DYNAMICS OF THE POLYMER ELECTROLYTE FUEL CELL:
EXPERIMENTS AND MODEL-BASED ANALYSIS

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZURICH
for the degree of
Doctor of Technical Sciences

presented by
PAUL HENDRIK RODATZ
Dipl. Masch.-Ing. ETH
born 18.9.1973
Germany

accepted on the recommendation of
Prof. Dr. L. Guzzella, examiner
Prof. Dr. A. Wokaun, co-examiner
Prof. Dr. A. Stefanopoulou, co-examiner

2003
Seite Leer / Blank leaf
CONTENTS

Acknowledgments v

Abstract vii

Notations xi

1 Introduction 1

1.1 General Aspects of Fuel Cells 1
1.2 Thermodynamic and kinetic considerations 3
  1.2.1 Reversible cell potential 3
  1.2.2 Voltage losses 5
  1.2.3 Fuel Cell Efficiency 8
1.3 Application Example: Experimental Fuel Cell Vehicle Hy.Power 9
1.4 Contributions 14

2 Experimental Setup 15

2.1 Fuel Cell Stack 16
2.2 Peripheral Components 20

3 Modeling 27

3.1 One Dimensional Fuel Cell Stack Model 28
  3.1.1 Mass Transport 29
  3.1.2 Electrochemistry 38
3.2 Air Supply System 42
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Experimental Investigation Steady State Conditions</td>
<td>49</td>
</tr>
<tr>
<td>4.1</td>
<td>Reproducibility and Error of Measurement</td>
<td>49</td>
</tr>
<tr>
<td>4.2</td>
<td>Stack Model</td>
<td>51</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Test Procedure</td>
<td>51</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Parameters of Reactants</td>
<td>53</td>
</tr>
<tr>
<td>4.2.3</td>
<td>Polarization Curves</td>
<td>57</td>
</tr>
<tr>
<td>4.2.4</td>
<td>Validation</td>
<td>65</td>
</tr>
<tr>
<td>4.3</td>
<td>System Model</td>
<td>66</td>
</tr>
<tr>
<td>4.4</td>
<td>Cell Voltage</td>
<td>67</td>
</tr>
<tr>
<td>5</td>
<td>Experimental Investigation Dynamics</td>
<td>79</td>
</tr>
<tr>
<td>5.1</td>
<td>Step in air stoichiometry</td>
<td>79</td>
</tr>
<tr>
<td>5.2</td>
<td>Current step</td>
<td>88</td>
</tr>
<tr>
<td>5.2.1</td>
<td>Experimental</td>
<td>89</td>
</tr>
<tr>
<td>5.2.2</td>
<td>Discussion</td>
<td>96</td>
</tr>
<tr>
<td>5.3</td>
<td>Current spike</td>
<td>99</td>
</tr>
<tr>
<td>6</td>
<td>Conclusions</td>
<td>111</td>
</tr>
<tr>
<td>References</td>
<td></td>
<td>115</td>
</tr>
<tr>
<td>Curriculum Vitae</td>
<td></td>
<td>125</td>
</tr>
</tbody>
</table>
ACKNOWLEDGMENTS

This research was carried out at the Institute of Energy Technology and the Measurement and Control Laboratory at the Swiss Federal Institute of Technology (ETH) Zurich, Switzerland from 1999 to 2003.

The support and trust of my supervisor, Prof. Dr. Lino Guzzella, is gratefully acknowledged.

Furthermore, I would like to thank Prof. Dr. A. Wokaun, Director of the General Energy Research Department (ENE), Paul Scherrer Institute, and Prof. Dr. A. Stefanopoulou, Director of the Powertrain Control Laboratory, University of Michigan for accepting to be my co-examiners.

I am indebted to the many people from the Paul Scherrer Institute who supported me throughout my work. My special thanks goes to Dr. Felix Büchi, the discussion with whom were of great help. Further, I would like to thank Akinori Tsukada, Dr. Philipp Dietrich, Renzo Marcolongo, Roberto Panozzo and Gino Paganelli for their support and help. I would also like to thank Martin Ruge of HTA Biel for supplying the drawings of the cell design.

My gratitude is assured to the entire staff of the Measurement and Control Laboratory, especially to Dr. Chris Onder and to those with whom I shared an office since they had to put up with me. The help of Hans Ulrich Honegger and Daniel Matter in constructing the test bench is highly appreciated.

Many more helped me with my work throughout the years. I would like to assure all of them of my gratitude.

Finally, my thanks go to my parents who encouraged me start this dissertation. My special thanks is reserved to my girl-friend for her wonderful support and the motivation she gave me in difficult times.
Fuel cells are considered to be a viable alternative to the internal combustion engine, since they have a higher efficiency, especially in part load conditions. In combination with hydrogen as fuel they enable a power conversion free from CO₂ emissions. Although extensive effort is undertaken to accelerate the commercialization of the fuel cell, most research is performed on single cells with a small active area and a power output of a few watts. Moreover, these cells are often operated at optimal conditions with regard to humidification, temperature and reactant flows.

In this thesis the transient behavior of a large PEM fuel cell stack is investigated. For this purpose a fuel cell test bench equipped with a fuel cell stack was built. The stack delivers 6 kW electric power. Experience obtained through the work on the fuel cell powered experimental Hy.Power vehicle was incorporated into this test bench. The test bench was designed and constructed to be as similar to the vehicle as possible, in order to obtain operating conditions that are typical for automotive applications. Many parts used in the test bench are also found in the vehicle.

From the data about the current-voltage relationship at different operating conditions a one-dimensional model was developed. This model considers the transport of the reactants (oxygen and hydrogen) and that of water orthogonal to the membrane surface. Beside other internal variables the model facilitates the computation of the membrane water content and the partial pressure of the reactants at the electrode-membrane interface. With these internal variables the magnitude of the Ohmic losses as well as of the activation polarization and eventually the cell voltage are determined. Even though the three-dimensional stack is reduced to a one-dimensional problem, the current-voltage relationship obtained from simulation agrees well with the experimental data. The computational burden is substantially smaller when compared to more extensive models.
This steady-state fuel cell model forms the foundation for the investigation of the transient behavior of the fuel cell stack. The measured voltage response to current steps, current spikes and air stoichiometry steps are compared to the voltage variation predicted by the steady-state simulation. The deviation between simulation and measurement allows to draw conclusions on the origin of the transient phenomena. The hydration/dehydration process of the fuel cell is found to be several orders of magnitude slower than the adaptation of the kinetics to new boundary conditions. The response of the fuel cell voltage to load changes is shown to follow a characteristic sequence. Furthermore, a slight, reversible decrease of the stack voltage with time is observed even when the operating parameters are not manipulated. The source of this decrease is analyzed and a procedure to lessen this decrease is proposed and tested.

