows good fitting results, the model may be not sophisticated enough to represent the fuel cell impedance. Moreover, it is known that the double layer effect is an effect related to an electrode-electrolyte interface [75], and the fuel cell is constructed with two of those interfaces. Therefore, the obtained data of the impedance measurements are also fitted on a third order equivalent circuit model, as is shown in Fig. 2.17.

The results of a least squares fit to the third order impedance network are presented in Table 2.8. The shift of the bulk resistor $R_{\infty}$ of the 1 A and 3 A measurement is consistent with the shift seen in the second order fit of Table 2.7, as was to be expected. The first double layer capacitor $C_{DL}$ and the adsorption inductor $L_{A}$ are relatively constant and the double layer resistors $R_{DL}$ and $R_{R}$ and the adsorption resistor $R_{A}$ are decreasing with increasing DC currents $I_{DC}$. However, the second double layer capacitor $C_{R}$ varies more in value than the other parameters.

When the error between the identified impedance models (second and third order) and the measured impedance is studied, the error of the second order model grows with increasing frequency, while the error of the third order model stays limited. This is graphically presented in Fig. 2.18.

The figure shows the absolute error of the simulated impedances with respect to the impedance data for two DC current settings, in order to show the difference between a low DC current set point ($I_{DC} = 1A$) and a high DC current set point ($I_{DC} = 5A$). The gray line shows the simulated impedance
Chapter 2. Characterization of PEM fuel cells

data of the second order model with respect to the electrochemical impedance data. It can be seen that for a low DC current set point the error increases with increasing frequency, while for a high DC current set point, this effect is negligible. For the third order model, the black line in Fig. 2.18, the absolute error is small for the low DC current set point and for the high DC current set point.

From the fitting results of the third order model, the value of the second double layer capacitor $C_R$ bounces around a certain constant value. This parameter has less influence in the higher current region than in the lower current region, because the second double layer resistor ($R_{DL}$), which is responsible for the amplitude of the semi-circle belonging to $\tau_{R}$, has a much smaller value at high DC currents than at low DC currents.

### 2.4 Conclusions

In this chapter the electrochemical theory of a single fuel cell is explained. Measurements have confirmed the predicted steady-state behavior of one cell. Furthermore, measurements have proven that the theory for a single cell may be used for a stack of cells in series.

It is also confirmed with measurements that the air flow, that is the oxygen supply for the fuel cell, has a major influence on the performance of the stack. This is seen in higher output powers, and a higher limiting current.

The direction of measuring the steady-state polarization of a stack influences the output voltage of a stack. This effect can be eliminated by adjusting the transition time of the steady-state measurement. There is no real steady state of a fuel cell, because it is dependent on the transition time. Therefore, it is better to use the term “quasi steady state” instead. The quasi steady state is

<table>
<thead>
<tr>
<th>$I_{DC}$ [A]</th>
<th>$R_{\infty}$ [Ω]</th>
<th>$C_{DL}$ [F]</th>
<th>$R_{DL}$ [mΩ]</th>
<th>$C_R$ [F]</th>
<th>$R_R$ [mΩ]</th>
<th>$L_A$ [mH]</th>
<th>$R_A$ [mΩ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.282</td>
<td>0.220</td>
<td>200</td>
<td>0.441</td>
<td>94.4</td>
<td>36.1</td>
<td>19.1</td>
</tr>
<tr>
<td>2</td>
<td>0.270</td>
<td>0.259</td>
<td>107</td>
<td>0.364</td>
<td>54.9</td>
<td>45.2</td>
<td>20.4</td>
</tr>
<tr>
<td>3</td>
<td>0.290</td>
<td>0.263</td>
<td>107</td>
<td>0.745</td>
<td>18.1</td>
<td>37.3</td>
<td>16.6</td>
</tr>
<tr>
<td>4</td>
<td>0.257</td>
<td>0.243</td>
<td>82.3</td>
<td>0.692</td>
<td>21.6</td>
<td>35.3</td>
<td>12.3</td>
</tr>
<tr>
<td>5</td>
<td>0.266</td>
<td>0.239</td>
<td>65.7</td>
<td>0.566</td>
<td>18.7</td>
<td>38.5</td>
<td>9.4</td>
</tr>
<tr>
<td>6</td>
<td>0.265</td>
<td>0.226</td>
<td>64.5</td>
<td>0.995</td>
<td>18.2</td>
<td>48.4</td>
<td>8.2</td>
</tr>
</tbody>
</table>
Figure 2.18: The gray line represents the absolute error in impedance between the identified second order impedance and the measured EIS data, the black line shows the absolute error in impedance between the identified third order impedance and the EIS data.

...dependent on the transition time.

Aging has a significant influence on the performance of the fuel cell. Measurements show that the internal resistance of an aged stack is almost twice as high as the internal resistance of an unaged stack.

Two measurement methods for identifying dynamics of the fuel cell are introduced. The step-response measurement gives an indication of the large-signal behavior of the stack, while electrochemical impedance spectroscopy gives the small-signal behavior.

Electrochemical impedance spectroscopy gives a lot of insight in the impedance of the fuel cell. The data recorded with this measurement technique can be interpreted into an equivalent electrical circuit consisting of resistors, capacitors and inductor. Measurement results show that a third order equivalent circuit represents the impedance of a fuel cell stack better than a second order impedance model.

The different ways of measuring a fuel cell described in this chapter, results in three different models for a fuel cell. That is, a steady-state model, a large-signal model, and a small-signal model. For simulations, it would be convenient to use just one model capable of simulating all three modes. In Chapter
3, the introduced measurement methods are used to create such a model.
Chapter 3
Dynastatic model of a PEM fuel cell

The demand for accurate fuel cell models rises with increasing applications for fuel cells. With the possibility to characterize a fuel cell in its different operational states, e.g. steady-state, large-signal behavior (step response) and small-signal behavior (impedance spectroscopy), it is possible to construct accurate models. Until now, the different characterization methods resulted in different models, that is, it was not possible to use the small-signal model in section 2.3.4 to simulate the steady-state characteristic of section 2.2.4. Nor was it possible to simulate the step response of section 2.3.3 with the model from section 2.2.4. Different applications of the fuel cell resulted in a linear increase of modeling possibilities.

There are, of course, possible applications that require only one of the mentioned operation states of the fuel cell. For instance, the production of chlorine-alkaline uses only the steady-state operation of the PEM fuel cell [106]. However, most of the applications will combine several operation conditions. For instance, automotive applications are certainly not only concerned with steady-state operation, but a combination between large-signal behavior (accelerating and decelerating), steady-state and small-signal behavior (driving at nearly constant speed).

Combined static and dynamic models found in the literature are often based on temperature variations and steady-state characteristics [3, 68], on steady-state and step-response measurements [32, 46, 53, 95, 113] or on steady-state
and impedance measurements [43, 66, 86, 87, 113]. The first type of dynamic model is well described in [3]. The second type is more often used by power electronics designers because switched power supplies are confronted with step load changes at the output terminals of the fuel cell [69].

This chapter describes how a combined dynamic and static, “dynastatic”, model can be constructed from existing small-signal, large-signal, and steady-state characteristics [114, 115, 117]. Furthermore, this chapter discusses the verification of the model. The implementation in simulation software can be found in appendix E. The model does not include additional temperature variables. However, the resulting model is based on measurement results, which includes the temperature variation implicitly in the modeling approach.

### 3.1 Model construction

The dynastatic model is explicitly build to include small-signal, large-signal and steady-state behavior. The fuel cell can be seen as a Thévenin source, that is, an ideal voltage source with an impedance in series. Electrochemical impedance spectroscopy (EIS) results in the most comprehensive description of that impedance. Therefore, the impedance model found with electrochemical impedance spectroscopy data will be used. The equivalent circuit shown in Fig. 3.1, is the basis for the fuel cell model. The impedance found in Fig. 2.17 is placed in series to a non-linear voltage source $E_{FC}$. The non-linear voltage source follows from the kinetic (2.52) or mixed mode (2.51) steady-state model.
3.1. Model construction

with omitted ohmic overpotential term (2.50), resulting in

\[ E_{FC} = E_{ocv} - A \ln \left( \frac{I_{FC}}{I_0} \right), \quad (3.1) \]

\[ E_{FC} = E_{ocv} - A \ln \left( \frac{I_{FC}}{I_0} \right) + B \ln \left( 1 - \frac{I_{FC}}{I_{lim}} \right). \quad (3.2) \]

The ohmic part of the original steady-state model (\( \eta_{ohmic} \)) will be replaced by a complex impedance \( Z \), which is shown in Fig. 3.1 as the gray area. This complex impedance \( Z \) is found with electrochemical impedance spectroscopy.

3.1.1 Resistors

The resistors found with EIS are graphically represented in Fig. 3.2. It is clear that the bulk resistor \( R_{\infty} \) has a constant character, and can therefore be approximated as a constant with value \( R_{\infty} = 0.272 \Omega \). The adsorption resistor \( R_A \) tends to slowly decrease with increasing current set points. Therefore, this resistor is approximated using

\[ R_A(I_{FC}) = R_A^0 - \alpha_A I_{FC}, \quad (3.3) \]

where \( R_A^0 = 23.5 \text{m}\Omega \) represents the initial value and \( \alpha_A = 2.62 \frac{\text{m}\Omega}{A} \) is the linear coefficient.

The two double layer resistors (\( R_{DL} \) and \( R_R \)) are showing non-linear behavior dependent on the fuel cell current. From Joule’s law it follows that the temperature dependency of a conductor is proportional to the square of the current through the conductor, that is,

\[ T \propto I_{FC}^2. \quad (3.4) \]

Therefore, in first approximation a function representing the resistors is proposed as being proportional to the square of the fuel cell output current. The implementation of the resistor functions is

\[ R_{DL}(I_{FC}) = R_{DL}^\infty + R_{DL}^0 e^{-\alpha_{DL}^* I_{FC}^2}, \quad (3.5) \]

and

\[ R_R(I_{FC}) = R_R^\infty + R_R^0 e^{-\alpha_R^* I_{FC}^2}. \quad (3.6) \]

The settling value for the first double layer resistor is \( R_{DL}^\infty = 75.2 \text{m}\Omega \), which represents the resistance for large output currents (\( I_{FC} \)). Furthermore, the initial value \( R_{DL}^0 = 172 \text{m}\Omega \) and the exponential rate coefficient \( \alpha_{DL}^* = 0.342 A^{-2} \).
The second double layer resistance is characterized with $R^\infty_{DL} = 18.4 m\Omega$, $R^0_{DL} = 97.0 m\Omega$ and a rate coefficient $\alpha^R_{DL} = 0.244 A^{-2}$. The fit is presented in Fig. 3.2(a).

However, from the measurement data presented in Fig. 3.2, the exact characteristic of the double layer resistors can not be determined in the low current region. This is due to the limitations of the measurement-set up to measure the injected small current variations so that the obtained voltage variations are undistort.

A second approach assumes that the temperature changes are small. In that case, the current-temperature relationship (3.4) can be linearized, resulting in

$$ T \propto I_{FC}. $$ (3.7)

Using this linear relationship, the resistor functions can be represented with

$$ R_{DL}(I_{FC}) = R^\infty_{DL} + R^0_{DL} e^{-\alpha_{DL} I_{FC}}, $$ (3.8)

$$ R_{R}(I_{FC}) = R^\infty_{R} + R^0_{R} e^{-\alpha_{R} I_{FC}}. $$ (3.9)

The values for the first double layer resistor are $R^\infty_{DL} = 67.8 m\Omega$, $R^0_{DL} = 313 m\Omega$ and the exponential rate coefficient $\alpha_{DL} = 0.884 A^{-1}$. The values for the second double layer resistor are $R^\infty_{R} = 15.3 m\Omega$, $R^0_{R} = 199 m\Omega$ and the rate coefficient $\alpha_{R} = 0.907 A^{-1}$. The fits are presented in Fig. 3.2(b).
3.1. Model construction

3.1.2 Open circuit voltage source

With the values for the different resistors known, the steady-state resistance $R_{\text{int}}$ can be determined. Because in steady-state operation the adsorption inductance $L_A$ is short circuiting the adsorption resistance $R_A$, the total internal resistance, which is dependent on the output current of the fuel cell stack ($I_{\text{FC}}$), is determined by

$$R_{\text{int}}(I_{\text{FC}}) = R_{\infty} + R_{\text{DL}}(I_{\text{FC}}) + R_R(I_{\text{FC}}). \quad (3.10)$$

Because there are two possibilities of determining the values for the double layer resistors, the results of the open circuit voltage source, shown in Fig. 3.3, are also presented in two forms. Figure 3.3(a) shows the open circuit voltage source of the fuel cell stack for double layer resistors presented with (3.5) and (3.6), while Fig. 3.3(b) presents $E_{\text{FC}}$ for the double layer resistors from (3.8) and (3.9).

The difference between Fig. 3.3(a) and Fig. 3.3(b) directly shows the problem in fitting the double layer resistors with the current temperature relationship of (3.4). The open circuit voltage source of the stack has a minimum value at $I_{\text{FC}} = 4\,A$, while the $E_{\text{FC}}$ in Fig. 3.3(b) has a continuously decreasing trend.

The open circuit voltage trend of Fig. 3.3(a) rises after $I_{\text{FC}} = 4\,A$, which eliminates the possibility of using the mixed mode steady-state model (3.2),

Figure 3.3: Open circuit source characteristics (○) and the fit (full line). In (a) a quadratic and in (b) a linear relationship between fuel cell current and operating temperature is used.
because the mixed mode model forces the output voltage to decrease sharply when approaching the limiting current. Therefore, this model is rejected.

The large discrepancy between the first measurement point \( (I_{FC} = 0 \, A) \) and the simulated value, which can be seen in Fig. 3.3(b), is related to the internal currents of the fuel cell, see also appendix B. These loss currents prohibit the fuel cell from producing its open circuit voltage. A schematic representation of the fuel cell including the internal current source is shown in Fig. 3.4.

In order to decide whether assumption (3.4) or (3.7) is best, the kinetic mode steady-state model is first fitted using the least squares method to the open circuit source of Fig. 3.3(a). To include the minimum in the characteristic (at \( I_{FC} = 4 \, A) \), the activation coefficient \( A \) has to be rewritten. This is done by integrating the current temperature dependency of (3.4) in the definition of the activation coefficient (2.29) and (2.28). The proposed open circuit voltage source is

\[
E_{FC} = E_{ocv} - (a + bI_{FC}^2) \ln \left( \frac{I_{FC}}{I_0} \right),
\]

(3.11)

where the activation coefficient is made dependent on the square of the fuel cell output current. In this equation the theoretical value for the reversible fuel cell voltage \( E_{ocv} = 4.68 \, V \) is used, resulting in the constant term of activation \( a = 0.216 \, V \), the activation resistive term \( b = 541 \, \mu \Omega \, A^{-1} \) and the exchange current \( I_0 = 972 \, \mu A \). The error made between the open circuit function (the full line of Fig. 3.3(a)) and the measured data points is less than 2% except for \( I_{FC} = 0 \, A \).

Second, the kinetic mode steady-state model is fitted to the data from Fig. 3.3(b). For this fit, the activation coefficient \( A \) is assumed to be constant, resulting in

\[
E_{FC} = E_{ocv} - A \ln \left( \frac{I_{FC}}{I_0} \right),
\]

(3.12)

where \( E_{ocv} = 4.68 \, V \), \( A = 0.164 \, V \) and \( I_0 = 117 \, \mu A \). The error between this
3.1. Model construction

Figure 3.5: Measured values and fitted as a constant (lines) of the two double layer capacitors ($C_{DL}$ and $C_R$), and the adsorption inductor ($L_A$).

function (the full line of Fig. 3.3(b)) and the obtained data is less than 1%, except for $I_{FC} = 0$ A.

Although both solutions for the double layer resistors are applicable to find a model for the open circuit voltage source $E_{FC}$, solution (3.12) is more attractive. Not only is the error between the fitted open circuit voltage source in favor of the linear current dependency of the double layer resistors, but also the complexity of (3.12) is lower than that of (3.11).

3.1.3 Capacitors and inductor

From EIS and the (quasi) steady-state characteristics, the internal resistance $R_{int}$ and internal voltage source $E_{FC}$ can be found. EIS also provides an indication of the values for the double layer capacitances and adsorption inductance. Literature indicates that these elements have constant values [6, 75]. Therefore, it would be convenient to simulate the step response of the fuel cell with constant values for these elements. Figure 3.5 shows the values for the double layer capacitances (o-mark for $C_{DL}$ and •-mark for $C_R$) and the adsorption inductance $L_A$ (c-mark).

From Fig. 3.5, it is clear that the first double layer capacitor $C_{DL} = 0.241$ F and the adsorption inductor $L_A = 40.2$ mH can be interpreted as constants.
The second double layer capacitor, however, can hardly be assumed as constant.

In section 2.3.4, it is explained why it is difficult to fit a value for the second double layer capacitor in the higher current set points. By fitting the step response to the proposed dynamic model of Fig. 3.1, including (constant) values for \( C_R \), the results indicate which value is to be used. The average value for all data points is \( C_R = 0.634 \) \( F \) (full line in Fig. 3.5), while the average value when omitting the last data point result in \( C_R = 0.562 \) \( F \) (dashed line in Fig. 3.5).

For the verification of these assumed constant values for the capacitors and inductor, a simulation of the step response is made and compared with the measured characteristic. In Fig. 3.6, the simulated and measured voltages of the fuel cell stack are shown in response to the current delivered. The simulated response is made while using \( C_R = 0.562 \) \( F \) for the second double layer capacitor.

The error between the measured and simulated step response is calculated using both modeling possibilities for the second double layer capacitor. The difference between the response for \( C_R = 0.562 \) \( F \) and \( C_R = 0.634 \) \( F \) is marginal, that is, less than 3 mV peak and an average difference of less than 8 \( \mu \)V over the complete time interval. The largest voltage peaks of the error occur at the switching of the load.

**Figure 3.6:** Multi-step response: simulated voltage in Matlab (gray dashed line), measured voltage (black line) and applied load current (thin gray line).
### 3.1. Model construction

#### Table 3.1: Analytical equations and values of the fuel cell model for cartridge # 0377.

<table>
<thead>
<tr>
<th>Model equations</th>
<th>Components</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{FC} = E_{ocv} - A \ln \left( \frac{I_{FC}}{I_0} \right)$</td>
<td>$E_{ocv}$</td>
<td>4.68</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>$A$</td>
<td>0.164</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>$I_0$</td>
<td>117</td>
<td>$\mu A$</td>
</tr>
<tr>
<td>$R_{\infty}$</td>
<td>$R_{\infty}$</td>
<td>0.272</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$R_D = R_D^\infty + R_D^0 e^{-\alpha_D I_{FC}}$</td>
<td>$R_D^\infty$</td>
<td>67.8</td>
<td>$m\Omega$</td>
</tr>
<tr>
<td></td>
<td>$R_D^0$</td>
<td>313</td>
<td>$m\Omega$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_D$</td>
<td>0.884</td>
<td>$A^{-1}$</td>
</tr>
<tr>
<td>$C_R = R_R^\infty + R_R^0 e^{-\alpha_R I_{FC}}$</td>
<td>$C_R$</td>
<td>0.562</td>
<td>$F$</td>
</tr>
<tr>
<td></td>
<td>$R_R^\infty$</td>
<td>15.3</td>
<td>$m\Omega$</td>
</tr>
<tr>
<td></td>
<td>$R_R^0$</td>
<td>199</td>
<td>$m\Omega$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_R$</td>
<td>0.907</td>
<td>$A^{-1}$</td>
</tr>
<tr>
<td>$L_A = R_A^0 - \alpha_A I_{FC}$</td>
<td>$L_A$</td>
<td>40.2</td>
<td>$mH$</td>
</tr>
<tr>
<td></td>
<td>$R_A^0$</td>
<td>23.5</td>
<td>$m\Omega$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_A$</td>
<td>2.62</td>
<td>$\frac{m\Omega}{A}$</td>
</tr>
</tbody>
</table>

The step-response simulation is made by calculating the immediate changes in the resistances caused by the change in output current (3.3), (3.8) and (3.9) and combining those values with the steady-state voltage source (3.12), except for the value of the internal voltage source when $I_{FC} = 0 \ A$. For that specific situation, an approximation of the internal voltage source is made, based on the value found in Fig. 3.3(b).

#### 3.1.4 Overview of the model

The equivalent circuit model of Fig. 3.1 is determined for cartridge # 0377\(^1\), with analytical expressions listed in Table 3.1. For the analytical equations of the double layer resistors $R_D$, and $R_R$, and for the open circuit voltage source $E_{FC}$, the linear relationship (3.7) between temperature changes and output current is used.

\(^1\)Cartridge # 0377 is used for most of the measurements, therefore, this cartridge has aged most. Further on in this chapter, a new cartridge is measured, which will result in different values for some of the model parameters.
3.2 Model verification

The model, with parameters as given in Table 3.1, is verified with simulations in Matlab of the steady-state, small- and large-signal response, and the results are compared with the measured data. First, the electrochemical impedance data will be verified. Second, the steady-state characteristics are checked, and last, the step response is inspected.

The definition of the error ($\varepsilon$) used in the verification is

$$\varepsilon = \frac{V_{FC, sim} - V_{FC, meas}}{V_{FC, meas}} \cdot 100\%,$$

and is the relative error between the simulated voltage $V_{FC, sim}$ and the measured voltage $V_{FC, meas}$ of the fuel cell.

Small-signal verification

The simulation of the frequency response of the model is done by implementing the complex impedance in Matlab. Afterwards, the calculated values of the impedance are compared to the measured ones. The relative error $\varepsilon$ between measurement and simulation is shown in Fig. 3.7. The top left graph shows the model error with a DC set point of $I_{FC} = 1$ A. The top right graph shows the error for $I_{FC} = 2$ A DC setting, the middle left for $I_{FC} = 3$ A, etc.

From the figure, it can be seen that the largest deviation appears for 1 A and 3 A DC set point. This can be explained by referring to Fig. 2.15, where the same measurements show a slight shift of the semi-circles over the real axis. This shift results in a higher measured bulk resistance $R_\infty$ than is used for the simulation, which results in a higher relative error.

The error at $I_{DC} = 4$ A increases at higher frequencies. This effect is also related to a difference in bulk resistance compared to the used simulation value. An error in the bulk resistance will be enlarged in the higher frequency range. This can be seen in the $I_{DC} = 1$ A, $I_{DC} = 3$ A and $I_{DC} = 4$ A plots.

From the results shown in Fig. 3.7, it can be concluded that the average error made in the small-signal behavior is lower than 4%. The peak error is 6%.

Steady-state verification

The error ($\varepsilon$) made in the steady-state simulation is presented as the $\circ$-marks connected with the dotted line in Fig. 3.8. As predicted, the error between
the measured output voltage at $I_{FC} = 0 \, A$ deviates most. The other verified points are very close to the obtained values, and the error differs at most 3\% (at $I_{FC} = 6 \, A$).

To reduce the error at very low output currents of the stack, the steady-state equation (3.12) is expanded with an internal current term $I_n$, as presented in Appendix B. The values for the open circuit voltage source ($E_{FC}$) are fitted to

$$E_{FC} = E_{ocv} - A \ln \left( \frac{I_{FC} + I_n}{I_0} \right),$$

(3.14)

and for the new expression the parameters change to $A = 193 \, mV$, $I_0 = 631 \, \mu A$ and the fuel crossover or internal current term will be $I_n = 470 \, mA$. The fuel cell stack is made from 4 membranes with an active area of $A_e = 60 \, cm^2$ each,
which leads to an internal current density of \( j_n = 2 \, mA/cm^2 \). This value is marked in the literature as “normal” [70].

The results of the steady-state verification using the internal current lead to the error plot with the full line and the \( \diamond \)-marks of Fig. 3.8. The error is reduced to 3.6% maximum at \( I_{FC} = 6 \, A \), and the error at \( I_{FC} = 0 \, A \) is almost 0%.

The internal current component only influences the behavior of the steady state in the activation polarization region. In the higher current region, the influence of the internal impedance of the fuel cell is high and the influence of the activation polarization diminishes.

**Step-response verification**

The verification of the step response is done in two ways. First, the error plot of the step response presented in Fig. 3.6 is simulated with Matlab with an open circuit voltage source without internal currents. The top graph of Fig. 3.9 shows the relative error as defined in (3.13) between measurement and simulation. The alternative, an open circuit voltage source (\( E_{FC} \)) with internal currents, is shown in the bottom graph of Fig. 3.9.

The error of the step response is highly dependent on the open circuit voltage source. As is seen in Fig. 3.9, the internal current term in the steady-state characteristic (3.14) influences the large-signal behavior, especially in the low output current region (activation polarization). It can also be seen in Fig. 3.9 that the errors of the large-signal behavior at \( I_{FC} = 6 \, A \), that is the steps in the time interval \( 155 < t < 180 \), are higher when the internal current is included than without this term. This is also related to the error in the steady-state be-
3.2. Model verification

**Figure 3.9:** Relative error between the measured and simulated step characteristics. In the top figure the FC voltage is simulated without internal current, while in the bottom figure it is simulated with internal current.

**Figure 3.10:** Absolute error between the measured and simulated step characteristics.
behavior, seen in Fig. 3.8.

The difference in absolute value between the simulated voltage and the measured characteristic is very small over the complete current range, as is shown in Fig. 3.10. However, the error in the higher current range increases relatively more because of a lower fuel cell output voltage, as can be seen in Figs 3.6 and 3.10.

The large peak errors in the activation polarization region seen in Fig. 3.9 and Fig. 3.10, are caused due to instantaneous changing of the resistor values as a result of a different load current. In practice, the change in resistance will not be so abrupt. The peaks have a limited duration of only a couple of microseconds.

3.3 Model based on a new stack

This section shows that the model developed on the aged fuel cell stack (#0377), can also be adopted for a new stack (#0183). The parameters of the model that are dependent on aging will be found, and can be used in state-of-health measurement. Furthermore, it is also possible to measure the influence of the air flow as a function of the model parameters. In this way, a comparison can be made between parameters that change over aging, and parameters of the model that change due to a difference in air flow.

3.3.1 Dynastatic model of a new cartridge

The new fuel cell stack (#0183) is measured with the low air flow supply using the electrochemical impedance spectroscopy method. The component values of the third order model presented in Fig. 3.1 are obtained for DC current set points ranging from $I_{DC} = 0.5A$ to $I_{DC} = 7.5A$. The resistor values are shown in Fig. 3.11(a). The linear temperature dependency of (3.7) is used to fit the two double layer resistors, yielding

\[
R_{DL} = 0.0813 + 0.154e^{-0.452I_{FC}}, \quad (3.15)
\]
\[
R_{R} = 0.0196 + 0.227e^{-0.919I_{FC}}. \quad (3.16)
\]

The bulk resistor is fitted to $R_{\infty} = 0.147\Omega$ and the adsorption resistor to $R_{A} = 23.5m\Omega$. In contrast to the aged cartridge, the fitted adsorption resistance shows a constant character.

The double layer capacitors and inductor values are presented in Fig. 3.11(b). The first double layer capacitor and adsorption inductor are fitted as constants,
with $C_{DL} = 0.201 F$ resp. $L_A = 0.123 H$. The second double layer capacitor, however, should certainly not be fitted as a constant. An analytical function\(^2\) dependent on the square of the output current is proposed as

$$C_R = \hat{C}_R e^{-\left(\frac{i_{FC}-\hat{I}_R}{\alpha_{cr}}\right)^2},$$

(3.17)

where $\hat{C}_R = 5.03 F$ is the maximum value of the double layer capacitor, $\hat{I}_R = 6.40 A$ represents the current at which the maximum value of the double layer capacitor is reached, and $\alpha_{cr} = 3.43 A$ is the exponential current coefficient.

The open circuit voltage source $E_{FC}$ can now be created from the quasi steady-state data and the resistances of the stack found with impedance spectroscopy. The results are shown in Fig. 3.12. The quasi steady-state values are obtained from step-response measurements, with a transition time of 30 seconds. The step-response measurements did not diverge to different DC values. However, the step train is repeated 20 times and the obtained values are averaged, resulting in a more accurate quasi steady-state characteristic.

For the least squares fit of the open circuit voltage source, the internal current component $I_n$ is added to (3.12) as is indicated in Appendix B. The fitted values

\(^2\)This function is a pure analytical representation of the obtained data, and to our knowledge, does not have any physical relationship to known electrochemical phenomena.
are $E_{ocv} = 4.68V$, $A = 0.214V$, $I_0 = 1.97mA$ and the internal current $I_n = 0.829A$, which implies a loss current density of $j_n = 3.45mA/cm^2$. This is higher than the value of the aged stack in section 3.2. The analytical stack model for the new fuel cell cartridge is presented in Table 3.2.

Veriﬁcation of the model

The veriﬁcation of the model is done using quasi steady-state data from step responses. The steady-state characteristic is presented in Fig. 3.13, where in the top graph the ◦-marks describe the measured values of the fuel cell voltage and the solid line shows the simulated voltage. The error made with the steady-state simulation is given in the lower graph, the maximum error being less than 3%.

The dynastatic model has also been implemented in Simulink, which is shown in Appendix E. The veriﬁcation of the Simulink model is also done with step-response simulations. An implementation of the non-linear double layer capacitor ($C_R$) in Simulink can be found in appendix E. The results are shown in the top graph of Fig. 3.14 for simulated (black line) and measured voltages (gray line). The dashed black line shows the fuel cell output current $I_{FC}$. The
3.3. Model based on a new stack

error made in the step response between the measured and simulated characteristic, as defined in (3.13), is presented in the lower graph. It can be seen that the error is largest when the current steps from a high value (= 6 A) to almost zero (≈ 0 A). The maximum error is, in that case, 10%, while in all other cases the error stays below 5%.

Simplification of the model

The model of the new stack has increased in complexity compared to the model of the aged stack because a more elaborated function for the second double layer capacitor $C_R$ is used. The question arises if it is not possible to use a simple constant value for $C_R$ as it was done in section 3.1.3. With the least squares fit of the double layer data, the 95% prediction bounds are generated. These bounds are used to create a band of “allowed” values for a constant

<p>| Table 3.2: Analytical equations and values of the new fuel cell (# 0183) model utilizing low air flow supply. |</p>
<table>
<thead>
<tr>
<th>Model equations</th>
<th>Components</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{FC} = E_{ocv} - A \ln \left( \frac{I_{FC} + I_n}{I_0} \right)$</td>
<td>$E_{ocv}$</td>
<td>4.68</td>
<td>V</td>
</tr>
<tr>
<td>$A$</td>
<td>0.214</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td>$I_n$</td>
<td>0.829</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>$I_0$</td>
<td>1.97</td>
<td>mA</td>
<td></td>
</tr>
<tr>
<td>$R_{\infty}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{DL}$</td>
<td>$R_{\infty}$</td>
<td>0.147</td>
<td>Ω</td>
</tr>
<tr>
<td>$R_{DL} = R_{DL}^\infty + R_{DL}^0 e^{-\alpha_{DL} I_{FC}}$</td>
<td>$C_{DL}$</td>
<td>0.201</td>
<td>F</td>
</tr>
<tr>
<td>$R_{DL}^\infty$</td>
<td>81.3</td>
<td>mΩ</td>
<td></td>
</tr>
<tr>
<td>$R_{DL}^0$</td>
<td>0.154</td>
<td>Ω</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{DL}$</td>
<td>0.452</td>
<td>$A^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$C_R = \hat{C}<em>R e^{-\left( \frac{I</em>{FC} - \hat{I}<em>R}{\alpha</em>{cr}} \right)^2}$</td>
<td>$\hat{C}_R$</td>
<td>5.03</td>
<td>F</td>
</tr>
<tr>
<td>$\hat{I}_R$</td>
<td>6.40</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{cr}$</td>
<td>3.43</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>$R_R = R_R^\infty + R_R^0 e^{-\alpha_R I_{FC}}$</td>
<td>$R_R^\infty$</td>
<td>19.6</td>
<td>mΩ</td>
</tr>
<tr>
<td>$R_R^0$</td>
<td>0.227</td>
<td>Ω</td>
<td></td>
</tr>
<tr>
<td>$\alpha_R$</td>
<td>0.919</td>
<td>$A^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$L_A = R_A^0 - \alpha_A I_{FC}$</td>
<td>$L_A$</td>
<td>123</td>
<td>mH</td>
</tr>
<tr>
<td>$R_A^0$</td>
<td>23.5</td>
<td>mΩ</td>
<td></td>
</tr>
<tr>
<td>$\alpha_A$</td>
<td>0</td>
<td>$\frac{Ω}{A}$</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.13: Steady-state simulation vs. measurements of the new cartridge # 0183; in the top figure the simulation and measurement is shown, and in the bottom figure the relative error between them.

Figure 3.14: Step-response simulation and measurement of cartridge # 0183 is shown in the top figure, and the relative error between them in the bottom figure.
3.3. Model based on a new stack

Figure 3.15: Relative error between the measured EIS-curve of stack # 0183 and the simulated curve with $C_R$ defined as (3.17) (full line) and $C_R = 1.13 \text{ F}$ (dashed line) for different DC set points: a) $I_{DC} = 1.5 \text{ A}$, b) $I_{DC} = 3.0 \text{ A}$, c) $I_{DC} = 5.0 \text{ A}$ and d) $I_{DC} = 6.5 \text{ A}$. 

The error made for small-signal behavior between the simulation with the proposed current dependent double layer capacitor (3.17) and the capacitor with constant value is presented in Fig. 3.15. The dashed lines show the relative error when the simulation is done with the constant value of the double layer capacitor. The full line represents the error when the simulation is performed with (3.17) describing the double layer capacitor.

The error is shown for different DC set points. Figure 3.15(a) shows the error at $I_{DC} = 1.5 \text{ A}$, Fig. 3.15(b) for $I_{DC} = 3.0 \text{ A}$, Fig. 3.15(c) for $I_{DC} = 5.0 \text{ A}$ and Fig. 3.15(d) for $I_{DC} = 6.5 \text{ A}$. It is clear from Fig. 3.15 that the error between the simulation for low to medium DC currents, that is Figs. 3.15(a), and 3.15(b), is almost the same for both ways of simulating the double layer capacitor $C_R$, while for the higher DC currents, that is Figs. 3.15(c), and 3.15(d), the relative
error between the measured EIS curve and the simulated EIS curve modeling a constant $C_R$ grows, especially in the 0.2 Hz to 3.5 Hz frequency range.

The average error recorded, that is, the average over all examined frequencies, is for the current dependent capacitor around 2%, while it is for the constant value of $C_R$ around 3.5%. However, the peak deviation with constant assumed capacitor can get higher than 10%. However, the average error made with the constant value of $C_R$ is low, which makes it an interesting option to keep the model simple.

### 3.3.2 High air flow model

The new fuel cell stack (# 0183) is also measured with a high air flow supply. The construction and the verification of the model are done in the same way as presented in section 3.3, and is presented in appendix F. The results of the

<table>
<thead>
<tr>
<th>Model equations</th>
<th>Components</th>
<th>Values</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{FC} = E_{ocv} - A \ln \left( \frac{I_{FC} + I_n}{I_0} \right)$</td>
<td>$E_{ocv}$</td>
<td>4.68</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>$A$</td>
<td>0.180</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>$I_n$</td>
<td>0.842</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>$I_0$</td>
<td>722</td>
<td>$\mu$A</td>
</tr>
<tr>
<td>$R_\infty$</td>
<td>$R_\infty$</td>
<td>0.116</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$C_{DL}$</td>
<td>$C_{DL}$</td>
<td>0.265</td>
<td>$F$</td>
</tr>
<tr>
<td>$R_{DL} = R_{DL}^\infty + R_{DL0}^0 e^{-\alpha_{DL} I_{FC}}$</td>
<td>$R_{DL0}^\infty$</td>
<td>16.4</td>
<td>$m\Omega$</td>
</tr>
<tr>
<td></td>
<td>$R_{DL0}^0$</td>
<td>133</td>
<td>$m\Omega$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{DL}$</td>
<td>0.283</td>
<td>$A^{-1}$</td>
</tr>
<tr>
<td>$C_R$</td>
<td>$C_R$</td>
<td>2.63</td>
<td>$F$</td>
</tr>
<tr>
<td>$R_R = R_R^\infty + R_R^0 e^{-\alpha_R I_{FC}}$</td>
<td>$R_R^\infty$</td>
<td>7.20</td>
<td>$m\Omega$</td>
</tr>
<tr>
<td></td>
<td>$R_R^0$</td>
<td>0.154</td>
<td>$\Omega$</td>
</tr>
<tr>
<td></td>
<td>$\alpha_R$</td>
<td>1.47</td>
<td>$A^{-1}$</td>
</tr>
<tr>
<td>$L_A$</td>
<td>$L_A$</td>
<td>123</td>
<td>$mH$</td>
</tr>
<tr>
<td>$R_A$</td>
<td>$R_A$</td>
<td>13.6</td>
<td>$m\Omega$</td>
</tr>
<tr>
<td>$C_R = \hat{C}<em>R e^{-\left( \frac{I</em>{FC} - \hat{I}<em>R}{\alpha</em>{cr}} \right)}$</td>
<td>$\hat{C}_R$</td>
<td>7.95</td>
<td>$F$</td>
</tr>
<tr>
<td></td>
<td>$\hat{I}_R$</td>
<td>6.99</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td>$\alpha_{cr}$</td>
<td>4.20</td>
<td>A</td>
</tr>
</tbody>
</table>
analytical expressions for the equivalent circuit model are listed in Table 3.3.

The second double layer capacitor $C_R$ is constructed twice, namely as a constant for simplification of the model, and as a function of the output power, as is presented in (3.17). The latter representation of the second double layer capacitor results in a better fit of the impedance data, but it makes the model unnecessarily more complex.

### 3.4 Parameter correlation between the models

In this chapter a model of a fuel cell stack is made for an aged and a new cartridge. Both had a low air flow supply. In this section, the correlation between the model parameters of the aged and new cartridge is made. Furthermore, a comparison between the same cartridge with a low and a high air flow supply can be made. It is interesting to compare the parameters of the models, to find the most indicative parameters for aging and for air flow supply.

A relative error $\epsilon$ defined as

$$\epsilon(\%) = \frac{x - x_{0183,low}}{x_{0183,low}} \cdot 100\%$$

(3.18)

is calculated per model parameter $x$. Because the new cartridge # 0183 is used with both air flow supplies, it is convenient to use the parameters of its model with low air flow supply as reference.

### 3.4.1 Aged and new stack parameters

First, the comparison between the models of the aged (Table 3.1) and the new cartridge (Table 3.2) are compared. The change in model parameters is listed in Table 3.4.

If both open circuit voltage sources are compared, then two parameters are markedly different. Firstly, the internal current $I_n$ of the aged cartridge is 43% lower than in the new stack. This parameter is strongly dependent on the material condition of the membrane.

Secondly, the exchange current $I_0$ is much lower in the aged stack than in the new stack (94%). The exchange current is linked to the value of the activation coefficient, however, the difference can not be explained with the lower value of $A$ for the aged stack. According to (2.48), a larger value for the exchange current results in a higher fuel cell current ($I_{FC}$) needed to start the
activation. In other words, if the exchange current is higher, then the performance of the fuel cell is better. The exchange current density (2.22) is dependent on the concentrations of the reactants and products of the reaction, and on the electrochemical reaction rate constant. If the platinum catalyst is deteriorated due to intensive use, it can be interpreted as lower concentration of reactants. This results in a lower exchange current density.

Probably the best parameter to indicate aging is the bulk resistance (\(R_\infty\)). This resistor increases with 85% in value for the aged cell. By measuring the impedance of the fuel cell around \(\pm 100\, Hz\) the bulk resistance can be easily found, as is shown in Fig. 2.15. Two impedance plots are shown in Fig. 3.16 in order to compare the changes in small-signal behavior of the aged (# 0377) and unaged (# 0183) cartridge. It is clear from these plots that the size of the semi-circles stay almost the same, but the characteristic of the aged cartridge is translated over the \(Z'\) axis.

Other parameters that change markedly are the adsorption inductor (\(L_A\)) and the second double layer capacitor (\(C_R\)). If the current dependency of \(C_R\) is taken into account, the second double layer capacitor deviates even more.