Conventional PI controllers do not consider the crosscoupling of variables in interconnected systems. Therefore, the control of the air supply system using PI controllers was marked by large overshoots. The performance was thus unsatisfactory, especially since the air supply has a major impact on the voltage response. In this thesis a dynamic model of the air supply system was developed. Thereby a good agreement between simulation and measurement data was obtained. This model was used to design a model-based controller for the air supply system. The performance of this controller is compared to that of a set of PI controllers and showed a significantly improved performance with regard to response time and decoupling of mass flow and pressure.
ZUSAMMENFASSUNG


NOTATIONS

1. Symbols

\( a \)  
water activity  
[-]

\( a_f \)  
fitting parameter Eq. 5.2  
[-]

\( a_1, a_2 \)  
parameters for pressure drop approximation  
[-]

\( A_{\text{eff}} \)  
effective nozzle/valve opening area  
\([\text{m}^2]\)

\( A_r \)  
fitting parameter to describe flooding of catalytic surface  
[-]

\( c_1 \ldots c_4 \)  
fitting parameters for torque map of E-Motor  
[-]

\( c_{\text{H}_2\text{O}, m} \)  
molar concentration of water in the membrane  
\([\text{mol/cm}^3]\)

\( C_1 \ldots C_4 \)  
fitting parameters for voltage trace  
[-]

\( d_H \)  
hydraulic diameter  
\([\text{m}^2]\)

\( D_0 \)  
fitting parameter for diffusion coefficient  
\([\text{cm}^2/\text{s}^1]\)

\( D_{ij} \)  
binary diffusion coefficient  
\([\text{cm}^2/\text{s}]\)

\( D_w \)  
diffusion coefficient of water in the membrane  
\([\text{cm}^2/\text{s}]\)

\( E \)  
reversible cell potential  
[V]

\( E^0 \)  
standard potential  
[V]

\( E_{\text{th}} \)  
theoretical cell potential using the HHV  
[V]

\( f \)  
friction factor  
[-]

\( F \)  
Faraday constant  
[C/mol]

\( G \)  
mass velocity  
[\text{kg/s m}]

\( i \)  
transmission ratio between E-motor and compressor  
[-]

\( i_0 \)  
exchange current density  
[A/cm\(^2\)]

\( i_{01}, i_{02} \)  
fitting parameters for exchange current density  
[-]

\( i_{fc} \)  
current density  
[A/cm\(^2\)]

\( i_L \)  
limiting current density  
[A/cm\(^2\)]

\( I_{fc} \)  
cell current  
[A]

\( I_m \)  
cell current assuming total hydrogen conversion  
[A]
\( k_0 \ldots k_3 \) coefficients relating water activity to water content
\( k_{Ap} \) flow parameter to account for pressure drop in inlet manifold
\( k_{oc1}, k_{oc2} \) fitting parameters for open-circuit voltage
\( k_p \) permeability of water in the membrane
\( K \) hydraulic resistance
\( l_{fc} \) flow channel length
\( m \) mass flow
\( M_i \) molar weight of species \( i \)
\( M_m \) dry equivalent weight of the membrane
\( n \) number of electrons participating in reaction
\( n \) speed
\( n_d \) electroosmotic drag coefficient
\( N_i \) molar flux of species \( i \)
\( p_{ci} \) critical pressure of species \( i \)
\( p_{H2O,m} \) partial pressure of water in the membrane
\( p_i \) partial pressure of species
\( p_{tot} \) system pressure
\( P \) power
\( Q_i \) factors considering heat dissipation in manifolds
\( R \) universal gas constant
\( R_{air} \) gas constant air
\( R_{ohm} \) Ohmic resistance
\( t \) time
\( t_0 \) time of step
\( t_E \) electrode thickness
\( t_m \) membrane thickness
\( T \) temperature
\( T_{ci} \) critical pressure of species \( i \)
\( Tq \) torque
\( u \) input signal
\( U \) voltage
\( U_{act} \) activation polarization
\( U_{cell} \) cell voltage
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U_{conc}$</td>
<td>concentration polarization</td>
<td>[V]</td>
</tr>
<tr>
<td>$U_D$</td>
<td>electrode potential</td>
<td>[V]</td>
</tr>
<tr>
<td>$U_{fc}$</td>
<td>stack voltage</td>
<td>[V]</td>
</tr>
<tr>
<td>$U_{oc}$</td>
<td>open-circuit voltage</td>
<td>[V]</td>
</tr>
<tr>
<td>$U_{ohm}$</td>
<td>ohmic polarization</td>
<td>[V]</td>
</tr>
<tr>
<td>$U_{std}$</td>
<td>standard deviation of cell voltage across stack</td>
<td>[mV]</td>
</tr>
<tr>
<td>$v$</td>
<td>flow velocity</td>
<td>[m/s]</td>
</tr>
<tr>
<td>$V$</td>
<td>manifold volume</td>
<td>[m³]</td>
</tr>
<tr>
<td>$V_{liq}$</td>
<td>accumulated liquid water</td>
<td>[cm³]</td>
</tr>
<tr>
<td>$x_0$</td>
<td>mass fraction of dispersed phase</td>
<td>[-]</td>
</tr>
<tr>
<td>$x_g$</td>
<td>gas phase quality ($x_g = m_g/(m_g + m_{liq})$)</td>
<td>[-]</td>
</tr>
<tr>
<td>$x_i$</td>
<td>mole fraction of species $i$</td>
<td>[-]</td>
</tr>
<tr>
<td>$y$</td>
<td>co-ordinate along the fuel cell flow channel</td>
<td>[-]</td>
</tr>
<tr>
<td>$z$</td>
<td>co-ordinate orthogonal towards membrane surface</td>
<td>[-]</td>
</tr>
</tbody>
</table>

**Greek letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>net water flux per molar flux of consumed hydrogen molecules</td>
<td>[-]</td>
</tr>
<tr>
<td>$\alpha_c$</td>
<td>transfer coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>$\varepsilon_g$</td>
<td>porosity of gas diffusion electrode</td>
<td>[-]</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy change</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>enthalpy change</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>$\Delta N_i$</td>
<td>molar flux of species $i$ orthogonal to membrane</td>
<td>[mol/cm²s]</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>entropy change</td>
<td>[J/molK]</td>
</tr>
<tr>
<td>$\eta_{el}$</td>
<td>voltage efficiency</td>
<td>[-]</td>
</tr>
<tr>
<td>$\eta_f$</td>
<td>faradaic efficiency</td>
<td>[-]</td>
</tr>
<tr>
<td>$\eta_{sys}$</td>
<td>system efficiency</td>
<td>[-]</td>
</tr>
<tr>
<td>$\eta_{th}$</td>
<td>thermodynamic efficiency</td>
<td>[-]</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>ratio of specific heat capacities</td>
<td>[-]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>water content in membrane</td>
<td>[-]</td>
</tr>
<tr>
<td>$\lambda_i$</td>
<td>stoichiometric coefficient of flow $i$</td>
<td>[-]</td>
</tr>
<tr>
<td>$\mu$</td>
<td>viscosity of water</td>
<td>[g/cm s]</td>
</tr>
<tr>
<td>$\Pi$</td>
<td>compression ratio</td>
<td>[-]</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------------</td>
</tr>
<tr>
<td>$\theta$</td>
<td>combined interia of compressor and E-motor</td>
<td>[kg m$^2$]</td>
</tr>
<tr>
<td>$\rho_m$</td>
<td>dry density of the membrane</td>
<td>[g/cm$^3$]</td>
</tr>
<tr>
<td>$\sigma_m$</td>
<td>membrane conductivity</td>
<td>[S/cm]</td>
</tr>
<tr>
<td>$\sigma_{m1,2}$</td>
<td>fitting parameters for membrane conductivity</td>
<td>[-]</td>
</tr>
<tr>
<td>$\tau_p$</td>
<td>tortuosity of gas diffusion electrode</td>
<td>[-]</td>
</tr>
<tr>
<td>$\tau_f$</td>
<td>time constant related to water build-up</td>
<td>[-]</td>
</tr>
<tr>
<td>$\nu_{fg}$</td>
<td>difference in specific volume between gas and liquid phases</td>
<td>[m$^3$/kg]</td>
</tr>
<tr>
<td>$\nu_g$</td>
<td>specific volume of gas phase</td>
<td>[m$^3$/kg]</td>
</tr>
<tr>
<td>$\omega$</td>
<td>speed</td>
<td>[s$^{-1}$]</td>
</tr>
<tr>
<td>$\Psi$</td>
<td>nozzle flow function (Eq. 3.36)</td>
<td>[-]</td>
</tr>
</tbody>
</table>