### Table 3.4: Parameter deviation between aged and new stack for low air flow supply.
The new stack (# 0183) is used as reference.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Aged stack (# 0377)</th>
<th>New stack (# 0183)</th>
<th>(\epsilon) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) [mV]</td>
<td>164</td>
<td>214</td>
<td>-23.4</td>
</tr>
<tr>
<td>(I_n) [mA]</td>
<td>470</td>
<td>829</td>
<td>-43.3</td>
</tr>
<tr>
<td>(I_0) [mA]</td>
<td>0.117</td>
<td>1.97</td>
<td>-94.1</td>
</tr>
<tr>
<td>(R_\infty) [m(\Omega)]</td>
<td>272</td>
<td>147</td>
<td>85.0</td>
</tr>
<tr>
<td>(R_{DL}^\infty) [m(\Omega)]</td>
<td>67.8</td>
<td>81.3</td>
<td>-16.6</td>
</tr>
<tr>
<td>(R_{DL}^0) [m(\Omega)]</td>
<td>313</td>
<td>154</td>
<td>103</td>
</tr>
<tr>
<td>(\alpha_{DL}) [A(^{-1})]</td>
<td>0.884</td>
<td>0.452</td>
<td>95.6</td>
</tr>
<tr>
<td>(R_R^\infty) [m(\Omega)]</td>
<td>15.3</td>
<td>19.6</td>
<td>-21.9</td>
</tr>
<tr>
<td>(R_R^0) [m(\Omega)]</td>
<td>199</td>
<td>227</td>
<td>-12.3</td>
</tr>
<tr>
<td>(\alpha_R) [A(^{-1})]</td>
<td>0.907</td>
<td>0.919</td>
<td>-1.31</td>
</tr>
<tr>
<td>(R_A) [m(\Omega)]</td>
<td>23.5</td>
<td>23.5</td>
<td>0</td>
</tr>
<tr>
<td>(\alpha_A) [m(\Omega)A(^{-1})]</td>
<td>2.62</td>
<td>0</td>
<td>(\infty)</td>
</tr>
<tr>
<td>(C_{DL}) [m(\mathcal{F})]</td>
<td>241</td>
<td>201</td>
<td>19.9</td>
</tr>
<tr>
<td>(C_R) [(\mathcal{F})]</td>
<td>0.562</td>
<td>1.13</td>
<td>-50.3</td>
</tr>
<tr>
<td>(L_A) [mH]</td>
<td>40.2</td>
<td>123</td>
<td>-67.3</td>
</tr>
</tbody>
</table>
3.4. Parameter correlation between the models

The dynastatic model found for the tested fuel cells does not provide information about the limiting current. This parameter was eliminated in the open circuit voltage source $E_{FC}$ because measurements confirm that the concentration coefficient $B$ approaches zero, shown in Table 2.2. Therefore, it would be convenient to find additional parameters that could give information about concentration issues.

The parameter deviation in a fuel cell due to a different air supply is also compared. Table 3.5 shows the model parameters and their relative error as defined in (3.18).

It was expected that all the resistors of the high air flow model would have lower resistance values than those of the low air flow model. This assumption is found to be true, as it can be seen in Table 3.5. Actually, the resistance values for high fuel cell currents deviates most, that is for the first double layer resistor $R_{DL}^\infty$ the difference is almost 80%, and for the second double layer resistor $R_R^\infty$ more than 63%.

The most convenient way to find an easy to obtain parameter indicating the air flow, is to measure the resistance at a fuel cell current $I_{FC}$ that approaches zero. The internal resistance of the model can be calculated from (3.8), (3.9), and (3.10) as

$$R_{int} = R_\infty + (R_{DL}^\infty + R_{DL}^0) + (R_R^\infty + R_R^0)$$

(3.19)

The internal resistance for the low air flow is $R_{int} = 630m\Omega$, while the internal resistance for the high air flow model is $R_{int} = 427m\Omega$. The relative error as

---

**Figure 3.16:** Graphically presented EIS results of the aged cartridge (# 0377, gray dashed line), and the new cartridge (# 0183, black line).
defined in (3.18) \( \epsilon = -32.2\% \) does not show the largest deviation, but is by far the easiest to measure. In contrast to aging, the bulk resistance \( R_\infty \) follows the trend of the other resistances, while with aging, the other resistances did not change as much as the bulk resistance. To illustrate the changes in the impedance plots as a result of the changing internal resistance, Fig. 3.17 shows that the high air flow supply differs in size and is translated over the \( Z' \) axis.

Furthermore, the exchange current \( I_0 \), which is the only changing parameter of the internal voltage source, also indicates the changed air flow very clearly. This is because the concentration of the reactant oxygen is supplied better, which is linked directly to the exchange current density (2.22).

The last parameter that changes a lot due to a different air flow is the value of the second double layer capacitor \( (C_R) \), especially when the constant parameter is used (over 130%). If a constant value is used in the model, the value of this parameter can easily be obtained by measuring it around 1 Hz under high load conditions. In that operating point the characteristic changes the most, as can be seen in Figs. 3.15(d), and F.5(d). However, it takes a lot of computing

<table>
<thead>
<tr>
<th>Parameters</th>
<th>High air flow supply</th>
<th>Low air flow supply</th>
<th>( \epsilon ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A ) ( [mV] )</td>
<td>180</td>
<td>214</td>
<td>-15.9</td>
</tr>
<tr>
<td>( I_n ) ( [mA] )</td>
<td>842</td>
<td>829</td>
<td>1.57</td>
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<tr>
<td>( I_0 ) ( [mA] )</td>
<td>0.722</td>
<td>1.97</td>
<td>-63.4</td>
</tr>
<tr>
<td>( R_\infty ) ( [m\Omega] )</td>
<td>116</td>
<td>147</td>
<td>-21.6</td>
</tr>
<tr>
<td>( R^{DL}_C ) ( [m\Omega] )</td>
<td>16.4</td>
<td>81.3</td>
<td>-79.8</td>
</tr>
<tr>
<td>( R^{DL}_R ) ( [m\Omega] )</td>
<td>133</td>
<td>154</td>
<td>-13.6</td>
</tr>
<tr>
<td>( \alpha^{DL} ) ( [A^{-1}] )</td>
<td>0.283</td>
<td>0.452</td>
<td>-37.4</td>
</tr>
<tr>
<td>( R^A_\infty ) ( [m\Omega] )</td>
<td>7.20</td>
<td>19.6</td>
<td>-63.3</td>
</tr>
<tr>
<td>( R^A_R ) ( [m\Omega] )</td>
<td>154</td>
<td>227</td>
<td>-32.2</td>
</tr>
<tr>
<td>( \alpha^A ) ( [A^{-1}] )</td>
<td>1.47</td>
<td>0.919</td>
<td>60.0</td>
</tr>
<tr>
<td>( R_A ) ( [m\Omega] )</td>
<td>13.6</td>
<td>23.5</td>
<td>-42.1</td>
</tr>
<tr>
<td>( C_{DL} ) ( [mF] )</td>
<td>265</td>
<td>201</td>
<td>31.8</td>
</tr>
<tr>
<td>( C_R ) ( [F] )</td>
<td>2.63</td>
<td>1.13</td>
<td>133</td>
</tr>
<tr>
<td>( L_A ) ( [mH] )</td>
<td>123</td>
<td>123</td>
<td>0</td>
</tr>
<tr>
<td>( C_R ) ( [F] )</td>
<td>7.95</td>
<td>5.03</td>
<td>58.1</td>
</tr>
<tr>
<td>( \tilde{I}_R ) ( [A] )</td>
<td>6.99</td>
<td>6.40</td>
<td>9.22</td>
</tr>
<tr>
<td>( \alpha_{ct} ) ( [A] )</td>
<td>4.20</td>
<td>3.43</td>
<td>22.4</td>
</tr>
</tbody>
</table>
power to recover this parameter in situ.

3.5 Conclusions

This chapter provides a way of constructing an accurate fuel cell model based on the electrochemical theory from Chapter 2. This model is capable of simulating the static and dynamic behavior of PEM fuel cells, a so-called dynastatic model.

The results obtained from electrochemical impedance spectroscopy are used to find the small-signal behavior. From the EIS data the values of the resistor parameters can be found, together with a first indication for the capacitors and inductor values of the third order equivalent circuit. The two double layer resistors \( R_{DL} \) and \( R_R \) are non-linearly dependent on the output current \( I_{FC} \). The bulk resistor \( R_\infty \) and the adsorption resistor \( R_A \) may be assumed constant.

Once the internal resistance is known, the open circuit voltage source \( E_{FC} \) of the equivalent circuit can be retrieved. In order to reduce the simulation error at no load, an estimation of the internal current \( I_n \) of the fuel cell is introduced. The additional internal current parameter is not only necessary to reduce the steady-state error, but also to reduce the error in the step response.

Finally, the indicative values of the capacitors and inductor from EIS can be used to find the optimal values with respect to the step-response measurements. When the capacitors and inductor values are fitted, the dynastatic model can be used to predict the system behavior under different operating conditions.
The dynastatic model provides also a way to obtain the state-of-health of
the fuel cell with respect to aging. The bulk resistor \( R_\infty \) provides a firm indi-
cation of aging. When the fuel cell is excited with a small sinusoidal signal of
about 100 Hz superimposed on an arbitrary DC current, the resistance found
is the bulk resistor. For aged cells, this parameter becomes significantly higher
than for new cells.

Furthermore, the dynastatic model gives also information about the air flow
supply. Due to the elimination of the limiting current \( I_{\text{lim}} \) parameter from the
open circuit voltage source \( E_{FC} \), no direct parameter of concentration limita-
tion is provided by the model. However, two parameters deviate greatly due
to a changed air flow. It is possible to determine the second double layer capac-
itor \( C_R \) around 1 Hz, but this parameter is difficult to obtain in situ, because
it needs a lot of computational power to retrieve it from the data. A more easy
way to determine concentration failure of the fuel cell system, is the measure-
ment of the internal resistance \( R^{\text{int}} \) at a system current \( I_{FC} \) approaching
zero. This parameter will deviate due to concentration loss, but is less depen-
dent on the bulk resistance \( R_\infty \) in contrast to aging.
Part II

Contamination in the fuel cell feedstock
Chapter 4

Biomass and fuel cells

Hydrogen has to be produced in order to gain electrical energy from a fuel cell. There are numerous ways to produce hydrogen, but not all methods are environmentally friendly. For instance, it is possible to electrolyze water to hydrogen and oxygen, but if the electricity needed for the reaction to take place is produced with fossil fuels, the complete process is not environmentally friendly.

To determine if a method is environmentally friendly or not, a workable definition of “green power” should be made. In this work, the definition of green energy is: “Electricity that is generated from sustainable energy sources” [103]. This definition leads to a second definition, that is, the definition of sustainable energy sources: “Sustainable energy sources are continuously replenished on the earth”. Examples of sustainable energy sources are wind, solar, geothermal, hydropower, and various forms of biomass [103].

Furthermore, the definition given above does not give clear boundaries for what may be included as sustainable energy sources and what may not. The definitions are quite political, which results in a vague term like “continuously replenished”, which does not give a clear definition of time. This leads to disputes on, for instance nuclear power and municipal waste. It depends on the organization wielding the term green energy if municipal waste and nuclear power are included in the definition of sustainable energy sources [103].
Why biomass?

In order to answer the question why biomass should be used to produce electricity, it should first be made clear what biomass is. A definition is: “Biomass is a very broad term which is used to describe material of recent biological origin that can be used either as a source of energy or for its chemical components” [64]. Plants, trees, manure, many household and industrial wastes (on the basis of plants) can be considered as biomass. Biomass can actually be seen as storage of solar energy [40, 64].

When biomass is used as an energy source, carbon dioxide (CO\textsubscript{2}) will be produced. However, if the production of biomass is managed well, the emission of CO\textsubscript{2} will not contribute to a rise in the atmospheric concentration of CO\textsubscript{2}, in contrast to burning fossil fuels. Because plants and trees continuously convert CO\textsubscript{2} into oxygen in order to grow, and release this CO\textsubscript{2} back when they are converted into energy, the balance of CO\textsubscript{2} is neutral. This circular balance is called CO\textsubscript{2}-neutral conversion of energy. Figure 4.1 shows the CO\textsubscript{2}-neutral conversion cycle graphically.

In this chapter the production of hydrogen from biomass is explained. It is known that with the conversion of biomass to hydrogen-rich gas, carbon monoxide (CO) is produced. This gas prevents the proper working of fuel cells due to a phenomenon called CO-poisoning. This effect, which already starts with trace amounts of CO, prohibits a proper functioning of the platinum cat-
4.1 Production of hydrogen from biomass

Although it is not the purpose of this work to research the conversion of biomass to hydrogen in full detail, this section will give a brief overview of three different conversion techniques. In Fig. 4.2 the route from biomass to its electrical application is shown. This section describes the second and third balloon in the figure, that is, the conversion of biomass to hydrogen-rich gas and (partially) the cleaning of the gas.

There are, however, several ways to convert biomass into a useful type of energy. A good overview of what is available and in which state of development the technology is can be found at the site of the Biomass Technology Group [18], and at the site of the Energieonderzoek Centrum Nederland [107]. Three selected conversion techniques described in this section may play an important role in the future of biomass conversion and electricity generation using fuel cells.
4.1.1 Gasification of biomass

Biomass gasification is a thermal conversion technique where a solid fuel is converted into combustible gas. Biomass is heated with a controlled supply of an oxidizing agent like oxygen, air or steam. The solid fuel converts to a gas mixture containing carbon monoxide (CO), carbon dioxide (CO$_2$), hydrogen (H$_2$), methane (CH$_4$), water (H$_2$O) and nitrogen (N$_2$). However, contaminants are also created, like tars, ashes and other small particles. These contaminants have to be removed before the gas is suitable for combustion [18].

If wood is used as the biomass fuel, a typical gas mixture contains about 50% N$_2$, 20% CO, 10% CO$_2$, 17% H$_2$ and 2% CH$_4$. Furthermore, some other impurities are present, which need to be removed dependent on the application [18]. The most critical contaminant is tar, and a lot of research is focused on that subject [58, 60, 81].

Of the three techniques described in this section, gasification of biomass is the closest to commercialization. The gas produced from biomass is suitable for gas engines, micro turbines and even (high temperature) fuel cells [18].

4.1.2 Pyrolysis of biomass

The second conversion technique presented here is pyrolysis. Pyrolysis is the thermal decomposition of biomass at temperatures higher than 200 °C in the absence of air. The end product of pyrolysis is a mixture of solids (char), liquids (oxygenated oils), and gases (methane, carbon monoxide, and carbon dioxide). The concentrations are determined by operating temperature, pressure, and oxygen content [63]. So, the major difference between gasification and pyrolysis is the absence of an oxidizing agent.

An implementation given by [18] is the so-called “flash-pyrolysis” method, in which biomass (for instance wood) is rapidly heated in order to break its complex structure to smaller parts. There is an optimum temperature in which the liquid product is maximized. It is possible to gain 70% of the biomass weight in oil [17, 18]. The solid product, char, is used to heat the reactor, in such a way that it is self-sustaining [18].

At this moment, the calculated bio-oil production costs are less than 85 €/ton, which is close to the price of fossil oil. Bio-oil can be used as fuel in boilers or furnaces. Normal Diesel engines need some adjustments for running on bio-oil, but the results are promising [18].

However, bio-oil can not be used as a feedstock for fuel cells, unless it is converted to hydrogen-rich gas. This can be done by gasification as is described in
section 4.1.1. A major advantage of using bio-oil for gasification over biomass is that the gasifiers for oil are well known in contrast to the gasifiers for solid materials [18].

4.1.3 Gasification of biomass in supercritical water

The last conversion technique discussed is supercritical water gasification. Supercritical water means that water is brought to a pressure and temperature which are above its critical point. Water becomes supercritical at pressures above 221 bar and temperatures above 374 °C. If the water is supercritical, then there is no distinction between its liquid and gaseous phase [104].

Supercritical water gasification is especially suitable for biomass containing a high water content, although it can be used for other types of feedstock [104]. The advantages over other types of biomass conversion are that the gasses are “relatively” clean, that is, polluting gasses like ammonia (NH₃), hydrogen sulfide (H₂S) and carbon dioxide (CO₂) stay in the liquid phase. Further advantages are that the oxidation can be complete, which means that there is no waste, carbon dioxide can get separated in concentrated form for reuse or storage and the gasses are produced under high pressure, which eliminates the use of compression of the gasses after the conversion [104].

The process can be optimized to maximize hydrogen production, or to minimize the production of methane or carbon monoxide [18]. A typical conversion composition is 4% CO, 33% CO₂, 56% H₂ and 7% CH₄. However, these values may get optimized for use with fuel cells (higher hydrogen content, lower carbon monoxide and methane content) [18, 104].

Because of the high hydrogen content and controllable pollution contents of the gas mixture, supercritical water gasification is an interesting option in combination with fuel cells. However, the status of biomass gasification in supercritical water is still far from commercialization, and a lot of research needs to be done [18].

On our request, the Biomass Technology Group [18] has researched the best composition of gasses using supercritical water gasification. The specific demands were maximization of the hydrogen content, which results directly in a minimization of methane, ethane, propane etc. and minimization of carbon monoxide contents. The components of the best gas mixture possible vary as follows: methane (CH₄ : ±[3 · · · 7]%), carbon dioxide (CO₂ : ±[30 · · · 35]%), hydrogen (H₂ : ±[50 · · · 60]%) and carbon monoxide (CO : ±[0.5 · · · 1.5]%). All concentration percentages are given in volume percentage (% = %v).
4.2 Influence of CO on the fuel cell stack

The influence of carbon monoxide on the performance of a PEM fuel cell can be researched by mixing small amounts of CO in the hydrogen feedstock. Literature indicates that amounts of less than 10 ppm do not significantly influence the performance of the fuel cell [27, 118]. However, 30 ppm or higher are of influence. Therefore, five different gas mixtures are used for the investigation of CO-poisoning. As is indicated in section 4.1, the gas mixture of the best hydrogen gasification consists of methane \((\text{CH}_4 : \pm 3 \cdots 7\%)\), carbon dioxide \((\text{CO}_2 : \pm 35 \cdots 35\%)\), hydrogen \((\text{H}_2 : \pm 60 \cdots 60\%)\) and carbon monoxide \((\text{CO} : \pm 0.5 \cdots 1.5\%)\). Because 0.5%v CO will poison the catalysts of the fuel cell in a very short time period, mixtures with lower concentrations CO were used\(^1\).

In order to study the impact of CO, different gas-mixtures were tested with the PEM fuel cell. Table 4.1 gives an overview of the used gasses for this purpose. As can be seen in the table, methane is replaced by nitrogen \((\text{N}_2)\), because a methane mixture might interfere with the safety regulations in the laboratory. Gas # 1 is pure hydrogen. All previous measurements were performed using this gas. Gas # 2 is a dummy gas, without CO contamination, which is used to show the influence of CO\(_2\) and N\(_2\) on the performance of the fuel cell. Gas # 3 contains 30 ppm CO, which is still low, but should have a reasonable influence on the performance of the PEM fuel cell. Gas # 4 (50 ppm CO) and gas # 5 (100 ppm) are mixtures with high impact on the performance of the fuel cell, which reduces the output power to nearly zero in a short time interval. With increasing CO contents, it becomes more challenging to efficiently operating the fuel cell.

<table>
<thead>
<tr>
<th>Gas</th>
<th>H(_2)</th>
<th>CO</th>
<th>CO(_2)</th>
<th>N(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.99%</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>60%</td>
<td>-</td>
<td>35%</td>
<td>5%</td>
</tr>
<tr>
<td>3</td>
<td>60%</td>
<td>30ppm</td>
<td>35%</td>
<td>5%</td>
</tr>
<tr>
<td>4</td>
<td>60%</td>
<td>50ppm</td>
<td>35%</td>
<td>5%</td>
</tr>
<tr>
<td>5</td>
<td>60%</td>
<td>100ppm</td>
<td>35%</td>
<td>5%</td>
</tr>
</tbody>
</table>

\(^1\)This implies that additional cleaning of the biomass gas is needed, in order to reduce the CO content of the gas mixture.
In order to have an indication of the operating performance of the fuel cell, one should understand the concept of CO-tolerance. By definition: “A fuel cell is CO-tolerant when the loss of the cell voltage is not higher than 15% compared to the cell voltage utilizing pure hydrogen under the same circumstances” [27].