2. Subscripts

- A: anode
- air: air
- amb: ambient
- aux: auxiliary components
- C: cathode
- cmp: compressor
- cons: consumed
- em: electric motor
- fc: fuel cell
- g: gaseous
- $H_2$: hydrogen
- $H_2O$: water
- im: inlet manifold
- liq: liquid
- $N_2$: nitrogen
- om: outlet manifold
- prod: produced
- sys: system
- tot: total system
- valve: pressure control valve
Superscripts

\( \infty \) stationary
\( \text{in} \) inlet
\( \text{liq} \) liquid
\( \text{out} \) outlet
\( \text{ref} \) reference state
\( \text{sat} \) saturated

3. Notation

\( \Delta \) difference
\( \bar{\ } \) average or mean value
\( . \) flux or flow
\( \frac{d}{dt} \) derivative in time

4. Abbreviations

CAN Controller Area Network
CO Carbon Monoxide
DMFC Direct Methanol Fuel Cell
ETH Swiss Federal Institute of Technology
HHV Higher Heating Value
LQG Linear Quadratic Gaussian (-controller)
MEA Membrane Electrode Assembly
PEFC Polymer Electrolyte Fuel Cell
PI Proportional Integrating (-controller)
CHAPTER 1

INTRODUCTION

1.1 General Aspects of Fuel Cells

The last decades have seen a continuous rise in interest in fuel cell technology. Tremendous effort in research and development as well as commercialization was undertaken. However, the observation and identification of the fuel cell effect dates back to the year 1839. Within only a couple of months, first C.F. Schönbein and then W.R. Grove noticed the combination of hydrogen with oxygen in the presence of platinum. Three years later Grove demonstrated the first lab-scale fuel cell, which he called gas battery. It consisted of a four-cell array and a small water electrolyzer [1].

However, the steam engine and later the internal combustion engine flooded the market with their relatively cheap technology and energy carriers. The need for an efficient and environmentally clean but complex conversion system with an expensive energy carrier had not yet been born. In the 1960th, the demand for clean and reliable energy sources in aerospace and military applications led to a revival of the fuel cell. In those niche markets the high material costs played only a minor role [2].

Many kinds of fuel cells have been developed and have shown promising results [3]. Among those the polymer electrolyte fuel cell (PEFC) is considered to be advantageous in mobile applications, especially in the automotive sector. Essential components of a PEFC are the membrane electrode assembly (MEA) and a flow field. The MEA consists of a proton
Figure 1-1: Single cell consisting of membrane electrode assembly and two flow field plates (left); Magnification of the reactive zone at the interface between gas diffusion electrode and membrane (right).

The electrolyte is a conducting polymer electrolyte (most commonly used is Nafion from DuPont [4]) sandwiched between two electrodes (see Figure 1-1). The electrodes have to be gas and liquid permeable and therefore possess a porous structure. In case of an H\textsubscript{2} PEFC, hydrogen is oxidized to H\textsuperscript{+} at the anode. Protons enter the electrolyte, while electrons flow in the external circuit. The protons migrate through the membrane to the cathode. There they recombine with oxygen to form water. A gas flow field is machined into the current collectors, thereby enabling the gas distribution. The voltage of a fuel cell is small, about 0.7 V when useful currents are drawn. Therefore, many cells are connected in series, forming a stack. A bipolar plate connects two electrodes with opposite polarities thereby implementing the serial addition in the stack.

Humidification properties of the membrane restrict the operation temperature to 100°C. Owing to this restriction PEFC have quick startup capabilities compared to other fuel cell types. The thinness of the MEAs allows for the fabrication of compact fuel cells. PEFCs have a substantially
higher part-load efficiency than internal combustion engines. As passenger vehicles are mostly operated under part-load conditions the use of PEFCs permits significantly lower fuel consumption.

Numerous problems need to be solved before a competitive fuel cell powered vehicle will be available on the market. Among the most pressing issues is the production of hydrogen and its onboard storage. Hydrogen is the only fuel that in combination with a fuel cell facilitates a CO$_2$-emission free power source. Alternatively, onboard reforming of hydrocarbons (such as methanol or gasoline) or direct methanol fuel cells (DMFC) are proposed, even though carbon dioxide emissions arise with these solutions.

1.2 Thermodynamic and kinetic considerations

In this chapter definitions of important parameters such as standard potentials and efficiencies are given.

1.2.1 Reversible cell potential

The Gibbs free-energy change, $\Delta G$, of a chemical reaction is a measure of the maximum net work obtainable from the reaction. Only if the entropy change, $\Delta S$, is zero, the free-energy change is equal to the enthalpy change, $\Delta H$, of the reaction, as maybe seen from the following equation [5]:

$$\Delta G = \Delta H - T\Delta S$$ (1.1)

If the entropy change is negative, which is the case for the reaction between H$_2$ and O$_2$ to water, the free-energy change is less negative than the enthalpy change. In case of the liquid-phase reaction between hydrogen and oxygen the respective values are [3]:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O_{(liq)}$$

$\Delta G = -237.3$ kJ/mol at 25°C

$\Delta H = -285.8$ kJ/mol at 25°C (1.2)

The Gibbs free-energy change depends on the temperature and state (liquid or gas) [3].
If there are no losses in the fuel cell, thus if the process is reversible, all this Gibbs free-energy change is converted into electrical energy. The reversible cell potential, $E$, is calculated from the following equation [5]:

$$E = -\frac{\Delta H - T \Delta S}{nF} = -\frac{\Delta G}{nF} \quad (1.3)$$

where $n$ is the number of electrons exchanged in the reaction (2 for the production of water from $H_2$ and $O_2$) and $F$ is the Faraday constant.

For the half-cell reactions and the overall reaction between hydrogen and oxygen the following standard potentials, $E^0$, (i.e., all reactants and products are in their standard state at one atmosphere and 25°C) are obtained [5].

**Anode:** $H_2 \rightarrow 2H^+ + 2e^- \quad E_A^0 = 0.0 \text{ V}$

**Cathode:** $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad E_C^0 = 1.23 \text{ V} \quad (1.4)$

**Cell:** $H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad E_{cell}^0 = 1.23 \text{ V}$

The dependence of the standard potential on the temperature is found by differentiating Eq. 1.3 with regard to the temperature $T$ at constant pressure $p$ [6]:

$$\left(\frac{\partial E^0}{\partial T}\right)_p = \frac{1}{nF}\left(\frac{\partial \Delta G}{\partial T}\right)_p = \frac{\Delta S}{nF} \quad (1.5)$$

After integrating Eq. 1.5 the following expression is obtained:

$$E^0(T) = E^0(T^0) + \frac{\Delta S}{nF}(T - T^0) \quad (1.6)$$
1.2 Thermodynamic and kinetic considerations

The Nernst equation provides a relationship between the standard potential, \( E^0 \), for the cell reaction and the equilibrium potential, \( E \), at different partial pressures \( p \) of reactants and products [5, 7].

\[
E = E^0 + \frac{RT}{2F} \ln \left( \frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2O}} \right) \tag{1.7}
\]

where \( R \) is the universal gas constant.