Before the influence of carbon monoxide can be investigated, it should be made clear that the other “non-reactive” gases in the mixture do not influence the performance of the fuel cell. Therefore, an initial test is conducted with the same fuel cell cartridge utilizing pure hydrogen gas (# 1) and the dummy gas (# 2 in which nitrogen and carbon dioxide are present). The steady-state characteristics of the cartridge are shown in Fig. 4.3. From the figure, it is clear that the influence of N\textsubscript{2} and CO\textsubscript{2} are marginal, except for higher output currents. This can be explained by the fact that non-consumable gasses do influence the partial pressure, and thus the concentration of the consumable gasses in the anode channel.
4.2.1 CO-poisoning

Section 4.1 points out that the conversion of biomass results in mainly methane (exchanged here with nitrogen), carbon dioxide and hydrogen. However, in all cases carbon monoxide is also produced. Carbon monoxide is a very good adsorbate for the platinum surface of the catalyst. However, CO is not part of the fuel cell reaction. This leads to a monolayer of adsorbed CO covering the active sites of the platinum catalyst, blocking the hydrogen from adsorbing to that surface [1, 4, 27, 29, 30, 90, 98, 118]. The monolayer CO prevents the fuel cell from operating, and eventually this will lead to a decrease in output power. In a way, CO poisons the fuel cell, hence the term CO-poisoning.

In the literature several methods for clearing the catalyst surface from CO are presented. These methods can be categorized in three different groups. Firstly, it is stated that by increasing the operating temperature of the fuel cell the balance between CO and CO\(_2\) can be pushed towards the CO\(_2\) side, which is a much weaker adsorbate for platinum than CO [4, 12, 102, 118]. This method, however, increases the evaporation of water from the membrane, which will increase its ionic resistance, and can eventually lead to the destruction of the fuel cell [47, 48, 49].

Secondly, by adding an oxidant to the anode gas stream, like pure oxygen, CO can get oxidized when it is adsorbed to the platinum [11, 12, 13, 62, 90, 118]. Unfortunately, oxygen is not selective, and only a small amount of the oxygen will react with CO. The rest of the oxygen will react with hydrogen, heating up the fuel cell and reducing the overall efficiency [4]. Furthermore, to operate the fuel cell with a mixture of anode gas and pure oxygen requires a complex control system, in order to monitor oxygen levels [27].

Lastly, the anode catalyst of the fuel cell can have a different composition of metals. By using bi-metal catalysts utilizing ruthenium (Ru) and platinum (Pt), self-oxidation of CO can be accomplished [4, 27, 29, 90]. However, this method has to be implemented during the manufacturing of the fuel cell. A commercially obtained fuel cell can not be altered to comply with this requirement.

Carbon monoxide has a higher oxidation potential than hydrogen. Therefore, the CO molecules adsorbed to the platinum catalyst will remain on the surface. If this mechanism of CO-poisoning is associated with the coverage of CO (\(\theta_{CO}\)), then the relationship between the current density of the gas mixture (\(j_{H_2,CO}\)) related to the current density of pure hydrogen (\(j_{H_2}\)) can be given by [12]

\[
j_{H_2,CO} = j_{H_2}(1 - \theta_{CO})^2.
\]

(4.1)

It is clear from (4.1) that the coverage of CO on the platinum electrode surface
4.2. Influence of CO on the fuel cell stack

4.2.2 Influence of 30 ppm CO

The influence of 30 ppm CO on the fuel cell performance was tested, and the steady-state polarization was recorded as is shown in Fig. 4.4. In comparison with Fig. 4.3, the output voltage of the cartridge differs significantly.

The transition time used for the characteristic shown in Fig. 4.4 is 60 s. The fuel cell is CO-tolerant for currents below 4 A. For higher currents, the output voltage drops below 15% of the hydrogen voltage level. The gray line and the gray dashed line shown in Fig. 4.4, show the CO-tolerance lines for the voltage-current and power-current characteristics, respectively. If the voltage of the CO gas mixture drops below the gray line, the fuel cell does not work in CO-tolerant mode.

Once the catalysts are poisoned with CO, the performance of the fuel cell will drop further over time. This can be demonstrated by lowering the anode
gas outlet flow to the amount exactly needed for the non-reactive gases to leave the fuel cell. In other words, the anode outlet flow does not contain hydrogen. If the electrical load is switched on at a certain moment, the individual cells will react to the CO mixture as is seen in Fig. 4.5.

The electrical load is switched on at $t = 20 \text{ s}$ from 0 A to 6 A. As is shown in Fig. 4.4, the fuel cell is not CO-tolerant for load currents above 4 A, which means that the fuel cell will get poisoned quickly. At $t = 60 \text{ s}$, the voltage of cell # 4 ($V_4$) drops below 0 V. Cell # 4 gets negatively biased by the other cells in the stack. From this moment on, the cartridge is not capable of maintaining the a constant output current of 6 A to the electrical load, but delivers an output current around 3 A.

Furthermore, cell # 3, which initially also dropped below 0 V, recovers to a positive voltage. However, the voltage level of cell # 3 stays lower than the voltages of cells # 1 and # 2. This effect gives an indication of the internal gas-channel layout of the cartridge. Because the CO-concentration will increase as a result of depletion of hydrogen through the anode gas channel, it is expected that the cells are chemically connected in series, starting at cell # 1 and ending at cell # 4.
4.2. Influence of CO on the fuel cell stack

In contrast to the chemical series connection from cell #1 to #4, the electrical series connection of the cells starts from cell #3 at the lowest potential via cell #4 and #1 to cell #2 at the highest potential. For clarity, the test-setup including gas-channel layout used for the measurement is shown in Fig. 4.6.

4.2.3 Self-oxidation of CO

Over hours of repeated measurements, cells #1 and #2 decrease slowly in output voltage, until cell #2 drops below 0 V and starts oscillating at a self-oxidizing frequency of $f_{so} = 0.125$ Hz, shown in Fig. 4.7. Cell #1 does not present this oscillating behavior but its voltage is low compared to the voltage shown in Fig. 4.5. Cells #3 and #4 are not included here because their behavior remains identical as in Fig. 4.5.

This oscillating behavior is described in the literature as CO self-oxidation [29, 98, 116]. However, this phenomenon is, to our knowledge, not reported yet for fuel cells having pure platinum catalysts.

Experimental observation indicates that the electrical potential of the individual cells is correlated to this phenomenon. This assumption was confirmed by investigating the cartridge with a reordered electrical layout, so that cell #1

Figure 4.6: Schematics of test-setup including gas-channel layout of fuel (dashed lines) and electrical connections (full lines).
has the lowest potential and cell # 4 the highest, as is shown in Fig. 4.8. The test led to the same results as presented in Fig. 4.7 for cells # 3 and # 4. Cells # 1 and # 2 gave low output voltages, comparable with the results of cell # 1 in Fig. 4.7.

To eliminate the possibility that the oscillations are related to the connecting wires, control circuitry or the DSP measuring system, the CO self-oxidizing test was repeated without any connection made to the measurement system.

Figure 4.7: CO self-oxidation of cell # 2 of cartridge # 0679.

Figure 4.8: Test-setup including gas-channel layout of fuel (dashed lines) and electrical connections (full lines). The electrical series connection of the cells have been altered compared to Fig. 4.6.
4.3 Regeneration of a CO-poisoned PEM fuel cell

Figure 4.9: Oscilloscope capture of CO self-oxidizing behavior of cell # 4 from cartridge # 0679. All connection wires, control-electronics and the DSP measurement system are removed from the test-setup for this measurement.

The cartridge (# 0679) was only connected to a load resistor, having the same resistance as the electronic load, as shown in Fig. 4.8. Cells # 3 and # 4 were monitored with an oscilloscope, and the results for cell # 4 are depicted in Fig. 4.9.

It is clear from Fig. 4.9 that the oscillations appear also without the measurement system. The frequency found in this measurement is well in the range of previous measurements. This confirms that connecting wires are not responsible for the oscillations. Furthermore, it also shows that the DSP system is able to capture the measurement data very precisely.

4.3 Regeneration of a CO-poisoned PEM fuel cell

Regeneration of a CO-poisoned fuel cell can be done in several ways. In section 4.2.1 the different methods of cleaning the CO from the catalysts are described. Except for the bi-metal catalyst option, the methods can be implemented in a chemical or an electrical way. This work is specifically focused on electrically regenerating a fuel cell.
The electrical pulsing technique, which is one of the electrical regeneration methods, is based upon short circuiting, an idea used earlier to humidify the fuel cell membrane \[50\]. Appendix C gives the optimization of the short-circuiting technique for humidification of the membranes, conducted on a cartridge. The operating temperature of the PEM fuel cell will increase during the pulses, which would imply that this technique could also be used to clean the catalyst surface from CO-poisoning. However, measurements have shown that the poisoning rate increases when short circuiting the membranes.

Although short circuiting a fuel cell with pure platinum catalysts was disappointing, literature indicates that this technique is very promising in combination with bi-metal catalysts, such as Ruthenium-Platinum \[27, 29, 98, 99\].

A closer analysis of the electrochemical structure of a hydrogen fuel cell reveals the theoretical possibility of reversing the reactions. That is to say, by applying a negative voltage pulse to the terminals of poisoned cells, with respect to their normal operation, trace amounts of oxygen could be introduced in the anode channel and the formed oxygen will oxidize the chemisorbed CO.

The mechanism of electro-oxidation of CO in an acidic environment can be described by

\[
\begin{align*}
\text{CO} + \text{Pt} & \rightleftharpoons (\text{CO-Pt}), & (4.2) \\
(\text{CO-Pt}) + \text{H}_2\text{O} & \rightleftharpoons \text{Pt} + \text{CO}_2 + 2\text{H}^+ + 2e^- , & (4.3)
\end{align*}
\]

where (4.2) represents the adsorption and desorption reaction of CO to platinum. The Pt–CO represents the bonded CO to platinum. The electro-oxidation reaction of CO is given in (4.3). In the same way, hydrogen reacts in the presence of platinum, that is

\[
\begin{align*}
\text{H}_2 + 2\text{Pt} & \rightleftharpoons 2(\text{H-Pt}), & (4.4) \\
2(\text{H-Pt}) & \rightleftharpoons 2\text{Pt} + 2\text{H}^+ + 2e^-. & (4.5)
\end{align*}
\]

The CO–Pt bond is stronger than the H–Pt bond, which results in the exclusion of hydrogen adsorption given in (4.4) \[13, 30\].

By introducing oxygen into the gas channel and by assuming that the oxidation of CO or H\(_2\) with O\(_2\) will only occur in the presence of an adsorbent, the oxidation of adsorbed CO with oxygen can be described by

\[
\begin{align*}
\text{O}_2 + 2\text{Pt} & \rightleftharpoons 2(\text{O-Pt}), & (4.6) \\
(\text{CO-Pt}) + (\text{O-Pt}) & \rightarrow 2\text{Pt} + \text{CO}_2. & (4.7)
\end{align*}
\]
4.3. Regeneration of a CO-poisoned PEM fuel cell

The oxidation of carbon monoxide as described in (4.7) can contribute to removing chemisorbed CO from the platinum catalyst. Furthermore, it is assumed that reaction (4.7) proceeds only in one direction. However, the introduced oxygen will also react with the adsorbed hydrogen in the following way

\[ 2(\text{H–Pt}) + (\text{O–Pt}) \rightarrow 3\text{Pt} + \text{H}_2\text{O}. \]

(4.8)

Reaction (4.8) is also assumed to proceed in one direction. This reaction is not desirable, because it does not contribute to the generation of electricity [13].

For the purpose of electrically regenerating the fuel cell the measurement setup must be adapted, which will be described in section 4.3.1. After that, the measurement results are presented, and finally the regeneration pulsing method is optimized.

### 4.3.1 Regeneration setup

The fuel cell test-setup must be adjusted in order to perform the measurements. Therefore, a programmable voltage source ("Source") is added to the test setup. Figure 4.10 shows how the source is attached to a single cell. It is possible to switch the source to the other cells of the cartridge using a network of parallel switches.

The current and voltage of the source from Fig. 4.10 are controllable by the DSP system. The source is powerful enough to reach voltages below -2.3 V with respect to the “normal” cell voltage, which should be enough to start electrolysis [82].
In section 4.2 it is shown that electrical reordering of the individual cells of the cartridge benefits the behavior of the stack with respect to CO self-oxidation. Therefore, the test-setup is expanded with three relay switches (S1, S2 and S3) as is shown in Fig. 4.11. These switches are controlled by the DSP system, so that the stack can be automatically reordered in two configurations.

The dashed lines in Fig. 4.11 shows the cell order as is presented in Fig. 4.8. If the switches are positioned in the opposite way, then the cells are electrically ordered as is shown in Fig. 4.6.

### 4.3.2 Regeneration of poisoned cells

The regeneration of the CO-poisoned fuel cells is performed by programming the external source of Fig. 4.10 to a voltage amplitude of \( A_p = -2.3 \, V \) with respect to the normal cell anode potential. After 20 seconds, a load current of 4 A is switched on. At \( t = 60 \, s \), the pulse source is switched on, and a negative voltage pulse is applied to a single cell of \( V_{cell} = -2.3 \, V \). The load current is switched off at the moment that one of the cell voltages drops below 0 V. Figure 4.12 shows the results of the test using gas #3 (see Table 4.1). The mark “EOM” indicates the End Of Measurement, that is, the switching off of the load current.
4.3. Regeneration of a CO-poisoned PEM fuel cell

Figure 4.12: Regenerative pulses on individual cells of cartridge #0679. The stack was ordered from cell #3 at the lowest potential via cell #4 and #1 to cell #2 at the highest potential. The mark “EOM” indicates the End Of Measurement.

It must be noted that the cells of the cartridge were ordered as is shown in Fig. 4.6. Cells #1 and #2, which have the highest potential of the stack, are regenerated very well due to the negative voltage pulse. The performance improved with 500%, and the CO self-oxidation disappears completely. The two lowest potential cells do not show significant improvement. To the contrary, after the pulse, between $t = 60\,\text{s}$ to $80\,\text{s}$, the voltages of cell #3 and cell #4 start to decline. The voltages of cell #3 and cell #4 are decreasing at an increasing rate until one of them drops below 0 V.

A conclusion of this measurement is that without reordering the cells of the fuel cell, regeneration with negative voltage pulses is not possible. In order to prove this hypothesis, a measurement script is developed, shown in Fig. 4.13.

This “automatic regeneration” script starts by comparing the individual voltages of the cells in the stack. If the voltage is lower than the CO-tolerance
boundary\textsuperscript{3}, the script marks the cell for regeneration. After the regeneration decision, the script detects if the cell with number \# is situated in the lower or the higher potential range. If the cell is in the lower potential range, the stack is reordered. If there is no potential error anymore, the cell is regenerated, and after the repetition time $\tau_p$ has finished, the script starts again.

The script is tested with a repetition time $\tau_p = 10$ s and a duty cycle of the pulse $D_p = 10\%$. The duty cycle is defined as the on-time of the pulse source during $\tau_p$. The amplitude of the pulse source was set to $A_p = -1.0$ V, because the currents of the external source will rise exponentially with increasing pulse amplitude to more than 60 A [52]. The gas used for this test is gas \# 4 (see Table 4.1), which is the gas containing 50 ppm CO. This is a higher concentration than is used for the measurement of Fig. 4.12, which can result in higher poisoning rates. The results of this test are presented in Fig. 4.14.

It is clear from Fig. 4.14 that cell \# 4 poisons at the fastest rate, because this cell is regenerated most. It can also be seen that since the stack is reordered automatically, cells \# 3 and \# 4 can be electrically regenerated. Furthermore, the performance improvement is for all cells more or less equal. For all cells, the voltage doubles after a negative pulse.

\textsuperscript{3}The CO-tolerance boundary is 85\% of the voltage produced with pure hydrogen supply.
4.3. Regeneration of a CO-poisoned PEM fuel cell

Figure 4.14: Regenerative pulses on individual cells of cartridge # 0679, using automation script (I).

Figure 4.14 shows small spikes in the voltages of the non-pulsed cells at the moment of pulsing a particular cell. This behavior can be explained by the construction of the stack. The cells are placed close to each other, which results in a linkage between cells, especially between cells that are electrically hardwired, that is, cells # 1 and # 2 and cells # 3 and # 4 [52].

4.3.3 Optimization of the regeneration pulse

One drawback of applying negative pulses to the fuel cell is that it takes a significant amount of power to do this. To apply pulses of \( V_{cell} = -2.3 \, V \), the external voltage source has to deliver \( I_{source} \approx 55 \, A \) or more. This may lead to excessive losses in wires and it consumes energy generated by the fuel cell stack. Therefore, the pulse amplitude with respect to the cell anode potential \( (A_p) \), frequency \( (f_p = \tau_p^{-1}) \) and duty cycle \( (D_p) \) should be as low as possible.

Furthermore, to make sure that the fuel cell works in CO-tolerant operation, the stack voltage may not go below 85% of its nominal voltage when it works with a pure hydrogen fuel supply. To optimize the pulses, a definition for stack efficiency is needed: Here we say that the efficiency \( (\eta_p) \) is the total surplus of
energy generated by the fuel cell stack when it operates with CO-containing fuel mixtures normalized to the energy created when utilizing pure hydrogen fuel (gas # 1, see Table 4.1), or

\[
\eta_p = \frac{E_{FC} - E_{loss}}{E_{FC,H_2}} \cdot 100\% ,
\]  

(4.9)

where \(E_{FC}\) is the energy produced by the fuel cell with poisoned gas, \(E_{loss}\) is the loss energy due to the pulse-source, and \(E_{FC,H_2}\) is the energy which would be created when the fuel cell operates with a pure hydrogen fuel supply under the same gas pressure.

In addition to the definition of the efficiency, some boundary conditions have to be defined. First, between the regenerating pulses none of the individual cell voltages may drop to or below 0 V. Second, none of the individual cells may start self-oxidizing, because those “uncontrolled” oscillations influence the control of the load. Lastly, although it may be that the highest efficiency can be reached at higher amplitudes of the pulses, the current supplied to the fuel cell must be kept as low as possible, in order to keep the design of a pulse source converter as simple as possible.

The first optimization is performed with gas # 3 (see Table 4.1). Each measurement takes 120 s, and the individual voltages of the cells, the stack current and voltage of the external pulse source are monitored. Furthermore, the pulse amplitudes range from \(A_p = -0.25\) V to \(A_p = -1.00\) V in steps of 0.25 V. The repetition time (\(f_p^{-1} = \tau_p\)) was chosen to be 1 s, 2.5 s, 5 s, 8 s and 10 s and the duty cycle (\(D_p\)) varies between 5\% and 25\% in steps of 5\%.

The efficiency is determined by (4.9), and the results of the \(A_p = -0.25\) V pulse and the \(A_p = -1.00\) V pulse are shown in Fig. 4.15.

It is clear from Fig. 4.15 that the stack efficiency performed with \(A_p = -0.25\) V varies between 65\% and 86\% (\(\tau_p = 2.5\) s and \(D = 5\%\)). This is CO-tolerant, however, some of the pulse points did not match the first boundary condition, that is, one of the voltages dropped below zero between the pulses.

Furthermore, from Fig. 4.15 it can be seen that the highest stack efficiency reached is found with \(A_p = -1.00\) V, where the repetition times and duty cycles are small. The efficiency reaches almost 94\%, and is CO-tolerant. The measurements with \(A_p = -0.75\) V are almost identical to the results with \(A_p = -1.00\) V. For \(A_p = -0.50\) V the measured points lie between the two contour plots of Fig. 4.15.

A summary of the measurement results is given in Table. 4.2. In this table, the maximum efficiencies are given for different amplitudes of the pulses. The
4.3. Regeneration of a CO-poisoned PEM fuel cell

Figure 4.15: Efficiency plots of pulse-regeneration (script I) with amplitudes of $A_p = -0.25 \, V$ (top figure) and $A_p = -1.00 \, V$ (bottom figure).

Maximum efficiency is reached at the presented repetition time $\tau_p$ and duty cycle $D_p$. The average pulse current ($I_{s,avr}$) and pulse power ($P_{s,avr}$) drawn from the pulse source are also given in Table 4.2. The most extreme overshoot of a pulse is never higher than double the value of the average pulse power and current.

For the data shown in Table 4.2, the first boundary condition for regeneration, i.e. none of the cell voltages may drop below zero in between the pulses, is not always fulfilled. In case of $A_p = -0.25 \, V$, the voltage of some cells may drop below zero.

Table 4.2: Results of the pulse optimization to make fuel cells CO-tolerant with gas # 4 (see Table 4.1) for pulse amplitudes varying between $A_p = -0.25 \, V$ and $A_p = -1.00 \, V$.

<table>
<thead>
<tr>
<th>$A_p [V]$</th>
<th>$\eta_{p,max} [%]$</th>
<th>$D_p [%]$</th>
<th>$\tau_p [s]$</th>
<th>$I_{s,avr} [A]$</th>
<th>$P_{s,avr} [W]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.25</td>
<td>86.3</td>
<td>5</td>
<td>2.5</td>
<td>7.36</td>
<td>7.25</td>
</tr>
<tr>
<td>-0.50</td>
<td>87.2</td>
<td>5</td>
<td>1.0</td>
<td>13.1</td>
<td>17.9</td>
</tr>
<tr>
<td>-0.75</td>
<td>93.0</td>
<td>5</td>
<td>2.5</td>
<td>17.7</td>
<td>35.1</td>
</tr>
<tr>
<td>-1.00</td>
<td>93.8</td>
<td>5</td>
<td>1.0</td>
<td>21.8</td>
<td>57.8</td>
</tr>
</tbody>
</table>
Figure 4.16: Efficiency plot of pulse-regeneration (script I) with amplitude \(A_p = -0.80\) V, and utilizing gas # 4 (Table 4.1).

This occurs for \(\tau_p = 10\) s and duty cycles of 20% or lower, and for \(\tau_p = 8\) s with duty cycles of 10% or less. For the other amplitudes, the individual voltages stay above zero.

The results of the first optimization show that a maximum of the stack efficiency should be found for amplitudes between \(-1.00 \text{ V} < A_p \leq -0.50 \text{ V}\), repetition time \(\tau_p\) below 5 s, and duty cycle below 10%. The second optimization round was performed for the following amplitudes: \(A_p = -0.60 \text{ V}\), \(A_p = -0.70 \text{ V}\), \(A_p = -0.80 \text{ V}\), and \(A_p = -0.90 \text{ V}\), with repetition times between 1 s and 2.5 s and duty cycles from 2% to 8%. The gas used for this optimization is again gas # 4 (see Table 4.1).

The results of the second optimization show that for the amplitudes \(A_p = -0.80 \text{ V}\) and \(A_p = -0.90 \text{ V}\), the highest stack efficiencies are reached at \(\tau_p = 2\) s and \(D = 6\%\). The optimization plot for \(A_p = -0.80\) V is shown in Fig. 4.16.

A summary of the measurement results is given in Table 4.3. The average pulse power of \(A_p = -0.80\) V is 2 W higher than the average pulse power for \(A_p = -0.70\) V. However, the maximum stack efficiency is almost 3% higher, while the difference between the average pulse power for \(A_p = -0.80\) V and \(A_p = -0.90\) V is 6.3 W and the efficiency increases with only 0.6%. Therefore,
an amplitude of $A_p = -0.80 \, V$ is preferable over higher or lower amplitudes.

The hypothesis that negative pulses applied to the cell terminals result in electrolysis of water in the anode channel of the fuel cell can not be confirmed, because the increase in efficiency also occurs with much lower negative voltage pulses than the theory predicts for electrolysis ($\approx -1.23 \, V$). Of course, this value is sensitive to temperature and pressure effects [82]. In the future, thorough investigation of the exact cause of the increase in CO-tolerance due to negative pulses and its reactions in the anode channel should be done.

### 4.3.4 Regenerating under higher CO concentrations

One of the problems of using higher CO concentrations in the fuel cell feedstock, is that the poisoning rate increases, as can be seen by comparing Figs. 4.12 and 4.14. In the former case, the CO concentration is 30 ppm, while in the latter case the concentration is 50 ppm.

Therefore, the regeneration script was replaced, the new flow diagram being shown in Fig. 4.17. The major changes compared to Fig. 4.13 are that there is no check on the voltage of the lowest cell related to the hydrogen voltage level, and the cell that is regenerated, is excluded from the next evaluation for lowest voltage. In other words, the cell with the lowest voltage not recently regenerated is pulsed.

It was expected that with fast repetition times between the pulses, none of the cell voltages will drop below 0 V. Furthermore, the voltages of the cells that suffer less from poisoning do not drop too much before they get regenerated.

Another advantage of using this regeneration script is that no preliminary knowledge of the fuel cell is needed for regeneration.

The optimization was conducted for four different amplitudes, that is, for $A_p = -0.75 \, V$, $A_p = -1.00 \, V$, $A_p = -1.25 \, V$, and $A_p = -1.50 \, V$. The repetition time of the pulses varies between 1 s and 5 s in steps of 1 s and the duty cycle is changed between $D_p = 1\%$ and $D_p = 4\%$.

<table>
<thead>
<tr>
<th>$A_p [V]$</th>
<th>$\eta_{p,\text{max}} [%]$</th>
<th>$D_p [%]$</th>
<th>$\tau_p [s]$</th>
<th>$I_{s,\text{avr}} [A]$</th>
<th>$P_{s,\text{avr}} [W]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.60</td>
<td>88.4</td>
<td>8</td>
<td>2.5</td>
<td>8.94</td>
<td>12.2</td>
</tr>
<tr>
<td>-0.70</td>
<td>90.0</td>
<td>8</td>
<td>2.5</td>
<td>11.9</td>
<td>19.1</td>
</tr>
<tr>
<td>-0.80</td>
<td>92.7</td>
<td>6</td>
<td>2.0</td>
<td>11.8</td>
<td>21.2</td>
</tr>
<tr>
<td>-0.90</td>
<td>93.3</td>
<td>6</td>
<td>2.0</td>
<td>13.9</td>
<td>27.5</td>
</tr>
</tbody>
</table>
The results are presented in Table 4.4. In contrast to the previously presented optimization figures, each pulse amplitude is associated with two average source currents and average pulse powers, which needs some explanation.

The first value of the pulse current amplitude is related to a highly poisoned cell, while the second value is related to a healthy cell. This is graphically represented in Fig. 4.18. In the top figure the current released by the external source is plotted against time, while in the bottom figure the cell voltages of cell #3 and #4 are given. Cell #4 is obviously more affected by CO-poisoning than cell #3. The external source has to produce a higher voltage in order to pulse cell #3 to (in this case) \( V_3 = -1.25 \text{ V} \). The voltage of the poisoned cell is much lower, and thus is the difference in voltage to overcome much smaller, and thus the current of the source is less.
In Fig. 4.19 the efficiency as defined in (4.9) is plotted for an amplitude of $A_p = -1.25$ V. The stack efficiency reaches values of more than 98% against pure hydrogen utilization. This means that the excessive power loss (156 W) of some of the pulses is compensated in a better performance of the cartridge.

Regeneration script II gives high stack efficiencies. However, the extra cost of high power pulses in contrast to more constant and lower current pulses for the external source can be a decisive consideration of using method I.

Therefore, a final implementation of the regeneration was made by combining the two scripts (I and II) from Fig. 4.13 and Fig. 4.17. Script III only regenerates a cell if its voltage drops below 85% of the hydrogen level. Furthermore, it is not allowed to regenerate the same cell if it was regenerated in the previous period. The results of these tests are summarized in Table 4.5.

It can be seen in Table 4.5 that for all the investigated amplitudes ($A_p$), pulses of $\tau_p = 5$ s with a duty cycle of $D_p = 2\%$ are found to be the optimal regeneration algorithm. It can also be seen, in comparison to Table 4.4, that the maximum efficiency is 1.5% lower with script III. However, the highest average pulse power needed is three times lower than the highest average pulse power needed for the regeneration method II. This advantage will reduce the complexity of the pulse-source design. Moreover, if the maximum efficiency from optimization script III (that is; $\eta_p = 97.2\%$ at $A_p = -1.00$ V) is compared with the same pulse amplitude ($A_p$) regeneration script II (that is $\eta_p = 96.1\%$), then it can be concluded that regeneration script III gives higher efficiencies with lower pulse powers.

The measurement results show that regeneration with knowledge of the fuel cell hydrogen performance is preferable over scripts without that knowl-

<table>
<thead>
<tr>
<th>$A_p [V]$</th>
<th>$\eta_{p, max}$ [%]</th>
<th>$D_p$ [%]</th>
<th>$\tau_p$ [s]</th>
<th>$I_{s, avr} [A]$</th>
<th>$P_{s, avr} [W]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.75</td>
<td>93.6</td>
<td>4</td>
<td>5</td>
<td>6.36</td>
<td>7.88</td>
</tr>
<tr>
<td>-1.00</td>
<td>96.1</td>
<td>4</td>
<td>5</td>
<td>8.90</td>
<td>15.3</td>
</tr>
<tr>
<td>-1.25</td>
<td>98.3</td>
<td>3</td>
<td>5</td>
<td>12.7</td>
<td>28.1</td>
</tr>
<tr>
<td>-1.50</td>
<td>98.9</td>
<td>2</td>
<td>4</td>
<td>16.2</td>
<td>43.6</td>
</tr>
</tbody>
</table>
Figure 4.18: External source current pulses (in the top figure) for pulsing poisoned (cell # 4) and healthy (cell # 3) (in the bottom figure). Automation script II is executed and gas # 5 in Table 4.1 is applied.

Figure 4.19: Efficiency plot of the performance of the fuel cell utilizing gas # 5 (see Table 4.1) and regenerative pulses (script II) of $A_p = -1.25\, V$. 
edge. However, in the future further investigation of the optimization script should be performed. In terms of efficiency, script II presented in Fig. 4.17 gives the best results. If, on the other hand, the energy loss, and thus the additional hydrogen used, is considered, then it can be more beneficial to use adjusted script I, that is with the exclusion of a previous cell.

4.4 Conclusions

In this chapter, the possibility of producing hydrogen rich gas from biomass was considered. The hydrogen contents of the gas mixture can reach levels of about 60%. It is also possible, by optimizing the gasification method, to reduce poisonous gasses, like CO, to levels below 1.5%. However, these levels of CO will still pollute the platinum catalysts of the fuel cell at high rates. Therefore, additional cleaning of the biogas is needed.

On the basis of measurements it is demonstrated that additional components in the hydrogen gas stream, like CO$_2$ and N$_2$, have a small impact on the performance of the fuel cell. However, small amounts of CO (as low as 30 ppm) markedly influence the performance of the fuel cell. The influence of CO can be observed in the decay of the fuel cell output voltage compared to the case of utilizing pure hydrogen. It is possible that one of the cells in a stack will drop below 0 V. It is also possible to observe low frequency oscillations of the cell voltage, with an average voltage round 0 V. These oscillations were identified as being self-oxidizing oscillations of CO from the platinum catalyst.

With respect to the behavior of the fuel cell to CO-poisoning, the order of the serial cells in a stack is important. Self-oxidizing behavior is only observed in cells at the highest electrical potential in a stack.

It is possible to electrically regenerate CO-poisoned fuel cells by forcing the

<table>
<thead>
<tr>
<th>$A_p$ [V]</th>
<th>$\eta_{p,max}$ [%]</th>
<th>$D_p$ [%]</th>
<th>$\tau_p$ [s]</th>
<th>$I_{s,avr}$ [A]</th>
<th>$P_{s,avr}$ [W]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.00</td>
<td>97.2</td>
<td>2</td>
<td>5</td>
<td>16.6</td>
<td>38.4</td>
</tr>
<tr>
<td>-1.10</td>
<td>96.4</td>
<td>2</td>
<td>5</td>
<td>18.8</td>
<td>48.0</td>
</tr>
<tr>
<td>-1.20</td>
<td>96.3</td>
<td>2</td>
<td>5</td>
<td>20.1</td>
<td>56.4</td>
</tr>
<tr>
<td>-1.30</td>
<td>97.0</td>
<td>2</td>
<td>5</td>
<td>21.6</td>
<td>64.4</td>
</tr>
</tbody>
</table>
cell terminals to a negative output voltage for a short time period. The electrical position of the cell that is regenerated is of critical importance. Only the cells at higher potential in the stack are regenerated well.

The optimization results of the shapes of the regeneration pulses show that the pulse amplitude $A_p$ has to be varied between -0.80 V for lower and -1.00 V for higher CO concentrations. The repetition time $\tau_p$ and the duty cycle $D_p$ are dependent on the regeneration method (script I, II, or III) and the CO concentration. Good results can be achieved for repetition times between 2 s and 8 s in combination with duty cycles ranging between 2% and 6%.

Finally, it is possible to operate a PEM fuel cell with pure platinum loaded catalysts on biogas with CO. Measurements show that the specific PEM fuel cell we used is CO-tolerant with a concentration of up to 100 ppm CO.
Chapter 5
Energetic, environmental and economical issues

The previous chapters have dealt with the technical path of the implementation of low-temperature fuel cells operating with contaminated feedstock, created from biomass. Although the results are promising, the success of the biomass-based electricity generation system is not only dependent on technological aspects. Economical and environmental issues do contribute to the viability of the system in total.

To give an overview of the economical and environmental impact of a biomass energy system using fuel cells, this chapter will summarize the major system issues. First, the energy balance of the different parts of the total system are investigated, and the efficiency of the PEM fuel cell is supported by measurements. From these values the energy balance is specified and compared to other electricity generation possibilities. Furthermore, the impact of the system on the environment is highlighted, and finally some economical issues are presented.

The global electricity generation system is schematically presented in Fig. 5.1. Because there is a range of parameters that can be changed, such as the method of gasification of the biomass, the cleaning method, the type of fuel cell used, and the design of the power electronic converter, it is outside of the scope of this report to include all the possibilities to derive the exact figures for the efficiencies per part of the system. Therefore, only the most representative aspects are considered.
Furthermore, the definition of efficiency is not unambiguous either. For example, in the overall efficiency of the system the logistics of the raw material can be taken into account, or not. Therefore, boundary conditions of the efficiencies are given in the overview.

5.1 Energy balance of the system

The energy balance of the system (Fig. 5.1) deals with the energy output of each block as a function of the energy input. The energy balance may start on different points, that is, it may start at the harvesting of the biomass, or even before that, but it may also start at the point where it enters the first stage of the conversion to electricity, which is the gasification step. In this chapter, the efficiency calculation will start at this first conversion step.

The efficiencies presented in the following are obtained from the literature, except for the efficiency of the fuel cell (the efficiency of the fuel cell cartridge # 1472, which was characterized in section 2.2.4, is directly measured).

Because the efficiency of the power-electronic conversion step in Fig. 5.1 is normally high (usually above 95%), easily predictable and dependent on the application, economical interest, and the investment, this step will not be taken into account for the energy balance calculation.

5.1.1 Efficiency of biomass conversion and gas cleanup

The efficiency calculation for biomass to hydrogen-rich gas conversion is highly dependent on the chosen method. If gasification in supercritical water is performed, then it should be taken into account that the process is new, and is
not yet fully optimized. On the other hand, processes that are known, like “normal” gasification of biomass, result in higher pollution ratios, and require additional cleaning steps afterwards.

Thermodynamic efficiencies found for biomass gasification in supercritical water are found up to 93% [24, 77]. But there are also negative efficiencies found for non-optimal feedstock processes [77]. This wide range of efficiencies makes a thorough analysis not possible.

There is, however, literature available about integrated biomass-cleaning conversion devices, like the so-called “Hotspot methanol processor” [38, 73], and an integrated fuel processor for portable hydrogen production [35, 36]. Both fuel processing devices are integrated with a fuel cell.

**Hotspot methanol processor**

This fuel processor operates by injecting fuel together with air into a large catalyst bed, where hydrogen is formed by partial oxidation in a localized reaction zone, called “the hot spot” [38]. The reaction that takes place is most closely represented by

\[
\text{CH}_3\text{OH} + 0.5\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2. \tag{5.1}
\]

For the hotspot methanol processor an integrated CO cleanup unit is present, operating on the basis of selective catalytic oxidation. From a gas-mixture containing 2.6% CO, 45.6% H\textsubscript{2}, 16.6% CO\textsubscript{2}, 18.2% N\textsubscript{2}, and 17% H\textsubscript{2}O, produced by the hotspot processor, the CO concentration in the outlet gas of the cleanup unit varied around 8 ± 5 ppm, and the concentration H\textsubscript{2} was reduced to 43% [38].

If the hotspot methanol processor is coupled to a PEM fuel cell system, and when the rejected hydrogen from the anode of the fuel cell is recuperated for providing energy to be used by the hotspot pre-heater, as is shown in Fig. 5.2(a), then the steady-state efficiency of the hotspot reactor reaches 95.4%, and the CO cleanup unit reaches 93.5%. The resulting efficiency of the hotspot methanol processor is \(\eta_{\text{Hotspot}} = 89\%\), referred to the higher heating value [38], which is clarified in section 5.1.2.

**Integrated fuel processor**

The integrated fuel processor operates on methanol. Its schematical layout is presented in Fig. 5.2(b). The methanol is first evaporated in the vaporizer, and fed to the reformer, where it reacts with steam in the presence of a catalyst to
a hydrogen-rich gas. The gas contains hydrogen, CO\textsubscript{2}, and small amounts of CO. The amount of CO in the fuel cell gas stream must be reduced to levels below 100 ppm. This is done in the CO cleanup reactor. The clean gas is fed to a PEM fuel cell in order to produce electricity. The left-over hydrogen from the anode of the fuel cell is directed to a burner, which will heat the vaporizer [35, 36].

In the reformer reactor, the following reactions take place

\begin{align}
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 3\text{H}_2, \quad (5.2) \\
\text{CH}_3\text{OH} & \rightarrow \text{CO} + 2\text{H}_2, \quad (5.3) \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2, \quad (5.4)
\end{align}

where (5.2) is the steam reforming reaction, (5.3) is the methanol decomposition reaction, and (5.4) is the water-gas shift reaction. From the last reaction, it can be concluded that an excess of water will reduce the production of CO. The selectivity of methanol to CO\textsubscript{2} is 97%, and to CO about 3% [35].

The polluted hydrogen-rich gas is mixed with a small quantity of air, and is then cleaned in a platinum-based catalytic CO selective oxidation reactor.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.2.png}
\caption{Sketch of an integrated solution for reforming hydrocarbons to electricity. The schematic is valid for a) the hotspot processor and b) for the integrated fuel processor.}
\end{figure}
The air is needed to oxidize CO. However, platinum is not only a good catalyst for the oxidation of CO with oxygen, but also for hydrogen. The selectivity of the CO oxidizer is assumed to be 50%, which means that an even amount of hydrogen and CO is oxidized [35, 36].

Following [35, 36], the system as presented in Fig. 5.2(b) has an exergetic efficiency of about 37%. In the calculation of that efficiency, the conversion ratio of hydrogen-rich gas to electricity in the fuel cell is assumed to be 50%. The efficiency of the fuel processor including the CO selective oxidizer is about \( \eta_{\text{Fuel processor}} = 74\% \).

### 5.1.2 Efficiency of the fuel cell

The low-temperature fuel cell has a rather difficult description of its efficiency. That is because its temperature (around 60 °C) does not give a definite indication of the state of water in (2.3).

The efficiency of a fuel cell can best be described by the ratio between the extracted electrical energy and the chemical energy released by “burning” the fuel. The change in enthalpy of formation (\( \Delta H \)) of reaction (2.3) gives the molar chemical energy for burning hydrogen. The efficiency\(^1\) of the fuel cell is defined as

\[
\eta_{\text{FC}, H_2} = \frac{\mathcal{E}_{\text{FC}}}{\Delta H} \cdot 100\%,
\]

where \( \mathcal{E}_{\text{FC}} \) is the electrical energy produced by the fuel cell with pure hydrogen feedstock.

The enthalpy of formation \( H \) and the entropy \( S \) of the reaction are dependent on the form of the water product. Table 5.1 shows the enthalpy of formation and the entropy of the reactants and products of (2.3) at standard pressure \( P^0 = 100kPa \) and room temperature \( T^0 = 298.15K \) [70].