1.2.2 Voltage losses

Useful electrical work is obtained from a fuel cell only when a reasonably large current is drawn. However, an increase in current leads to a decrease of the actual cell voltage from the reversible cell potential due to irreversible losses in a practical fuel cell. Several sources contribute to these irreversible losses (also called overpotential or polarization), although they originate primarily from three sources: activation polarization, \( U_{act} \), Ohmic losses, \( U_{ohm} \), and mass transport or concentration losses, \( U_{conc} \).

Polymer electrolyte fuel cells (PEFC) exhibit qualitatively similar voltage/current relationships, as illustrated in Figure 1-2. The semi-exponential behavior at low current densities is due to the activation polarization of the oxygen reduction reaction. In the intermediate current density region the pseudolinear behavior is caused predominantly by Ohmic losses. At high current densities the cell potential decays rapidly due to mass-transport limitations. The highest voltage is obtained at zero current. Its value should be given by the standard potential of the chemical reaction (i.e., 1.23 V at standard conditions for reaction in Eq. 1.2). However, under practical conditions, the open-circuit potential (voltage at zero current) settles at values slightly below 1 V. This deviation can be explained if the open-circuit potential is considered to be a mixed potential due to the simultaneous occurrence of the four-electron (direct reduction) and two-electron (indirect...
reversible cell potential

Figure 1-2: Typical polarization curve of a H₂/air fuel cell with major loss contributions.

reduction via hydrogen peroxide as an intermediate) oxygen reduction reactions. Impurity oxidation can also contribute to this deviation (for more details see [3] and [8]).

Activation polarization results from the control of the electrochemical rate on the electrode surface by sluggish electrode kinetics. Similar to a chemical reaction the electrochemical reaction has to overcome an activation barrier which depends on the electrode surface (electrocatalyst). It is influenced by processes involving the adsorption/desorption of reactant species and/or product species, the transfer of electrons through the double layer, and the nature of the electrode surface (rough or smooth surface). Generally, the activation polarization is described by the Tafel equation [7]:

$$U_{act} = \frac{RT}{\alpha C_nF} \ln \left( \frac{i_C}{i_0} \right)$$  (1.8)
where $\alpha_c$ is the transfer coefficient, $i_{fc}$ the cell current density, and $i_0$ the exchange current density.

Ohmic losses are caused by resistance to the flow of ions within the ion conducting electrolyte and resistance to the flow of electrons through the electrode materials. These losses are expressed by Ohm’s law [7, 9]:

$$U_{ohm} = I_{fc}R_{ohm}$$

where $I_{fc}$ is the cell current and $R_{ohm}$ the overall cell resistance (including electronic, ionic, and contact resistances).

Concentration losses are typically observed at high reaction rates when the reactants are rapidly consumed and a concentration gradient is formed between the electrode surface and the bulk. Slow diffusion of the reactants gases in the electrodes is a major contributor to concentration losses, although slow transport through the electrolyte to or from the reaction site also plays a role. If the limiting current density $i_L$ is known, the concentration losses are calculated as follows [7]:

$$U_{conc} = \frac{RT}{nF} \ln \left(1 - \frac{i_{fc}}{i_L}\right)$$

Activation polarization and concentration losses can occur at both electrodes. The effect of polarization is a shift of the electrode potentials to new values. Thus, the anode (cathode) voltage is described by the reversible electrode potential increased (decreased) by electrode polarization [7]:

$$U_{A/C} = E_{A/C} \pm |U_{act,A/C} + U_{conc,A/C}|$$
The overall cell voltage, $U_{\text{cell}}$, is given by the difference between cathode and anode voltage diminished by the Ohmic losses in the cell [7]:

$$U_{\text{cell}} = U_C - U_A - U_{\text{ohm}}$$
$$= (E_C - |U_{\text{act}, c}| - |U_{\text{conc}, c}|) - (E_A + |U_{\text{act}, a}| + |U_{\text{conc}, a}|) - U_{\text{ohm}}$$

(1.12)

1.2.3 Fuel Cell Efficiency

It is not straightforward to define the efficiency of a fuel cell. For the case of a fuel cell working ideally, that is without any irreversibility, the free-energy change may be totally converted to electrical energy. Hence, the thermodynamic efficiency is given by [5]:

$$\eta_{\text{th}} = \frac{\Delta G}{\Delta H}$$

(1.13)

Using the higher heating value of hydrogen (see Eq. Eq. 1.2) a maximum efficiency value of 83% is obtained [7].

The voltage efficiency is used to describe the quality of a fuel cell, when comparing different cell designs. It is defined as [9]:

$$\eta_{\text{el}} = \frac{-nF}{\Delta H}U_{\text{cell}} = \frac{U_{\text{cell}}}{E_{\text{th}}} \quad \text{with} \quad E_{\text{th}} = \frac{-\Delta H}{nF}$$

(1.14)

$E_{\text{th}}$ is the theoretical standard electrode potential obtained from the enthalpy change. In this work the higher heating value (HHV) will be used, here $E_{\text{th}}$ is 1.48 V [3, 10]. Often, instead of the enthalpy change $\Delta H$ the voltage efficiency is referenced to the Gibbs free-energy change $\Delta G$. This does not allow any fair comparisons to other energy conversion systems, such as the internal combustion engine, and thus should be avoided.
The faradaic efficiency describes the relationship between the observed current, \( I \), and the theoretically expected current, \( I_m \), on the basis of the hydrogen inlet flow, assuming that all hydrogen is consumed [5]:

\[
\eta_f = \frac{I_{fc}}{I_m}
\]  

(1.15)

The faradaic efficiency may be less than unity due to low hydrogen utilization, parallel electrochemical reactions, and hydrogen crossover [5].

The system efficiency, \( \eta_{sys} \), further considers the power consumption of the auxiliary components (such as air compressor, cooling system, recirculation pumps, etc.) [5]. This value allows for judgements about the quality of the overall fuel cell system.

\[
\eta_{sys} = \frac{P_{fc} - P_{aux}}{m_{H2} \cdot \Delta H}
\]  

(1.16)

where \( P_{fc} \) is the gross electric power output of the fuel cell, \( P_{aux} \) the auxiliary power demand, and \( m_{H2} \) the inlet hydrogen flow.

1.3 Application Example: Experimental Fuel Cell Vehicle Hy.Power

In the course of this work extensive know-how was obtained during the development and operation of the so-called Hy.Power vehicle shown in Figure 1-3. The construction of the fuel cell system hardware and the implementation of the control algorithm provided numerous insights into the complexity of a fuel cell system for automotive applications. Valuable information was gathered on critical aspects such as reactant supply, water management, and cell voltage distribution. Since the experience gained from this vehicle served as a basis for further investigations, the vehicle is briefly described in this section.
The Hy.Power vehicle is a fuel cell powered electric vehicle, assisted by a supercapacitor storage. It was designed and constructed in a joint project by the Paul Scherrer Institute (PSI), the Swiss Federal Institute of Technology (ETH) and various industrial partners and has been demonstrated on numerous occasions since its completion in 2002.

An array of six PEFC stacks with 125 cells each and a combined nominal output of 48 kW forms the main power source of the vehicle. Each cell has an active area of 204 cm$^2$. The six stacks are electrically connected as two parallel strings of three stacks each in series in order to match the voltage requirement of the powertrain. The reactant gases and the cooling liquid are fed in parallel through a manifold plate [11].