The change in Gibbs free energy, \( \Delta G \), is used to calculate the standard reversible cell voltage \( E_{\text{rev}}^0 \) of a fuel cell, as given in (2.12). The change in Gibbs free energy can be derived from (2.6) and (2.7), and is described by

\[
\Delta G = \Delta H - T\Delta S,
\]

where \( \Delta H \) is the change in enthalpy of formation, \( \Delta S \) is the change in entropy, and \( T \) is the temperature.

\(^1\)This efficiency does not include recuperation of the heat produced by the fuel cell. If the heat is used for other processes, the efficiency will rise.
The change in enthalpy of formation can be calculated from the values in Table 5.1 as

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O(g),
\]

\[
\Delta H_{LHV} = H_{H_2O(g)} - H_{H_2} - \frac{1}{2}H_{O_2} = -241.83 \text{[kJ/mole]},
\]  

(5.7)

when the product water is in gaseous form, and

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O(l),
\]

\[
\Delta H_{HHV} = H_{H_2O(l)} - H_{H_2} - \frac{1}{2}H_{O_2} = -285.84 \text{[kJ/mole]},
\]  

(5.8)

when the water is produced in liquid form. In the former case the enthalpy of formation is referred to the lower heating value or LHV. In the latter case it is referred to the higher heating value, or HHV. The difference in enthalpy of formation is the molar enthalpy of vaporization of the water, or the latent heat [70].

The change in entropy can be calculated in the same way as the enthalpy of formation

\[
\Delta S_{LHV} = S_{H_2O(g)} - S_{H_2} - \frac{1}{2}S_{O_2} = -44.33 \text{[J/mole·K]},
\]  

(5.9)

Table 5.1: Values of the enthalpy of formation \( H \) and entropy \( S \) for the hydrogen fuel cell reaction (2.3) at \( T^0 = 298.15K \) and \( P^0 = 100kPa \) [70].

<table>
<thead>
<tr>
<th></th>
<th>( H ) [kJ/mole]</th>
<th>( S ) [J/mole·K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2O(l) )</td>
<td>-285.84</td>
<td>70.05</td>
</tr>
<tr>
<td>( H_2O(g) )</td>
<td>-241.83</td>
<td>188.83</td>
</tr>
<tr>
<td>( H_2 )</td>
<td>0</td>
<td>130.59</td>
</tr>
<tr>
<td>( O_2 )</td>
<td>0</td>
<td>205.14</td>
</tr>
</tbody>
</table>
5.1. Energy balance of the system

\[
\Delta S_{HHV} = S_{H_2O(l)} - S_{H_2} - \frac{1}{2}S_{O_2} = -163.11 \left[ \frac{J}{\text{mole} \cdot K} \right]. \tag{5.10}
\]

The Gibbs free energy can be obtained by combining (5.6) with (5.7), (5.9), and \( T = 333K \). This results in the Gibbs free energy with reference to the lower heating value \( (\Delta G_{LHV} = -227.07 \text{kJ/mole}) \), while (5.6), (5.8), (5.10), and the same temperature result in the Gibbs free energy referred to the higher heating value \( (\Delta G_{HHV} = -231.52 \text{kJ/mole}) \).

The enthalpy of formation, the entropy, and the Gibbs free energy can also be calculated by using the molar heat capacity for steam, hydrogen and oxygen [70]. The found values for the enthalpy of formation, entropy, and the Gibbs free energy are verified with the molar heat capacity calculation method. The difference between the two calculation methods is less than 0.04%, which makes it legitimate to use it in further calculations.

As the change in Gibbs free energy specifies the maximum electrical “work” that can be performed from a mole of hydrogen, and the change in enthalpy of formation gives the maximum of chemical energy per mole hydrogen, then it can be seen that with the definition of efficiency given in (5.5), there is a limit in this efficiency. This limit can be expressed as

\[
\eta_{FC,\lim} = \frac{\Delta G}{\Delta H} \cdot 100\% \tag{5.11}
\]

which is for the lower heating value \( \eta_{FC,\lim,LHV} = 93.9\% \), and for the higher heating value \( \eta_{FC,\lim,HHV} = 80.9\% \). If these theoretical limitations of efficiency are compared to the Carnot limit of approximately 65% when hydrogen is “burned” spontaneously at 585 °C to do work and the exhaust temperature is 25 °C [70], then it is clear that the limits \( \eta_{FC,\lim} \) are quite high [70].

Efficiency measurements of a cartridge fed with pure hydrogen

The efficiency \( \eta_{FC} \), as defined in (5.5) is obtained from measurements on the fuel cell cartridge # 1472. For this measurement, the cartridge is fed with pure hydrogen. The purge valve is closed, so that all hydrogen that is put into the cartridge must be converted to water, or is lost in another way. Between the cartridge and the hydrogen canister a flow meter is placed. The flow meter
was calibrated with a “soap film flow meter”\(^2\). This is not the most accurate way of calibrating a flow meter, but it will give a good indication of the amount of hydrogen that is fed to the cartridge. The pressure of the hydrogen is kept constant.

In order to determine the fuel cell efficiency, the steady-state characteristic of the cartridge is correlated to the amount of hydrogen used. Every steady-state current set point is imposed for a minute. Since the flow meter is calibrated in dl/min, the measured value results in the volume of the hydrogen used in one minute. The mass of the used hydrogen is calculated from the volume using its density at room temperature (0.0899 g/l). The amount of moles (0.496 mole/g) is then calculated from the measured mass of the hydrogen used [84].

To proceed from the amount of hydrogen (in mole) to chemical energy, the problem of higher or lower heating value arises. Therefore, both energy levels are calculated, as plotted in Fig. 5.3 (\(\eta_{LHV}\) for the lower heating value, and \(\eta_{HHV}\) for the higher heating value), together with the electrical output power \((P_{FC})\).

It can be seen in Fig. 5.3, that the maximum efficiency is reached at a quarter of the output current needed to reach the maximum output power. This is also mentioned in literature [106]. The efficiency (LHV) has a maximum of 54%, which is lower than other fuel cell systems presented in the literature [102, 106].

Furthermore, it can be seen in Fig. 5.3 that the efficiency drops to 37% (LHV) in the maximum power point \((I_{FC} = 10.5A)\). Hence, for a given application a trade-off should be chosen in order to optimize the most economical way of using the fuel cell.

**Efficiency with contaminated feedstock**

Most likely the fuel cell is not used with pure hydrogen. Therefore, the efficiency calculated previously should be multiplied by the efficiency value \((\eta_p)\) of the pulsed operation under contaminated feedstock, that is CO poisoning. Following the results in section 4.3, the efficiency that can be reached with the regeneration pulsing technique is more than 98%, that is using regeneration script II.

\(^2\)A soap film flow meter calibration works by injecting gas in a calibrated tube with known volume markings, where a soap film travels in a certain time depending on the flow of the gas between two predefined marks on the tube, that is a predefined volume. If a standard flow meter is connected in series with the soap film flow meter, the value of the flow meter is correlated to the volume of gas that passes in a certain time through the flow meter.
So, the maximum efficiency that can be expected from the measured fuel cell system suffering CO contamination mitigated by electrical regeneration is expected to be

$$\eta_{FC,max} = \eta_{FC} \cdot \eta_p = 54\% \cdot 98\% = 52.9\%,$$

(5.12)

where $\eta_{FC}$ is the efficiency of the fuel cell under pure hydrogen feedstock, as is shown in Fig. 5.3, and $\eta_p$ is the efficiency of the regeneration of CO poisoning, as defined by (4.9).

### 5.1.3 Exergy of the system

The term *Exergy* is defined as “the maximum work that can be done by a matter or a certain amount of energy in relation to its environment” [109, 121]. Fairly good examples of what exergy exactly means, can be found in [121].
The fuel processors, as discussed earlier, use the fuel cell anode gas and also its heat. These “products” were not taken into account in the fuel cell efficiency definition from the previous subsection. If the heat is used, then the efficiency will have a higher value, which means that the exergetic losses of the fuel cell are lower.

For the exergetic analysis in [35, 36], calculations were made for a fuel cell that has a lower heating value efficiency of 50%. The measured efficiency of the fuel cell in this work is also about 50%, which means that the exergy analysis in [35] provides a good indication of what can be expected from a current biomass-fuel cell system, that is, the exergetic efficiency from (bio-)methanol to electricity is indicated to be 37% [35, 36].

However, the fuel cell LHV efficiency has a great impact on the overall exergy loss [35]. A small increase in LHV efficiency of the fuel cell results in a large decrease of total exergy loss [35]. At present time the efficiency of PEM fuel cells has increased to over 60% [106], so a great gain in total system efficiency may be expected within a few years.

### 5.2 Environmental impact

Disturbing reports on climate change reach the news with increasing frequency, with a climax in February 2007, when the Intergovernmental Panel on Climate Change (IPCC) concluded that global warming is most probably caused by human activities [65]. Since 1750, the concentration of greenhouse gases like carbon dioxide ($\text{CO}_2$), methane ($\text{CH}_4$), and nitrous oxide ($\text{N}_2\text{O}$) has dramatically increased [65, 78, 105].

In the last century the average temperature of the earth has increased with 0.7 $^\circ\text{C}$, and it is expected that it will increase to between 1.5 and 6 $^\circ\text{C}$ at the end of this century, depending on the actions taken concerning greenhouse gas emissions [79, 78, 105]. The rise in temperature will eventually lead to a rise in sea-level, longer grow-seasons, and softer winters with more extreme weather [79, 78, 105].

The possible negative scenarios are acknowledged by many countries, and the will to work on a global reduction of greenhouse gasses is stated in the Kyoto Protocol$^3$ [93, 101]. The countries of the European Union (EU) have

---

$^3$Unfortunately, the largest polluting country in the world, that is the United States of America [25], does not want to agree with the protocol, because developing countries are not, or less restricted, in greenhouse gas emissions [93].
tightened the protocol with a restriction on the maximum allowed global temperature rise of 2 °C. Therefore, industrial countries should reduce greenhouse gas emissions to between 15 to 30% in 2020 [105]. The most important options to do this, are to invest in CO₂ neutral energy sources, filter and capture CO₂, reduce greenhouse gas emissions, reforestation, and promote sustainable forest management [105].

This work attempts to contribute to the technical implementation of the first mentioned action to stabilize the CO₂ content in the atmosphere, namely to research a CO₂ neutral energy source. A system containing biomass as energy source can be less polluting for the environment than systems using fossil fuels. This is true for an energy flow as is given in Fig. 5.4.

The CO₂-neutral conversion shown in Fig. 5.4 can be broken down in different ways, that is, one could harvest the biomass, without reforestation, or the biomass is used for energy generation, but not over the complete cycle. This can be the case when the biomass is harvested in a different continent, and the means of transport to the generation plant is done with fossil fuels. Following [93, 101], the contribution to greenhouse gas emission from navigation and aviation is not restricted in the Kyoto Protocol, because it is not clear who is responsible for that emission (most of the emissions will occur in international territories). This raises the question of how sustainable the energy from bio-oil really is [41]. Nevertheless, using biomass as a primary source of energy will
shift the balance of CO\(_2\) emission more towards a CO\(_2\)-neutral conversion, and thus will help to achieve the aims of the Kyoto Protocol.

The Kyoto Protocol offers countries the possibility to invest in other countries in order to gain Emission Reduction Units (ERU). One ERU is equal to one megaton CO\(_2\), so investing in emission reduction in other countries will help to achieve the Kyoto goal. These investments can be done in several ways, and one of them is to invest in so-called “sinks”. A sink is a CO\(_2\) container of biological origin, or just biomass. If these sinks are used only as carbon containers, it will reduce the CO\(_2\) concentration in the atmosphere. However, if the biomass is used for energy generation, then there will be no or less reduction of CO\(_2\) [93].

5.3 Economics of the system

One of the key issues of a new technology is the economical potential of the system. In other words, is it profitable to invest in a biomass-fuel cell generation system or not? In view of the environmental arguments, which were summarized in section 5.2, it has potential to invest in systems similar to the one presented in this report, because industrial countries, which have agreed with the Kyoto Protocol, are obliged to reduce CO\(_2\) emissions.

An economical question arises: is the system as described, capable to compete with other energy generation systems that are already available? The biomass-fuel cell system as described in section 5.1 is a system for small energy demands. Therefore, it could be compared to other low power systems\(^4\), like battery systems, and small internal combustion engines.

If the energy balance analysis starts from the same fuel, as shown in Fig. 5.5(a) for methanol, then the chemical to electrical conversion efficiency of the fuel processor-fuel cell system from section 5.1 is between 37 and 45\%. The conversion efficiency from a power plant-battery system lies between 25 and 40\%, depending on the battery type, and the efficiency of a combustion engine ranges between 7 and 27\%, depending on the size of the combustion engine. If the combustion engine is small, that is for powers below 1 kW, then the efficiency is comparable with the lower figure, while for large combustion engines, that is larger than 100 kW, the higher figure is applicable [35, 36, 38, 73].

If, however, a methanol plant with an exergetic efficiency of about 55\% [36] is considered in the efficiency calculation for the fuel processor-fuel cell system,

\(^4\)For this comparison, a maximum electrical power of 10 kW is considered.
as is presented in Fig. 5.5(b), then the total system efficiency will drop to about 21 to 25%. Of course, the internal combustion engine system should also start from its raw material, which is crude oil. The conversion efficiency of crude oil to gasoline is 90%, which brings the maximum obtainable efficiency of the engine between 6 and 24%. The best efficiency of the internal combustion engine system is comparable to the fuel processor-fuel cell system. Energetically, this makes the biomass-fuel cell system a promising alternative for the future.

### 5.3.1 Energy availability

One of the questions that arises is if it is possible to obtain the energy demand of the world, which is 400 EJ to date [88], from sustainable energy sources. An overview of the yearly amount of available sustainable energy is given in Fig. 5.6. As a comparison, the global energy use (left top box), and the amount of
fossil fuels\textsuperscript{5} (boxes at the right side) are also shown in the figure [34, 85, 88]. Biomass is not necessarily more expensive than fossil fuels, as is illustrated in Fig. 5.7 [42]. However, the current production costs for electricity from various sustainable energy sources\textsuperscript{6} vary between 0.04 $\text{€}$/kWh and 0.80 $\text{€}$/kWh, while the costs for electricity from fossil fuels range between 0.03 $\text{€}$/kWh and 0.05 $\text{€}$/kWh [88]. This makes the current production techniques not yet competitive with fossil fuels.

### 5.3.2 Cost of a fuel cell

The fuel processors described in section 5.1 are not commercially available, so a reasonable description of their cost is not available. The PEM fuel cell, however, is commercially available, and a recent cost analysis is also accessible [26].

Figure 5.8 shows the relative costs of the different parts of a 80 kW fuel cell stack [26]. As can be seen in the figure, the electrodes are the most cost-intensive parts of the stack, followed by the membrane, gas diffusion layers

\textsuperscript{5}For the potential fossil fuel energies, the identified and additional conventional and non-conventional oil reserves, the identified and additional conventional gas reserves, and identified coal reserves are used in Fig. 5.6 [88].

\textsuperscript{6}The production cost for electricity from biomass ranges between 0.07 $\text{€}$/kWh and 0.19 $\text{€}$/kWh.
Prices of fuels at industrial energy plants in baltic countries (min, average and max, in 2004).

Figure 5.7: Biomass may be cheaper than fossil fuels [42]. Note that there is no cost indication of biomass at this moment from reliable literature.

(GDL), and the bipolar plates. Additional costs are the assembly of the stack, and the Balance Of System (BOS), which is a collection of construction materials, not belonging to other categories.

In comparison to earlier cost models, the relative electrode costs have increased significantly (from between 43% and 52% to 77%) [9]. The electrode costs are mainly related to the platinum catalyst. Although the platinum loading has decreased over the years (from 0.8 mg/cm² in 2000 to 0.3 mg/cm² in 2004 [26]), the price of platinum has significantly increased, as can be seen in Fig. 5.9 [67].

The price per troy ounce of platinum has increased since half 2001 from about 400 $/troy oz to over 1200 $/troy oz. The cost analysis described in [9] used prices of before 2000, while [26] describes the costs of the fuel cell at the end of 2005.

The addition of Ruthenium as catalyst in fuel cells was cost effective until the end of 2006. The Ruthenium prices increased exponentially in the last half
Figure 5.8: Relative costs of the different parts of a PEM fuel cell stack (80 kW) for transportational purposes [26].

Figure 5.9: Cost development of Platinum and Ruthenium in $ per troy ounce (1 troy oz ≈ 31.10 gr) in the period from July 1992 to February 2007.
5.4. Conclusions

The fuel cell stack baseline cost is $67/kWe\textsuperscript{7} (net electric power) \cite{26}. In the calculation, the power density of the membrane was assumed to be 600 mW/cm\textsuperscript{2}. The electrode costs represent 77\% of the total cost, which is due to a higher platinum loading (0.75 mg/cm\textsuperscript{2}) for the 2005 cost analysis in contrast to the 2004 analysis. The platinum loading can, however, be reduced to 0.3 mg/cm\textsuperscript{2}, as was used in the 2004 analysis. This would reduce the overall price of a fuel cell stack significantly (down to $45/kWe). The price analysis is based on a production volume of 500,000 units per year \cite{26}.

The goal for a fuel cell powertrain cost for passenger vehicles was set to $30/kWe in 2015 by the U.S. Department of Energy (DOE). With a fuel cell stack as described above, the total powertrain cost is estimated to date at $125/kWe. To accomplish the DOE goal, the cost of the fuel cell stack should decrease to $20/kWe. The 2005 target cost for the fuel cell stack was set to $65/kWe, which was obtained \cite{26}.

5.4 Conclusions

If the energy balance of a fuel cell generation system based on biomass feedstock is compared with other electricity generation systems, then it can be concluded that such a system is feasible. Compared to the efficiency of an internal combustion engine (between 6 and 24\%), the fuel processor - fuel cell system exergetic efficiency (between 21 and 25\%) is already competitive.

The amount of sustainable energy available on the earth is more than enough to fulfil the energy demand of the modern society. A combination of different sustainable energy generation systems will contribute to a CO\textsubscript{2}-neutral balance. More efforts than described in the Kyoto Protocol are needed to reach the goal of less than 2 \degree C rise in global temperature in 2100, and the biomass - fuel processor - fuel cell system can contribute to that goal.

To make the transition from an internal combustion engine to a fuel cell based propulsion system in automotive application on economical grounds, the price of a fuel cell stack per kWe must be reduced from $67 now, to $20 in 2015. However, the decision for this transition should not be made only on the basis of economical arguments, but also on environmental issues.

\textsuperscript{7}The commercial price of a fuel cell stack is to date about €1000/kWe \cite{83}.
Part III

Conclusions
Chapter 6
Conclusions and recommendations

6.1 Conclusions

Characterization, analysis and modeling of PEM fuel cells

Analysis of a fuel cell was done by measuring single cells and a series stack of cells. The electrochemical steady-state theory is supported by measurements on both single cells and stacks. Measurements show that the electrochemical theory of a single cell may be used on a stack of cells.

Measurements also show that the oxygen supply has a major influence on the performance of the stack. A higher air flow results in a higher output power ($P_{FC}$) and a higher limiting current ($I_{lim}$). On the other hand, aging reduces the performance of the fuel cell. Measurements show that the internal resistance ($R_{int}$) of an aged stack is higher than that of a new one.

The steady-state scan direction of the measurement, that is the sequence increment of the discrete current steps ($I_{FC}$), influences the output voltage level ($V_{FC}$) of a stack. This effect can be eliminated by adjusting the transition time ($\tau$) of the steady-state measurement. The steady-state voltage of a fuel cell is dependent on the transition time of the fixed current. Therefore, it is better to use the term “quasi steady state” instead. The quasi steady state is the fuel cell steady-state characteristic fixed to a certain transition time.

The dynamics of a fuel cell were researched using a large-signal (step re-
response), and a small-signal measurement technique (electrochemical impedance spectroscopy). Electrochemical impedance spectroscopy (EIS) gives much insight into the impedance of the fuel cell. The data recorded with this measurement technique can be implemented in an equivalent electrical circuit consisting of resistors, capacitors and an inductor. Measurement results show that a third order equivalent circuit represents the impedance of a fuel cell stack better than a second order impedance model.

Steady state, step response, and impedance spectroscopy measurements result in three different models for a fuel cell. For simulations, it would be convenient to use just one model capable of simulating all three modes. Such a model is the dynastatic model, which combines the dynamic and static fuel cell behavior in a single model.