Jointly developed by PSI and Montena SA, the supercapacitors installed in the vehicle each have a rated capacitance of 1600 F with a rated voltage of 2.5 V [12]. Altogether, the 282 pair-wise connected supercapacitors provide a storage capacity of 210 Wh and are able to provide 50 kW for a duration of about 15 s [13]. The maximum voltage of the supercapacitor module is 360 V.
Figure 1-4 describes the configuration of the powertrain. The vehicle is driven by an AC motor with a permanent power output of 45 kW, a peak power output of 75 kW, and a maximum torque of 255 Nm (all values apply to an input voltage of 280 V). The input voltage of the motor inverter is kept at a constant high voltage, thereby assuring the highest possible motor torque and a good efficiency over the whole speed range. Fuel cell and supercapacitors are connected to a DC link by means of DC-DC converters [14]. A supervisory controller is used to actively regulate the power flow between motor inverter, fuel cell and supercapacitors. A one-step transmission without a clutch completes the powertrain.

Two 26-liter tanks store the hydrogen at a pressure of up to 350 bar. This amounts to roughly 1.05 kg of hydrogen, which is equivalent to about 4 liters of gasoline. The vehicle has a range of 50 to 100 km depending on the driving cycle. The total weight of the test vehicle is about 2000 kg.

The parallel arrangement of six fuel cell stacks requires the equal distribution of the reactant flow across 19500 channels (6 stacks * 125 cells per stack * 26 flow channels per cell). Maximum power output is generated only if the reactants flows into the array are distributed equally across all cells and flow channels. Especially on the hydrogen side this is difficult to accomplish as the hydrogen flow is considerably smaller than the air flow.
When the power output was increased beyond 20 kW, the voltage became unstable (see Figure 1-5). Larger than expected amounts of liquid water accumulated at the anode. As a consequence, the anode was increasingly flooded by water. Hydrogen was thus prevented from reaching the reaction site and the local reactant was starved causing the reaction to break down. The magnitude of this phenomenon rose with increasing current as more water was produced in the course of the reaction. In one attempt to improve matters a purge valve was installed through which hydrogen was continuously purged to the surrounding. This led to an increased hydrogen flow in the fuel cell and hence to an easing of the anode flooding. However, this improvement was gained at the cost of efficiency as hydrogen was wasted to the surrounding.

Figure 1-6 shows the responses of the fuel cell voltage and current to an increase in the power demand. The fuel cell power is increased gradually with a flat gradient of 1 kW/s. Nevertheless, a negative overshoot of the voltage and a positive overshoot of the current are clearly visible. The voltage
overshoot results from a temporary shortage of the reactants (oxygen and hydrogen) due to a slow response of the supply system. The current overshoots to compensate the voltage drop as the fuel cell is power controlled.

The experimental vehicle was a major success. During the operation time a total distance of about 1000 km was travelled and the vehicle was demonstrated on numerous occasions, such as the Geneva Motor Show or the Earth Summit in Johannesburg in 2002. Most of the critical aspects that were encountered during the operation of the vehicle, such as water accumulation and sluggish gas supply, are related to transient phenomena. The objective of the work presented here is to facilitate the understanding of transient phenomena, which typically arise in large-scale fuel cell stacks in automotive applications. For this purpose, a stack almost identical to those used in the Hy.Power vehicle was obtained. The test bench into which the stack is integrated is described in the next chapter.
1.4 Contributions

During the work on the fuel cell powered Hy.Power vehicle extensive knowledge and experience were obtained. The operation of this experimental vehicle was very successful, nevertheless some critical aspects were revealed, especially during load transients. For further investigations and analysis of these phenomena a fuel cell test bench was constructed. This test bench is equipped with a large PEM fuel cell stack (6 kWₑ) and reproduces the conditions found in automotive applications. In this thesis the transient behavior of a large PEM fuel cell stack operated under automotive conditions is explained. In particular the response to air stoichiometry steps, current steps and current spikes is analyzed. The experiments clearly show that the proposed application of current spikes significantly enhances the performance and improves the voltage stability.

The performance of the Hy.Power vehicle was impaired by the sluggish response of the air supply system. To improve matters, in this thesis a model-based MIMO controller is designed for the air supply system to control the mass flow and the pressure. This controller shows a significantly improved performance over PI controllers with regard to response time and decoupling of mass flow and pressure. With this controller the load on the fuel cell can be ramped up from zero to full load in less than 50 ms.

Furthermore, in this thesis the cell voltage distribution at different operating conditions is investigated and parameterized. The derived models agree well with the experimental data.

A one-dimensional model of this large fuel cell stack was developed which allows to simulated the performance over a wide operating range. The model requires the identification of only ten parameters. The current-voltage relationships at different system pressures, at different stack temperatures and at different air stoichiometric values are successfully reproduced. The computational burden is small compared to more extensive models, nevertheless a high accuracy is obtained. The model allows the computation of the water balance and the partial pressure of the reactants at the membrane-electrode interface.
The test bench (see Figure 2-1) described in this section is closely related to the fuel cell system used in the experimental vehicle Hy.Power. The test bench was designed and constructed to be as similar to the vehicle as possible. Many parts used in the test bench are also found in the vehicle. However, the piping in the test bench is longer than in the vehicle in order to avoid any physical constraints caused by components placed too closely to each other.

**Figure 2-1:** View of test bench with direct hydrogen fuel cell stack with 100 cells and nominal electric power output of 6 kW.
2.1 Fuel Cell Stack

Prior to the build-up of the fuel cell array of the Hy.Power vehicle, a prototype stack was constructed to test the design. Jointly developed by the Paul Scherrer Institute and the Center for Product-Design of the Swiss Federal Institute of Technology (ETH), the stack was thoroughly tested and evaluated. After the successful completion of Hy.Power project the stack was obtained for further studies on the test bench described in this chapter.

The fuel cell stack consists of 100 cells with an active area of 204 cm\(^2\) each (see Figure 2-2). Under optimal conditions with regard to pressure, humidity, reactants flow, and temperature, the electrical output capability of the stack is 6 kW at 0.6 V/cell. The cells are electrically connected in series, while the reactant gases and the cooling liquid are fed to the cells in parallel. The two

![Figure 2-2: CAD graph and photo of the 100-cell stack supplied by Paul Scherrer Institute [16].](image-url)
main parts of a fuel cell are the bipolar plates and the membrane-electrode-assemblies (MEA). The bipolar plates distribute air and hydrogen to the MEA and comprise the cooling channels. Furthermore, together with the sealing they have to prevent any mixing of the various media and to ensure that none of them leak to the exterior. Finally, the bipolar plates have to conduct the current between the cells. In the prototype stack new bipolar plates were used, which were developed and optimized with regard to volume, weight and manufacturing processes. The main objective in the design process was to achieve a low manufacturing cost to demonstrate the potential for mass production. This was accomplished with a mould-to-size process using a graphite-polymer compound [15].

The performance of two 125-cell stacks, one with moulded plates and the other with milled plates, was compared in [15]. The results showed that with milled plates a slightly higher voltage is achieved at high current densities. This is attributed to the higher conductivity of the milled material leading to lower Ohmic losses at high current densities. However, the moulded plates possess a smaller tolerance in channel depth, resulting in a more even flow distribution across the channels and a smaller voltage variation between the cells. A higher tolerance in absolute thickness of the moulded plates was observed, but this did not noticeably affect the performance of the assembled stack.

The bipolar plates consist of two half-plates which are glued together (Figure 2-3). Each flow field has 26 flow channels, which have a meander-like structure. With this design only slight deviations in channel length are achieved. The shortest channel has a length of 417 mm, whereas the longest channel is 420 mm long [16]. The design of the flow field is identical on the air and hydrogen side. Nevertheless, the relative flow between air and oxygen is a mix between co-flow, counter-flow and even cross-flow, as visualized in Figure 2-4.