The dynastatic model is constructed using electrochemical impedance spectroscopy data to find the values of the resistor parameters and an indication for the capacitor and inductor values of the third order equivalent circuit. The two double layer resistors ($R_{DL}$ and $R_R$) are non-linearly dependent on the output current ($I_{FC}$). The bulk resistor ($R_{\infty}$) and the adsorption resistor ($R_A$) may be assumed constant. Once the internal resistance ($R_{int}$) is known, the open circuit voltage source ($E_{FC}$) of the equivalent circuit is fixed. In order to reduce the simulation error at no load, an estimation of the internal current ($I_n$) of the fuel cell is made. The additional internal current parameter is not only necessary to reduce the steady-state error, but also to reduce the error of the step response. Finally, the indicative values of the capacitors ($C_{DL}$ and $C_R$) and inductor ($L_A$) from EIS can be used to find the optimal values with respect to the step-response measurements. When the capacitors and inductor values are fitted, the dynastatic model is complete.

The dynastatic model provides a way to obtain the state-of-health of the fuel cell with respect to aging. The bulk resistor ($R_{\infty}$) provides a firm indication of aging. When the fuel cell is excited with a small sinusoidal signal of about 100 Hz superimposed on an arbitrary DC current ($I_{DC}$), the bulk resistor is found. For aged cells, this parameter becomes significantly higher than for new cells.

Furthermore, the dynastatic model also gives information about the oxygen supply. Due to the elimination of the limiting current ($I_{lim}$) parameter from the open circuit voltage source ($E_{FC}$), no direct parameter of concentration limitation is provided by the model. However, two parameters deviate greatly due to a changed air flow, that is the second double layer capacitor ($C_R$) and the internal resistance ($R_{int}$). It is possible to determine the second double layer capacitor around 1 Hz, but this parameter is difficult to use in situ because it
6.1. Conclusions

needs a lot of computational power to obtain and compare. An easier way to determine concentration failure of the fuel cell system is the measurement of the internal resistance \( R_{int} \) at a system current \( I_{FC} \) approaching zero. This parameter will deviate due to concentration loss, but, in contrast with aging, it is less dependent on the bulk resistance \( R_{\infty} \).

**Contaminated feedstock and fuel cells**

The possibility of producing hydrogen rich gas from biomass was considered. The hydrogen contents of the gas mixture can reach levels of about 60%. It is also possible, by optimizing the gasification method, to reduce poisonous gasses, like CO, to levels below 1.5%. However, these levels of CO will pollute the platinum catalysts of the fuel cell very fast. Therefore, additional cleaning of the biogas is needed.

On the basis of measurements it is demonstrated that additional components in the hydrogen gas stream like \( \text{CO}_2 \) and \( \text{N}_2 \) have a small impact on the performance of the fuel cell. However, small amounts of CO (as low as 30 ppm) markedly influence the performance of the fuel cell. The influence of CO was observed in the decay of the fuel cell output voltage compared to the case of utilizing pure hydrogen.

It is possible that the voltage of one of the cells in a stack will drop below 0 V. It is also possible to observe low frequency oscillations of one of the cell voltages. These oscillations were identified as self-oxidizing oscillations of CO from the platinum catalyst.

With respect to the behavior of the fuel cell to CO-poisoning, the order of the serial cells in a stack is important. Self-oxidizing behavior is only observed in cells at the highest electrical potential in a stack.

It is possible to electrically regenerate CO-poisoned fuel cells by forcing the cell to a negative output voltage with respect to its normal polarization. The electrical position of the cell that is regenerated is of critical importance. Only the cells with higher potential in the stack are regenerated well.

The optimization results of the shapes of the regeneration pulses show that the pulse amplitude \( A_p \) has to be varied between -0.80 V for lower and -1.00 V for higher CO concentrations. The repetition time \( \tau_p \) and the duty cycle \( D_p \) are dependent on the regeneration method (script I, II or III) implemented and the CO concentration. Satisfying results were achieved for repetition times between 2 s and 8 s in combination with duty cycles ranging between 2% and 6%. This pulsing technique makes it possible to operate a PEM fuel cell with pure platinum loaded catalysts on biogas with CO. Measurements show that
the specific PEM fuel cell measured is CO tolerant with CO concentrations of up to 100 ppm.

**Energetic, environmental en economical issues**

If the energy balance of a fuel cell generation system based on biomass feedstock is compared with other electricity generation systems, then it can be concluded that such a system is feasible. Compared to the efficiency of an internal combustion engine (between 6 and 24%), the fuel processor - fuel cell system exergetic efficiency (between 21 and 25%) is already competitive.

The amount of sustainable energy sources available on the Earth is more than enough to satisfy the energy demand of the modern society. A combination of different sustainable energy generation systems will contribute to a CO$_2$-neutral balance. More efforts than described in the Kyoto Protocol are needed to reach the goal of less than 2 $^\circ$C rise in global temperature in 2100, and the biomass - fuel processor - fuel cell system may contribute to that goal.

### 6.2 Recommendations

The dynastatic model presented in Chapter 3 can be simplified or expanded to the needs of the user, depending on the goal. The dynastatic model is a model implementation that allows the user to simulate small-signal, large-signal, and steady-state behavior. Moreover, it can help in determining the state-of-health of the fuel cell stack. This report describes only two possibilities of using the model for state-of-health monitoring, namely aging and oxygen supply failure. It is very well possible that with additional research, more parameters can be found from electrical measurements.

The electrical regeneration as presented in Chapter 4 shows promising results. The auxiliary components are cheap, it does not need complicated controls, and, because it does not include special treatments in the manufacturing stage, the method is easily applicable on low-temperature fuel cells. Note that the long-term effect of the pulsing method on the fuel cell performance was not included in this work. To implement this method in commercial fuel cell stacks, the rate of deterioration of the membrane and catalysts should be investigated in comparison to other methods.

The exact mechanism of regeneration based on pulsing technique is not fully understood. Better understanding of the electrochemistry when pulsing may contribute to an improvement of the implementation. If the method
oxidizes CO with water, then the method could benefit from additional humidification of the hydrogen gas stream. This might prevent dry-out of the membrane. However, if another mechanism causes the desorption of CO from platinum, the fragile water balance of the low-temperature fuel cell might get disturbed from additional humidification.

In Chapter 5 it is shown that the energy balance of a fuel processor-fuel cell system is reasonable when compared to an internal combustion engine system. This is positive, because the internal combustion engine system has evolved over the past century to a commercially mature product while the fuel processor-fuel cell system did not have that chance yet. It may be expected that the new technology, when researched as intensively as the internal combustion engine system in the past 100 years, will gain in system performance and efficiency. So, with sufficient investments and research, the biomass-fuel cell system will contribute to a CO$_2$-neutral energy generation cycle.
Chapter 6. Conclusions and recommendations
Part IV

Appendices
# Appendix A

## Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
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<td>$\alpha_{cr}$</td>
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<td>Efficiency of the fuel cell with operational pulsing source</td>
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<td>Surface coverage of adsorbed species onto a surface</td>
</tr>
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<td>Diffusion-flux constant</td>
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<td>$\kappa_m$</td>
<td></td>
<td>Transmission coefficient</td>
</tr>
<tr>
<td>Symbol</td>
<td>Dimension</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>$\mu_k$</td>
<td>$[J/mole]$</td>
<td>Chemical potential of species $k$</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>$[J/mole]$</td>
<td>Electron potential</td>
</tr>
<tr>
<td>$\bar{\mu}_k$</td>
<td>$[J/mole]$</td>
<td>Electrochemical potential of species $k$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>$[1/s/cm^2]$</td>
<td>Electrochemical rate</td>
</tr>
<tr>
<td>$\nu_j$</td>
<td>$[1]$</td>
<td>Stoichiometric coefficient</td>
</tr>
<tr>
<td>$\rho$</td>
<td>$[\Omega \cdot cm^2]$</td>
<td>Reaction resistance</td>
</tr>
<tr>
<td>$\sigma_w$</td>
<td>$[\Omega/\sqrt{s}]$</td>
<td>Warburg constant</td>
</tr>
<tr>
<td>$\tau_D$</td>
<td>$[s]$</td>
<td>Dielectric relaxation time</td>
</tr>
<tr>
<td>$\tau_R$</td>
<td>$[s]$</td>
<td>Reaction relaxation time</td>
</tr>
<tr>
<td>$\tau_p$</td>
<td>$[s]$</td>
<td>Repetition time of the regeneration pulses</td>
</tr>
<tr>
<td>$\varphi_G$</td>
<td>$[V]$</td>
<td>Galvani potential</td>
</tr>
<tr>
<td>$\psi(x)$</td>
<td>$[V]$</td>
<td>Inner potential of phase $x$</td>
</tr>
<tr>
<td>$A$</td>
<td>$[V]$</td>
<td>Activation polarization coefficient</td>
</tr>
<tr>
<td>$A_p$</td>
<td>$[V]$</td>
<td>Amplitude of the pulse source</td>
</tr>
<tr>
<td>$a_j$</td>
<td>$[V]$</td>
<td>Activity of species $j$</td>
</tr>
<tr>
<td>$a$</td>
<td>$[V]$</td>
<td>Tafel polarization constant</td>
</tr>
<tr>
<td>$A e$</td>
<td>$[cm^2]$</td>
<td>Effective active area of a membrane</td>
</tr>
<tr>
<td>$A_{cpe}$</td>
<td>$[S]$</td>
<td>Admittance of constant phase element [89]</td>
</tr>
<tr>
<td>$B$</td>
<td>$[V]$</td>
<td>Concentration polarization coefficient</td>
</tr>
<tr>
<td>$b$</td>
<td>$[V]$</td>
<td>Tafel slope constant</td>
</tr>
<tr>
<td>$CPE$</td>
<td>$[S]$</td>
<td>Constant phase element</td>
</tr>
<tr>
<td>$C_{DL}$</td>
<td>$[F]$</td>
<td>Double layer capacitor</td>
</tr>
<tr>
<td>$C_R$</td>
<td>$[F]$</td>
<td>Reaction capacitor or second double layer capacitor</td>
</tr>
<tr>
<td>$\hat{C}_R$</td>
<td>$[F]$</td>
<td>Maximum value of the double layer capacitor amplitude</td>
</tr>
<tr>
<td>$C$</td>
<td>$[J/(kg\cdot K)]$</td>
<td>Average heat capacity</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>CO$_2$</td>
<td></td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>$c_j$</td>
<td>$[mole/cm^3]$</td>
<td>Concentration of species $j$</td>
</tr>
<tr>
<td>$c_{s,j}$</td>
<td>$[mole/cm^3]$</td>
<td>Surface concentration of species $j$</td>
</tr>
<tr>
<td>$c_{v,j}$</td>
<td>$[mole/cm^2]$</td>
<td>Bulk concentration of species $j$</td>
</tr>
<tr>
<td>$D_j$</td>
<td>$[cm^2/s]$</td>
<td>Diffusion coefficient of species $j$</td>
</tr>
<tr>
<td>$D_p$</td>
<td></td>
<td>Duty cycle of the pulse source</td>
</tr>
<tr>
<td>$E^0$</td>
<td>$[V]$</td>
<td>Equilibrium potential of chemical reaction</td>
</tr>
</tbody>
</table>
$E_{FC}$\text{[V]} Non-linear voltage source of the dynamic fuel cell model

$E_{rev}$\text{[V]} Reversible cell voltage, or EMF

$E_{ocv}$\text{[V]} Fuel cell open circuit voltage

$E^0_{rev}$\text{[V]} Standard reversible voltage

$\mathcal{E}_{ch}$\text{[J]} Chemical energy

$\mathcal{E}_{el}$\text{[J]} Electrical energy

$\mathcal{E}_{FC}$\text{[J]} Energy produced by a fuel cell operated with a certain feedstock

$\mathcal{E}_{loss}$\text{[J]} Energy loss

$\mathcal{E}_{FC,H_2}$\text{[J]} Energy produced by a fuel cell operated with pure hydrogen

$e^-$\text{[C]} Electron charge

$F$\text{[C]} Faradays constant (96485)

$f_{so}$\text{[Hz]} Self-oxidizing frequency

$G$\text{[J m\text{-}mole]} Gibbs energy

$\Delta G$\text{[J m\text{-}mole]} Change in Gibbs energy

$\Delta G^\ddagger$\text{[J m\text{-}mole]} Standard-state free energy of activation

$H$\text{[J m\text{-}mole]} Enthalpy

HHV Higher heating value: Total energy with recovery of the energy from water vapor to liquid

$H_2$ Hydrogen

$H_2O$ Water

$h$\text{[J \textcdot s]} Planck’s constant (6.626 \cdot 10^{-34})

$I_0$\text{[A]} Exchange current

$I_{s,avr}$\text{[A]} Average pulse current

$I_{FC}$\text{[A]} Fuel cell current

$I_{lim}$\text{[A]} Limiting current

$I_n$\text{[A]} Fuel crossover current and internal loss currents

$I_R$\text{[A]} Maximum double layer capacitance current for $C_R$

$i(t)$\text{[A]} Time varying current

$j^0$\text{[mA cm^{-2}]} Exchange current density

$J$\text{[mA cm^{-2}]} Diffusion flux density

$j$\text{[mA cm^{-2}]} Current density

$j_{lim}$\text{[mA cm^{-2}]} Limiting diffusion current density

$j_n$\text{[mA cm^{-2}]} Fuel crossover current density

$K$\text{[cm]} Reaction rate constant
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K^{(1)}$</td>
<td>Hybrid matrix of a two-port</td>
</tr>
<tr>
<td>$k_m$</td>
<td>Reaction rate constant</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann’s constant $(1.38 \cdot 10^{-23})$</td>
</tr>
<tr>
<td>$k^0$</td>
<td>Intrinsic rate constant</td>
</tr>
<tr>
<td>$L_A$</td>
<td>Adsorption inductor</td>
</tr>
<tr>
<td>LHV</td>
<td>Lower heating value: Total energy without recovery of the energy from water vapor to liquid</td>
</tr>
<tr>
<td>$M$</td>
<td>Mass</td>
</tr>
<tr>
<td>$N_2$</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of cells in FC stack</td>
</tr>
<tr>
<td>$\dot{N}$</td>
<td>Molar flow rate</td>
</tr>
<tr>
<td>$n_j$</td>
<td>Number of particles $j$</td>
</tr>
<tr>
<td>$n$</td>
<td>Stoichiometric coefficient</td>
</tr>
<tr>
<td>$O_2$</td>
<td>Oxygen</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure</td>
</tr>
<tr>
<td>$P$</td>
<td>Average pulse power</td>
</tr>
<tr>
<td>$P_{\text{ave}}$</td>
<td>Polymer Electrolyte Membrane</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>$\dot{q}$</td>
<td>Energy term</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant $(8.314)$</td>
</tr>
<tr>
<td>$R_{\text{int}}$</td>
<td>Internal steady state resistance of a fuel cell</td>
</tr>
<tr>
<td>$R_{\infty}$</td>
<td>Bulk resistance</td>
</tr>
<tr>
<td>$R_{DL}$</td>
<td>First double layer resistance</td>
</tr>
<tr>
<td>$R_{DL}^∞$</td>
<td>Double layer resistance for $(R_{DL}(I_{FC} \to \infty))$</td>
</tr>
<tr>
<td>$R_{DL}^0$</td>
<td>Double layer resistance for $(R_{DL}(I_{FC} \to 0))$</td>
</tr>
<tr>
<td>$R_R$</td>
<td>Second double layer resistance</td>
</tr>
<tr>
<td>$R_R^∞$</td>
<td>Double layer resistance for $(R_R(I_{FC} \to \infty))$</td>
</tr>
<tr>
<td>$R_R^0$</td>
<td>Double layer resistance for $(R_R(I_{FC} \to 0))$</td>
</tr>
<tr>
<td>$R_A$</td>
<td>Adsorption resistance</td>
</tr>
<tr>
<td>$R_A^0$</td>
<td>Adsorption resistance for $(R_A(I_{FC} \to 0))$</td>
</tr>
<tr>
<td>$S$</td>
<td>Entropy</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T^0$</td>
<td>Standard room temperature $(298.15 \text{ K})$</td>
</tr>
<tr>
<td>$U$</td>
<td>Internal energy</td>
</tr>
<tr>
<td>$V$</td>
<td>Volume</td>
</tr>
<tr>
<td>$V_{\text{FC}}$</td>
<td>Fuel cell stack output voltage</td>
</tr>
<tr>
<td>$v_{\text{cell}}$</td>
<td>Single cell output voltage</td>
</tr>
<tr>
<td>Symbol</td>
<td>Unit</td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>(v(t))</td>
<td>[V]</td>
</tr>
<tr>
<td>(W)</td>
<td>[Ω]</td>
</tr>
<tr>
<td>(w_{ch})</td>
<td>[J]</td>
</tr>
<tr>
<td>(Y(\cdot))</td>
<td></td>
</tr>
<tr>
<td>(Z(\cdot))</td>
<td></td>
</tr>
<tr>
<td>(Z)</td>
<td>[Ω]</td>
</tr>
<tr>
<td>(Z')</td>
<td>[Ω]</td>
</tr>
<tr>
<td>(Z'')</td>
<td>[Ω]</td>
</tr>
<tr>
<td>(z_j)</td>
<td></td>
</tr>
</tbody>
</table>

**Subscript**

- \(a\): Anodic part of a variable
- \(c\): Cathodic part of a variable
- \(d\): Dissolved state of a molecule
- \(g\): Gas state of a molecule
- \(l\): Liquid state of a molecule
- \(prod\): Product of a redox reaction
- \(react\): Reactants of a redox reaction
- \(s\): Solid state of a molecule
Energy loss results from the waste of fuel and electrons passing through the electrolyte. The electrolyte should only transport ions through the cell, however, a certain amount of fuel diffusion and electron flow is always possible. The fuel loss and current is small, and its effect is usually not very important. However, it does have a marked effect on the open circuit voltage of low temperature fuel cells [70].

The two phenomena of fuel crossover: 1) $\text{H}_2$ crossing the membrane and reacting at the cathode, and 2) the internal crossover of electrons through the membrane from anode to cathode, can be considered as an internal current [70]. The flow of fuel and electrons will be small (only a few $\frac{mA}{cm^2}$), but in low-temperature fuel cells it causes a noticeable voltage drop under open circuit conditions.

Because the internal current caused by the fuel crossover is very small, it is difficult to measure. However, it is possible to calculate the internal current by measuring the fuel consumption at open circuit. To calculate the internal current density one must know the active area of the membrane, the hydrogen consumption, and the number of cells. The internal current is calculated with the following expression [70]:

$$H_{2,usage} = \frac{I_n N}{n F} \left[ \frac{\text{mole}}{s} \right],$$

(B.1)
In these expressions $N$ stands for the number of cells and $n$ for the number of electrons involved in the reaction (for pure hydrogen: $n = 2$). To obtain the current density ($j_n$), one has to divide $I_n$ by the cell active area ($A_e$). The expression for the activation overpotential (2.28) can now be refined to

$$\eta_{act} = b \ln \left\{ \frac{j + j_n}{j_0} \right\} [V]$$

(B.3)
Appendix C

Electrical humidification of the membranes

The main transport mechanism of protons through the polymer electrolyte is diffusion [70, 102]. From the half cell reactions of the fuel cell, (2.1), and (2.2), it is clear that water forms at the cathode. The membrane is made from a material that easily absorbs a great amount of water. Via back diffusion, water will go from the cathode to the anode, that is, if the cathode holds more water than the anode. In contrast to back diffusion, there is a process called electro-osmotic drag, which is a mechanism that drags water molecules with each proton from the anode to the cathode. If there is a balance between the two transport mechanisms of water, the fuel cell will not dry out [70].

There are three phenomena responsible for the balance of water in the fuel cell. Firstly, oxygen is supplied using a fan to move air over the cathode, water will be evaporated and removed from the cathode. The evaporation is directly coupled to the cell temperature, and will be lower at low-temperatures than at high temperatures. If Joule’s law of energy dissipation is used to translate temperature variations of the fuel cell membrane to current densities (3.4), then it can easily be seen that the temperature will rise with the square of the current density.