The channel geometry on the air side and on the hydrogen side differ only in channel depth. The channel width at the bottom is 0.85 mm on both sides and the channel opens with an angle of 10° to allow a better fabrication. The air channels have a depth of 0.55 mm as opposed to 0.35 mm on the hydrogen side. The shoulder width amounts to 0.8 mm [16].
The channels for the cooling media are integrated into the back of the hydrogen half-plate (see Figure 2-3). Hence, the cooling channels are situated in the partition between anode and cathode after the two half-plates are glued together.

The MEA is made up from commercially available membranes (Nafion 112, DuPont [4]) and electrodes (ELAT, E-Tek, 0.5 mg Pt/cm² [17]), while the respective preparation and assembly procedures were newly developed [18, 19].

The Nafion membrane and other alternative polymer electrolyte materials consist of a polymer structure with pendant sulfonic acid groups. By swelling the membranes with water, the SO₃H-groups dissociate into mobile hydrated H⁺ ions and immobile SO₃ ions. The mobility of the H⁺ ion and thus the conductivity of the membrane depends strongly on the water content [20]. Therefore, proper water management of the membrane is essential for an efficient and reliable operation of the fuel cell [21].
Nafion membranes are generally characterized by their equivalent weight and their thickness. The equivalent weight describes the dry weight of the polymer per mol sulfonic acid group and presents a measure for the mass based concentration of the $\text{SO}_3\text{H}$ groups. For Nafion 112 the first two digits indicate an equivalent weight of 1100 g/mol. The thickness of the membrane is characterized by the third digit and amounts to 2/1000 inches (~50 $\mu$m) in the dry state. Compared to other commonly used membranes, such as Nafion 115 or Nafion 117, Nafion 112 is a thin membrane. Typically, thinner membranes show a better performance due to the smaller overall electrolyte resistance. A further advantage is the more effective water diffusion, leading to a better hydration of the anode, thus lower Ohmic losses even at high current densities [22].
Electrodes for PEFC are generally porous gas diffusion electrodes to ensure the supply of the reactant gases to the reaction zone. Gas diffusion occurs through the backing layer and the carbon support to the catalyst particles. A three-phase boundary between the gas phase, the electronic conductor (carbon supported catalyst particles) and the ionic conductor (solid polymer electrolyte) is prerequisite for the reaction to take place. Usually the catalyst is impregnated with some ionomeric solution (such as Nafion solution) before pressing the electrode onto the membrane. This ensures a good contact between catalyst particle and ionomer material, extends the reaction zone and increases the catalyst utilization [23].

2.2 Peripheral Components

The setup of the fuel cell system, which is discussed in this chapter, was realized with help of Hans Ulrich Honnegger (ETHZ), Renzo Marcolongo (PSI), Akinori Tuskada (PSI) and Daniel Matter (ETHZ).

The direct hydrogen fuel cell system (Figure 2-5) may be divided into three subsystems according to the fluid they handle:

- The air subsystem has to supply the process air at the required pressure, flow rate, temperature, and humidity.
- The H₂ subsystem has to supply hydrogen at the required pressure and flow rate.
- The cooling subsystem has to guarantee adequate cooling of the fuel cell stack and to ensure a small temperature gradient across the stack.

The air supply to the cathode is handled by a twin-screw compressor (Opcon OA1040) and a continuous pressure valve (Bürkert). A supersonic atomizer (Lechler) is used for the humidification of the air stream. Air pressure and temperature are measured at the inlet as well as at the outlet of the fuel cell stack, whereas the humidity is measured only at the inlet. The air mass flow sensor is placed in front of the compressor.
Figure 2-5: Diagram of test bench setup, consisting of air supply, hydrogen supply, and cooling.
With regard to the air supply of the fuel cell system, four states need to be controlled: mass flow, pressure, inlet temperature, and humidity, but only three actuators are available, namely the compressor, the pressure valve, and the humidification device. By injecting liquid water droplets into the hot air leaving the compressor the air stream is cooled and the humidity is increased. Therefore, the inlet temperature and the humidity are coupled and cannot be controlled independently in this setup. Excessively high inlet temperatures may damage the fuel cell membrane whereas a low humidity results in poor stack efficiency. To enhance the water evaporation a vessel filled with porous material was installed after the injection device. With this vessel the humidification was improved but it also made the humidity control difficult since the porous material has a large water storage capability thus introduces a large time lag. A open-loop control scheme is used to control the amount of injected water, which is set sufficiently high as to guarantee that no critical temperature levels are reached at the stack inlet. With this approach the air stream stabilizes at a temperature around 45 °C and a relative humidity of 100%. However, as a consequence the inlet temperature and the humidity cannot be varied in this setup.

The control of air mass flow and air pressure was achieved with either a state-based controller or with two independent closed-loop control systems. In the latter approach, the mass flow control loop consists of the compressor, a mass flow sensor (TSI 4020), and a simple PI controller. Similarly, the pressure control loop is made up of the continuous pressure valve (Bürkert), a pressure sensor (Bürkert), and another PI controller. Although mass flow and pressure interact (e.g. an increase in mass flow translates into a higher pressure if the valve position is kept unchanged), experiments have proven that the fuel cell acts as a sufficient damping element and that PI controllers provide satisfactory results. Nevertheless, state-based controllers decouple pressure and mass flow more effectively and show a superior behavior with regard to response time and to deviations from the setpoint (see Chapter 5.2).

Hydrogen is stored in a high-pressure tank at up to 200 bar. Using a reduction valve (Gloor) and a control valve (Bürkert) hydrogen is fed to the fuel cell stack. Excess hydrogen is recirculated by means of an ejector (Festo) [24, 25]. In addition, pressure waves are used to assist the removal of water droplets in the flow channels. These pressure waves are generated in three
2.2 Peripheral Components

different ways. First, the fuel cell is periodically supplied (in short intervals of less than 0.5 s) with hydrogen at pressures higher than the operating pressure. Second, also periodically, hydrogen is sucked from the exit of the fuel cell into a low pressure vessel generating low pressure pulses. The pump used to build up the vacuum in this vessel discharges the hydrogen to the entrance of the fuel cell. Finally, hydrogen is purged to the environment through a valve at the exit of the fuel cell (this option is not used under regular operating conditions). The pump used to build up the vacuum can also be used to actively recirculate hydrogen. Similar to the air subsystem, hydrogen pressure and temperature are measured at the inlet as well as at the outlet of the fuel cell stack, whereas the humidity is measured only at the inlet. The hydrogen massflow sensor is placed in front of the stack.

In order to achieve the best performance of the fuel cell stack, mass flow, pressure, inlet temperature, and humidity need to be controlled on the hydrogen side as well. Because of the stringent limitations on space and weight in an automotive application no humidification device was installed in the hydrogen feed. However, since part of the hydrogen is recirculated, dry hydrogen from the tanks is mixed with hydrogen which already passed through the stack and thereby took up water. Experiments have shown that in thin membranes (such as Nafion 112) the water flux due to back-diffusion to the anode can effectively compensate the flux due to the electroosmotic drag (protons moving from the anode to the cathode pull water molecules with them - typically 1 to 2.5 water molecules are dragged per proton [26]). Hence, the water is more evenly distributed in a thin membrane [22]. Due to the fact that the hydrogen flow is considerably smaller than the air flow, the capacity of hydrogen to carry water is also considerably smaller. Therefore, the lack of a proper humidification device in the hydrogen feed is not considered to be of major concern as the humidification of the air flow is much more important [27, 28]. Furthermore, since the hydrogen expands from high-pressure tanks prior to entering the fuel cell, the danger of excess temperature does not arise. Therefore, in this setup neither temperature nor humidity are controlled on the hydrogen side.