Secondly, the electro-osmotic drag is directly coupled to the current density of the cell. At high current densities, the electro-osmotic drag will be high, because a lot of protons are transported from the anode to the cathode, and at low current densities the electro-osmotic drag will be low [70].
Lastly, the creation of water at the cathode is also correlated to the current density. At high current densities, the redox reaction (2.3) will take place more often than at low current densities.

When the advantages of high and low current densities could be combined, the water controlling steps could be optimized, making sure that the fuel cell stays in optimal operation. If, for instance, the current density stays low, except for predefined moments, the temperature stays low, because temperature variations are slow [3]. This will reduce the evaporation of water at the cathode, but stimulates a higher reaction rate, which will create more water at the cathode, and thus stimulates back-diffusion in order to humidify the anode. In this way, it is possible to use the redox reaction itself for humidifying the membrane.

The working principles of the Avista Labs SR-12 fuel cell system are based on this humidifying method [49, 50]; the membrane is humidified by repeatedly shorting the output terminals of the individual cells. In order to control the humidification of the membranes, short-circuiting switches (Mosfets) are paralleled to individual cells, as is shown in Fig. C.1. The switches are controlled by the DSP system.

To test the effect of the pulsing technique for humidification, the average power of the fuel cell ($P_{FC}$) is recorded as a function of the pulse repetition time ($\tau_{hum}$) and duty cycle ($D_{hum}$). The humidification is tested at a low fuel cell current ($I_{FC} = 1 \text{ A}$), shown in Fig. C.2, and a high fuel cell current ($I_{FC} = 5 \text{ A}$), shown in Fig. C.3. The literature [50] gives an indication for the repetition-time span and duty cycle of the pulses, that is, the repetition time may not be longer than 4 minutes, and the duty cycle may not exceed 20%.

The repetition time is varied over 0.5 s, 1 s, 2 s, 5 s, 10 s, 20 s, 50 s, 100 s and

**Table C.1:** Advantages and disadvantages of low and high current densities for control water of the membrane.

<table>
<thead>
<tr>
<th>Low $j_{FC}$</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T(\circ C) \downarrow$</td>
<td>Low reaction rate</td>
<td></td>
</tr>
<tr>
<td>Low evaporation at cathode</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low electro-osmotic drag (eod)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Balance (eod) - back diffusion</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>High $j_{FC}$</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>High reaction rate</td>
<td>$T(\circ C) \uparrow$</td>
<td></td>
</tr>
<tr>
<td>High mobility charge carriers</td>
<td>High eod (drying anode)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High evaporation at cathode</td>
<td></td>
</tr>
</tbody>
</table>
**Figure C.1:** Auxiliary circuit for regeneration (humidification) of the membrane of the fuel cell. Every single cell has its own parallel Mosfet.

**Figure C.2:** Humidification optimization for $I_{FC} = 1\, A$ load current, where the output power ($P_{FC}$) is given as a function of the repetition time ($\tau_{hum}$) and the duty cycle ($D_{hum}$).
200 s. The duty cycle is tested between 0% and 2.0%. It is clear from Fig. C.2 that a better performance is obtained if the cells are pulsed, due to the fact that at a duty cycle of 0% the output power is lowest. The best results are shown for repetition times of $\tau_{hum} = 100$ s with a duty cycle of $D_{hum} = 0.6\%$.

From Fig. C.3, it can be concluded that pulsing with a duty cycle of $D_{hum} = 0.5\%$ gives the highest output power. It may be concluded that the most satisfying results of the humidifying pulse technique may be expected with repetition time of $\tau_{hum} \approx 100$ s and a duty cycle of $D_{hum} \approx 0.5\%$.

**Figure C.3:** Humidification optimization for $I_{FC} = 5\,A$ load current, where the output power ($P_{FC}$) is given as a function of the repetition time ($\tau_{hum}$) and the duty cycle ($D_{hum}$).
Appendix D

Modeling the internal fuel cell impedance

D.1 Two-port network theory

A two-port is a black-box containing ideal electrical components, such as resistors, capacitors and inductors. A two-port has only four variables, namely the voltage and current at side “1” \((v_1 \text{ and } i_1)\) and the voltage and current at side “2” \((v_2 \text{ and } i_2)\). The direction of the voltages and currents are defined as given in Fig. D.1.

The relationship between the voltages and currents of the two sides can be described with a matrix. Depending on the objective of the two-port, an

\[ Z^1 \]
\[ Y^1 \]
\[ K^1 \]

Figure D.1: A two-port, defined by its impedance \((Z^1)\), admittance \((Y^1)\), or hybrid matrix \((K^1)\).
impedance matrix $Z^{(i)}$, defined as

$$\tilde{v} = Z^{(i)} \tilde{i},$$

$$\begin{bmatrix} v_1 \\ v_2 \end{bmatrix} = \begin{bmatrix} Z_{11} & Z_{12} \\ Z_{21} & Z_{22} \end{bmatrix} \begin{bmatrix} i_1 \\ i_2 \end{bmatrix},$$  \hspace{1cm} (D.1)$$

an admittance matrix $Y^{(i)}$

$$\tilde{i} = Y^{(i)} \tilde{v},$$

$$\begin{bmatrix} i_1 \\ i_2 \end{bmatrix} = \begin{bmatrix} Y_{11} & Y_{12} \\ Y_{21} & Y_{22} \end{bmatrix} \begin{bmatrix} v_1 \\ v_2 \end{bmatrix},$$  \hspace{1cm} (D.2)$$

or a hybrid matrix $K^{(i)}$ can be chosen. For the impedance matrix, in order to describe the voltages $\tilde{v}$, the currents $\tilde{i}$ of the two-port are assumed to be known. In contrast to the impedance matrix, the admittance matrix describes the characteristics of the currents $\tilde{i}$ when the voltages $\tilde{v}$ are known. If, however, one voltage and one current are known, the relationship is best described using a hybrid matrix [23].

If, at the output of a two-port, a complex variable impedance ($Z_o$) is connected, then the input impedance can be calculated [23] as being

$$Z_i = Z_{11} - \frac{Z_{12}Z_{21}}{Z_{22} + Z_o} = \frac{Z_{11}Z_o + \text{det}(Z)}{Z_{22} + Z_o},$$  \hspace{1cm} (D.3)$$

where $\text{det}(Z) = Z_{11}Z_{22} - Z_{12}Z_{21}$. Equation (D.3) is known as a bilinear function, that is, the input impedance of a two-port is bilinearly dependent on the variable output impedance. In other words, $Z_i = f(Z_o)$, which implies that every point in the complex $Z_o$-plane is transferred to a point in the complex $Z_i$-plane [23].

A bilinear function can be reversed;

$$Z_o = \frac{-Z_{22}Z_i + \text{det}(Z)}{Z_i - Z_{11}},$$  \hspace{1cm} (D.4)$$

which also results in a bilinear function. One of the properties of a bilinear function is that a circle in the complex $Z_o$-plane is transferred to a circle in the complex $Z_i$-plane [23].

**D.2 Complex impedance**

Figure D.2 shows three cascaded two-ports. These three two-ports represent the impedance of the fuel cell found with electrochemical impedance spec-
troscopy. Their impedance is described with

\[ Z^{(1)} = \frac{1}{j\omega C_{DL}} \left[ \begin{array}{c} 1 \\ 1 + j\omega C_{DL} R_{\infty} \\ 1 + j\omega \right] \right), \]  
(D.5)

\[ Z^{(2)} = \frac{1}{j\omega C_{R}} \left[ \begin{array}{c} 1 \\ 1 \\ 1 + j\omega R_{R} / C_{R} \end{array} \right], \]  
(D.6)

\[ Z^{(3)} = \left[ \begin{array}{c} j\omega L_{A} \\ j\omega L_{A} \\ j\omega L_{A} \end{array} \left( R_{A} + j\omega L_{A} \right) \right]. \]  
(D.7)

### D.2.1 Projection of \( Z^{(3)} \)

The impedance of the fuel cell is found by short-circuiting the output of two-port \( Z^{(3)} \), so \( V_{A} = 0 \). From (D.3) and (D.7) follows the input impedance of \( Z_{A} \)

\[ Z_{i}(Z^{(3)}) = Z_{A} = \frac{j\omega L_{A} R_{A}}{R_{A} + j\omega L_{A}}, \]  
(D.8)

which can be normalized, and then becomes

\[ Z_{An} = \frac{Z_{A}}{R_{A}}. \]  
(D.9)

With a normalized frequency \( \Omega_{A} \) of

\[ \Omega_{A} = \omega \frac{L_{A}}{R_{A}}, \]  
(D.10)
relationship (D.8) becomes

\[ Z_{An} = \frac{j\Omega_A}{1 + j\Omega_A}. \]  

When the normalized frequency changes from 0 to \( \infty \), the response of (D.11) is a semi-circle\(^1\) shown in Fig. D.3.

### D.2.2 Projection of \( Z^{(3)} \) to the complex \( Z^{(2)} \)-plane

Because the impedance of the second two-port (\( Z^{(2)} \)) can be written as a bilinear function, the semicircle shown in Fig. D.3 is projected as a semicircle in the complex \( Z^{(2)} \) plane. Therefore, the analysis of the second two-port starts by neglecting the influence of the first two-port, and assuming that the impedance of the third two-port (\( Z_A \)) is constant. From (D.6) follows the input impedance of \( Z_R \)

\[ Z_i(Z^{(2)}) = Z_R = \frac{(R_R + Z_A)}{1 + j\omega C_R(R_R + Z_A)}, \]  

(D.12)

Normalizing (D.12) results in

\[ \Omega_R = \omega C_R(R_R + Z_A), \]  

\[ Z_{Rn} = \frac{Z_R}{(R_R + Z_A)} \]

\(^1\)If instead of half the normalized frequency, the complete range of frequencies is used (\( -\infty < \Omega < \infty \)), Fig. D.3 would become a complete circle [108].
When the normalized frequency $\Omega_R$ varies from 0 to $\infty$, the impedance of the two-port is described in the complex $Z_R$-plane as is shown in Fig. D.4(a).

The cascade of impedance $Z_A$ with $Z_R$ ensures that the semicircle of $Z_A$ is projected as another semicircle in the complex $Z_R$ plane. The projection of $Z_A$ in the complex $Z_R$ plane depends on the relation between $\Omega_A$ and $\Omega_R$. If $\Omega_A \gg \Omega_R$, that is, the time constant of the third two-port is much higher than the time constant of the second two-port, then the impedance response of the two two-ports is given in Fig. D.4(b). For this figure, the values of the resistors were chosen to be $\omega = 1$.

From Fig. D.4(b) it can be concluded that the semicircle of the third two-port is transposed and (possibly) rotated in the complex $Z_R$ plane, due to its coupling to the second two-port. This is according to the bilinear function theory [23].

### D.2.3 Projection of $Z^{(2)}$ to the complex $Z^{(1)}$-plane

The projection of $Z_R$ in the $Z_{DL}$ plane is made in the same way as it is done for the projection of $Z_A$ in the $Z_R$ plane. The response of the first two-port is equal to Fig. D.4(a), except for a shift over the real axis of $R_{\infty,n}$, which is the
normalized value of $R_{\infty}$:

\begin{align}
\Omega_{DL} &= \omega C_{DL}(R_{DL} + Z_R), \\
Z_{DL,n} &= \frac{Z_{DL}}{(R_{DL} + Z_R)} \\
&= R_{\infty,n} + \frac{1}{1 + j\Omega_{DL}}.
\end{align}

For the bilinear projection of $Z_R$ in the complex $Z_{DL}$ plain, the normalized frequencies are chosen to be $\Omega_A \gg \Omega_R \gg \Omega_{DL}$. Furthermore, the resistors are equal to unity and the normalized resistor $R_{\infty,n} = 0.4$. The results are plotted in Fig. D.5.

The projection can be altered if the time-constants of the two-ports are closer nearer to each other. The resistors in the two-ports cause shifting of the semi-circles over the real axis. The circle diameters are also dependent on the resistors of the two-ports.

**Figure D.5:** The normalized projection of Fig. D.2 in the complex $Z_{DL}$ plane.
Appendix E

Dynastatic model implementation

The implementation of the stack model in simulation software for electrical circuits may cause problems. The (non-) linear behavior of the resistors as a function of the output current make the model hard to implement. Simulink and the Power Systems toolbox, however, provide an environment which is able to implement the fuel cell model as is presented in Table 3.1. The program allows to use analytical functions to describe electrical current and voltage sources.

The complete implementation of the stack model is shown in Fig. E.1, where the open circuit voltage source of the fuel cell \( E_{FC} \) is implemented as is shown in Fig. E.1(b). The linear adsorption resistor \( R_A \) is implemented as presented in Fig. E.1(c) and the double layer resistors \( R_{DL} \) and \( R_R \) are shown in Fig. E.1(d) and Fig. E.1(e), respectively.

The Simulink model contains a subsystem called “current profile load”. In this subsystem, an arbitrary load profile can be implemented. To verify the model against the measurements, the step train of Fig. 3.6 is implemented in the current profile. The simulation result is compared to the measured voltage, as is shown in Fig. E.2.

The error, as defined in (3.13), between the measurement and the original Matlab simulation is shown in Fig. E.3 as the gray line. The black line in Fig. E.3 shows the error between the Simulink model and the measurement.

Figure E.3 indicates that the difference between the analytical approach and the electrical circuit based simulation is small. Also, the maximum error be-
Figure E.1: Simulink model of the fuel cell stack (a) and its subsystems: (b) open circuit source $E_{FC}$, (c) adsorption resistor $R_A$, (d) first double layer resistor $R_{DL}$ and (e) second double layer resistor $R_R$. 

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Figure E.2: Multi-step response: Simulink simulation of the fuel cell voltage (black line) vs. the measured voltage (gray line), also shown in Fig. 3.6.

Figure E.3: Relative error between the measured step-response and the step-response computed by Matlab (gray line), and the relative error between the measured step-response and the step-response calculated by Simulink (black line).
Figure E.4: Top: Simulink simulation (○-mark) and measured data (●-mark). Bottom: the relative error between simulation and measurement.

The relative error between simulation and measurement is small. Therefore, the Simulink model is a useful tool for the development of electronics.

Finally, the steady-state simulated operation of the stack is compared to the measured data. Figure E.4 shows the results of the simulation and the measurement. The relative error is small, and is almost equal to the Matlab simulation (Fig. 3.8).
Appendix F

Model construction of the new cartridge operating at high air flow supply

The electrochemical impedance spectroscopy is executed with DC current set points ranging from $I_{DC} = 0.5\,A$ up to $I_{DC} = 10\,A$. By using the least squares fit method onto the obtained data the resistor values are found, as is shown in Fig. F.1(a). Furthermore, Fig. F.1(b) shows the fitted results for the double layer capacitors and the adsorption inductor.

It is clear from Fig. F.1 that the variables of the high air flow model for stack # 0183 change in the same way as is seen with the low air flow supply of the same stack (Fig. 3.11). That is, the resistors, capacitors and inductor show the same trends that were observed with the low air flow supply. Therefore, the non-linear relationship of the second double layer capacitor $C_R$ to the output current of the fuel cell ($I_{FC}$) is equivalent to (3.17).

The values found for the resistors of the equivalent circuit model are

\[ R_{\infty} = 0.116\,\Omega, \quad (F.1) \]
\[ R_{DL} = 0.0164 + 0.133e^{-0.283I_{FC}}\,\Omega, \quad (F.2) \]
\[ R_R = 0.00720 + 0.154e^{-1.47I_{FC}}\,\Omega, \quad (F.3) \]
\[ R_A = 0.0136\,\Omega, \quad (F.4) \]
and the values for the double layer capacitors and adsorption inductor are

\[ C_{DL} = 0.265 F, \]  
\[ C_R = 7.95e^{-\left(\frac{I_{FC} - 6.99}{4.19}\right)^2} F, \]  
\[ L_A = 0.123 H. \]  

The internal resistances of the fuel cell model can now be calculated and used to find the open circuit voltage source \( E_{FC} \). The result of this calculation is shown in Fig. F.2, where the o-marks show the measured values and the solid line the fitted characteristic of (3.14).

The open circuit voltage source for the new fuel cell stack with high air flow supply is characterized by

\[ E_{FC} = 4.68 - 0.180 \ln \left( \frac{I_{FC} + 0.842}{722 \cdot 10^{-6}} \right), \]  

where the internal current is found to be \( I_n = 0.842 A \), which is slightly higher than the obtained value for the low air flow supply.

In order to reduce the complexity of the model, the second double layer capacitor is assumed to be constant in the same way as described in section 3.3.1. The value from a least squares fit is \( C_R = 2.63 F \).

The complete fuel cell stack model for the new stack (# 0183) with high air flow supply is presented in Table 3.3.
Verification of the model

The model of the stack with high air flow supply is also verified with steady-state, step-response and EIS characteristics. The verification of the steady-state characteristic is shown in Fig. F.3. The ◦-marks in the top graph present the measured data of the fuel cell stack. The full line shows the simulated characteristic. The lower graph shows the relative error between the measured and the simulated data. The maximum error between the quasi steady-state and simulated characteristic is 2%, which is quite small.

The verification of the model with the measured data of the step response is shown in Fig. F.4. The maximum error, as defined in (3.13), of the measured and simulated step response (lowest graph) is dependent on the amplitude of the step. With large amplitudes, which are shown in the first 220 seconds, the relative error is large, that is, higher or equal to 10%. However, when smaller steps are taken, the maximum error drops below 2% (240 s < t < 500 s).

Because the difference in deviation between small and large steps is seen in both the low and the high air flow model, it leads to a usage restriction for this model. That is, the model is accurate for large-signal behavior as long as the current steps do not vary too much in amplitude.

Figure F.2: Open circuit voltage source characteristics of the measured (◦-mark) and fitted data (line) for the new stack # 0183 with high air flow supply.
Figure F.3: Steady-state simulation (line) and measurements (x-mark) (top figure) and the relative error between them (bottom figure) of cartridge # 0183 operating with a high air flow supply.

Figure F.4: Multi-step response simulation vs. measurements (top figure) and the relative error between them (bottom figure) of cartridge # 0183 operating with a high air flow supply.
Figure F.5: Relative error between the measured EIS-curve obtained from cartridge # 0183 with a high air flow supply and the simulated curve with a variable $C_R$ (full line) and a constant $C_R = 2.63 \, F$ (dashed line) for different DC set points: a) $I_{DC} = 1.5 \, A$, b) $I_{DC} = 3.0 \, A$, c) $I_{DC} = 5.0 \, A$ and d) $I_{DC} = 7.0 \, A$.

The verification of the small-signal response is performed with two different second double layer capacitors. The results are shown in Fig. F.5, where the error for the constant value of $C_R$ is presented with a dashed line, while the error for the non-linear capacitor is presented with a full line.

It is clear from Fig. F.5 that the peak deviation in the medium to large DC current set points, Fig. F.5(c) and Fig. F.5(d), is largest for the frequency range of 0.5 Hz to 3.5 Hz. However, this peak is smaller than observed in the measurement with low air flow supply, as is shown in Fig. 3.15.

The average error for the low to medium DC current region is small ($\epsilon \leq 2\%$) for both constant $C_R$ and current dependent $C_R$. For the medium to high DC current region, the error rises to 5% for the current dependent capacitor, and to 6% for the constant $C_R$. 
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After his Ph.D. defense, Paul will join the company “Dutch Aero”, where he will work on Electrochemical Machining.
Paul Wingelaar worked towards his Ph.D. exam in the Electromechanics and Power Electronics (EPE) group in the Eindhoven University of Technology from 2003 to 2007. As an Electrical Engineer, he approaches the Fuel Cell from an electrical point of view. Traditionally, the approach to characterize fuel cells is by performing steady-state measurements. However, electrical engineers are more interested in the dynamic behavior of an electricity source. By keeping close to the electrochemistry, the “dynastatic” model, which is constructed from impedance spectroscopy, steady-state, and step response measurements, can be used in electrical and chemical modeling.

In order to contribute to a CO₂-neutral energy generation system, biomass gas is used as the feedstock for the fuel cells. Because biogas contains trace amounts of CO, which is a contaminant for low-temperature fuel cells, Paul searched for an electrical regeneration method for the polluted catalysts. The found and described regeneration method includes applying negative voltage pulses to the individual cells of the stack, and changing the electrical position of the cells in the stack. This regeneration method electro-oxidizes the adsorbed CO to CO₂, which will disconnect from the catalyst surface.