Although the fuel cell stack is fed with a surplus of hydrogen, from a system point of view the fuel supply is a filling process. As a consequence only one degree of freedom exists to control either mass flow or pressure. A large
pressure difference across the membrane between the air and hydrogen side would damage the membrane. Therefore, precautions have to be taken to avoid any large pressure deviations by controlling the hydrogen pressure or the pressure difference across the stack (realized again with a PI controller). The mass flow then adjusts itself according to the pressure drop across the pressure-regulating valve. Under steady-state conditions the hydrogen mass flow into the system equals the hydrogen consumed by the electrochemical reaction. In transient conditions there is lag, which causes a shortage of hydrogen and possibly even a local starvation of the reaction. This phenomenon is avoided by the above-mentioned recirculation of a certain amount of hydrogen, i.e., by supplying hydrogen to the fuel cell continually at larger than stoichiometric values. Without this arrangement only very limited dynamics would be achievable. More details about the hydrogen supply are found in [29].

The configuration of the cooling system is rather straightforward. The liquid cooling loop designed to cool the cells, consists of a continuous-controlled pump and a radiator with two fans of different size (standard automotive parts). The fans are operated independently, although only in an on-off mode. As the cells are fed in parallel, it is difficult to obtain an equal flow through all cells. Slight deviations in flow resistance among the channels cause the flow to differ from channel to channel and from cell to cell. Especially at reduced flows an even flow distribution is difficult to achieve. Low flows lead to insufficient cooling. Therefore, hot spots in the membrane may occur, as some cells may not be properly fed with cooling liquid. This is avoided by not operating the pump in the region with small flows. Sufficient flows in all cells are thus achieved even at low fuel cell loads, although at the expense of a slightly higher power consumption. Furthermore, the effect of intensive cooling with an accompanying falling stack temperature has to be accepted, although this effect is lessened by bypassing the radiator. The pump is controlled by a PI controller, whereas binary controllers control the fans.

The control algorithms are centrally managed by a dSpace DS1003 Processor Board. Matlab/Simulink is used to program the control algorithms. Logical sequences were programmed with the help of the Matlab toolbox Stateflow. Euler’s method was chosen as a solver, with a fixed step size of 5 ms. The communication between the sensors and the dSpace system, as well
as the communication to the actuators are handled by a CAN-Bus. For this purpose the highly flexible WAGO 750 CANopen series is installed, which is a modular I/O system. Modules are available for almost every type of sensor signal or actuator output, and the configuration can be expanded easily by adding additional elements. The load for dissipating the electric power is a Höcherl & Hackl electronic load, type DS5010, capable to sustain loads of up to 100 A or 5 kW. The fuel cell stack is equipped with a single cell measuring device [30] for monitoring purposes. This device was realized with the help of Gino Paganelli (ETHZ/PSI) and Roberto Panozzo (PSI).
CHAPTER 3

MODELING

The objective of the model presented in this work is the development of a tool for the calculation of the cell performance (i.e., the cell voltage over the current density of the fuel cell) and a tool for the investigation of transient phenomena (such as reactants transport, partial membrane dehydration, deactivation of the catalyst surface through flooding or the build up of an oxide layer). These phenomena have typically time constants in the range of a few seconds to several minutes. Dynamic effects with time constants of less than one second (such as diffusion lag or double layer capacity) are not considered.

Effort was carried out to simplify the analytical aspects as much as possible and to ease the burden on simulation time and parameter identification. The proposed transient model is based on chemical-physical knowledge of the phenomena occurring inside the cell, although some empirical equations are used. In the first section of this chapter a one-dimensional, isothermal steady state model is developed. This model is applied in Chapter 4 to outline the major characteristics of the mentioned 100-cell fuel cell stack. In Chapter 5 the model is expanded to facilitate a discussion of the observed transient voltage response of the fuel cell. In the second part of this chapter, a transient model of the air supply system is developed, which includes the dynamics of the compressor/electric-motor unit as well as the dynamics of the manifold filling/emptying processes.
3.1 One Dimensional Fuel Cell Stack Model

The three-dimensional stack problem is reduced to a one-dimensional problem, in which the relevant dimension is orthogonal to the membrane surface. The stack model considers the transport through the following five regions of the cross-sectional area within the fuel cell, as schematically illustrated in Figure 3-1: the flow channels and the gas diffusion electrodes on either side, and the Nafion membrane. The model includes the transport of the gaseous components through the porous electrode and water transport through the membrane. The former is based on diffusion corrected for porosity, whereas the latter is based on electroosmotic drag, diffusion and convection.

Electrode kinetics are considered only at the cathode, where the major losses occur, whereas the anode potential is assumed to be equal to its equilibrium value. For further simplification, the Ohmic resistance in the fuel cell is entirely made up from conductivity losses in the membrane.
3.1 One Dimensional Fuel Cell Stack Model

3.1.1 Mass Transport

The model presented in this section requires several simplification and the definition of a set of assumptions:

1. The temperature of the solids (bipolar plates, electrodes, and membranes) is assumed to be uniform and constant since the solid materials have a high thermal conductivity [31].
2. The feed gases have no temperature gradient over the channel length. The gases reach the stack temperature almost instantaneously upon entering the flow channels [23].
3. Heat transfer by conduction in the gas phase is negligible [31].
4. Flow conditions within the channel are plug-flow, i.e., the flow velocity is constant across the channel cross section [31, 32].
5. An ideal gas mixture of the reactant flows is assumed in the channel cross section.
6. The electroosmotic drag coefficient and the diffusion coefficient of water in the membrane are assumed to be determined by the water content of the anode side [31].
7. The electronic conductivity of the current collectors is sufficiently high for the voltage losses in the connectors to be negligible. Contact resistance between electrolyte and membrane caused by insufficient compression is negligible [31].
8. Only water in the form of vapor enters the stack.
9. The current density is assumed not to vary along the channel (see remark below).
10. The water content in the membrane varies linearly between cathode and anode, since the membrane is very thin [32].
11. The anodic overpotential is sufficiently small to be neglected [33, 34, 35].
12. The backwards reaction at the cathode is irrelevant [5].
13. Losses due to hydrogen cross-over are negligible [36, 37].
14. The catalyst layer is assumed to be ultrathin, so that gas transport resistance through the catalyst layer can be neglected [32, 33, 38].
Assumption 9 has significant implication on the model development. Büchi et al. [39] measured the local current density distribution of a single cell with a flow field identical to that used in the 100 cell stack. These measurements showed that under well humidified conditions the assumption of a constant current density is justified due to the specific design of the flow field (deviations from the mean value are less than 10%). However, with poor humidification large variations across the cell surface were observed (deviations of more than 25% have been measured). At low air stoichiometries segments near the air inlet had the highest performance, whereas at high stoichiometries these segments had the lowest performance. To accurately predict the current distribution either the development of a two-dimensional model or extended measurements with a segmented cell are necessary. These requirements contradict the objective to develop a simple model as far as possible. Hence, assumption 9 is retained and is understood to be an approximation.

The molar fluxes of reactants and products in the channels are averaged by the algebraic mean of the inlet and outlet fluxes of the respective specie.

The inlet fluxes are proportional to the current density and are given by the following equations:

\[ N_{H_2,O_A}^{in} = \lambda_{H_2} \cdot \frac{i_{fc}}{2F} \]

\[ N_{H_2O,A}^{in} = \lambda_{H_2} \cdot \frac{i_{fc}}{2F} \frac{x_{H_2O,A}^{in}}{1-x_{H_2O,A}^{in}} \]

\[ N_{O_2,C}^{in} = \lambda_{air} \cdot \frac{i_{fc}}{4F} \]
\[ N_{H_2O, C}^{in} = \lambda_{air} \cdot \frac{i_{fc}}{4F} \left( \frac{x_{H_2O, C}^{in}}{1 - x_{H_2O, C}^{in}} \cdot x_{air}^{air} \right) \] (3.4)

\[ N_{N_2, C}^{in} = \lambda_{air} \cdot \frac{i_{fc}}{4F} \left( \frac{1 - x_{air}^{air}}{x_{O_2}^{air}} \right) \] (3.5)

where \( i_{fc} \) is the current density and \( F \) the Faraday constant. The subscripts A/C denote the anodic/cathodic side of the cell. The dry gas mole fraction of oxygen in air \( x_{air}^{air} \) is set to 0.21. \( \lambda_{air} \) and \( \lambda_{H2} \) denote the stoichiometric coefficient of the air and hydrogen flow. The definitions of which are as follows:

\[ \lambda_{H_2} = \frac{m_{H_2}^{in}}{(M_{H_2} \cdot n_{cells} \cdot I_{fc})/(2F)} \]

\[ \lambda_{air} = \frac{m_{air}^{in}}{(M_{air} \cdot n_{cells} \cdot I_{fc} \cdot 4.86)/(4F)} \]

where \( m \) is the mass flow at the stack inlet, \( M_{H_2}, M_{air} \) the molar weight of hydrogen and air, \( n_{cells} \) the number of cells in the stack and \( I_{fc} \) the stack current.

Since the dew point of the anode and cathode inlet flow is known from measurements the water inlet fraction can be calculated:

\[ x_{H_2O}^{in} = \frac{p_{sat}(T^{sat})}{p_{tot}} \] (3.6)
where $p_{tot}$ is the total system pressure, $T_{\text{sat}}$ the dewpoint of the inlet flow and $p_{H_2O}^{\text{sat}}$ the saturation pressure of water.

From the flow balance, the inlet flow minus the flow that is consumed or produced at the membrane-electrode interface is the outlet flow. The mole fluxes $\Delta N_i$ of the components $i$ orthogonal to the membrane surface are defined as follows:

$$\Delta N_{H_2} = \frac{i_{fc}}{2F} \quad \Delta N_{H_2O,A} = \frac{\alpha \cdot i_{fc}}{2F}$$

$$\Delta N_{O_2} = \frac{i_{fc}}{4F} \quad \Delta N_{N_2} = 0 \quad \Delta N_{H_2O,C} = \frac{(1 + \alpha) \cdot i_{fc}}{2F}$$

The sign is defined to be positive for any flux from either the anode or the cathode flow channels towards the membrane. The variable $\alpha$ is the net water flux per molar flux of consumed hydrogen molecules [40]. The value of $\alpha$ is defined as positive for water transported from the anode to the cathode side. This is the case if the flux due to the electroosmotic drag is larger than the flux due to back-diffusion [41]. The flux of nitrogen is set to zero as nitrogen is neither consumed nor produced in the fuel cell reaction [40].

In Eq. 3.7 through 3.8 no distinction is made between water vapor and liquid water. The transport properties of vapor and liquid are thus considered identical in the continuity equations. However, when the partial pressure of the reacting gas has to be considered for the calculation of the electrode kinetics, the fraction of liquid water was subtracted and only the real mole fraction was used.

**Gas Diffusion in the Electrode**

Diffusion of the reactants in the porous backing is described by the Stefan-Maxwell equation, as used in the one-dimensional model published by Springer et al. [33]:

*Chapter 3 Modeling*
3.1 One Dimensional Fuel Cell Stack Model

\[ \frac{dx_i}{dy} = RT_{fc} \sum_{j=1, i \neq j}^{k} \frac{x_i N_j - x_j N_i}{p D_{ij} (\varepsilon_g / \tau_p)} \]  

(3.9)

where \( x_i \) is the mole concentration of component \( i \). The parameters \( \varepsilon_g \) and \( \tau_p \) take into account the porosity and the tortuosity of the gas diffusion electrode. The binary diffusion \( D_{ij} \) are calculated according to the estimation from Slattery and Bird [42] at low pressures. The pressure-diffusivity product is estimated from critical temperature \( T_c \), critical pressure \( p_c \) and mass \( M \) of the components \( i \) and \( j \) [43]:

\[ p D_{ij} = a \left( \frac{T}{T_{ci} T_{cj}} \right)^{b/3} \left( T_{ci} T_{cj} \right)^{5/12} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2} \]  

(3.10)

where \( a = 0.0002745, b = 1.832 \) for \( H_2, O_2 \), and \( a = 0.000364, b = 2.334 \) for water vapor.

Applying Eq. 3.9 together with Eq. 3.7/3.8 on water at the anode, as well as on oxygen and water at the cathode yields the following equations [40]:

\[ \frac{dx_{H_2O,A}}{dy} = \frac{RT_{fc} \cdot i_{fc}}{2F p_A D_{H_2O,H_2} (\varepsilon_g / \tau_p)} [x_{H_2O,A} (1 + \alpha) - \alpha] \]  

(3.11)

\[ \frac{dx_{H_2O,C}}{dy} = \frac{RT_{fc} \cdot i_{fc}}{2F} \left[ \frac{(1 - x_{H_2O,C} - x_{O_2}) (1 + \alpha)}{p C D_{H_2O,N_2} (\varepsilon_g / \tau_p)} + \right. \]  

\[ \left. \frac{0.5 x_{H_2O,C} + x_{O_2} (1 + \alpha)}{p C D_{H_2O,O_2} (\varepsilon_g / \tau_p)} \right] \]  

(3.12)

\[ \frac{dx_{O_2}}{dy} = -\frac{RT_{fc} \cdot i_{fc}}{2F} \left[ \frac{x_{O_2} (1 + \alpha) + 0.5 x_{H_2O,C} + 0.5 (1 - x_{H_2O,C} - x_{O_2})}{p C D_{H_2O,O_2} (\varepsilon_g / \tau_p)} + \right. \]  

\[ \left. \frac{0.5 x_{H_2O,C}}{p C D_{O_2,N_2} (\varepsilon_g / \tau_p)} \right] \]
Eq. 3.11 to 3.13 can be integrated across the electrode thickness, \( t_E \), to obtain the species concentration at the respective electrode-membrane interface.

The net water flux per molar flux of hydrogen is calculated as follows [32]:

\[
\alpha = 2 \left( n_d - D_w \frac{F}{i_{fc}} \frac{dc_{H_2O,m}}{dy} - c_{H_2O,m} \frac{k_p F}{\mu i_{fc}} \frac{dp_{H_2O,m}}{dy} \right) \tag{3.14}
\]

where \( n_d \) is the electroosmotic drag coefficient, \( D_w \) the diffusion coefficient of water in the membrane, \( c_{H_2O,m} \) the molar concentration of water in the membrane, \( p_{H_2O,m} \) the partial pressure of water in the membrane, \( k_p \) the permeability of water in the membrane and \( \mu \) the viscosity of water, respectively. The second term on the right-hand side describes the effect of water back-diffusion resulting from a concentration gradient and the third term describes the effect of convection due to a gradient in the partial pressure of water.

Since the membrane is very thin (~50 \( \mu \)m), a single-step linear difference assumption between the anode side and the cathode side is used for the calculations of the concentration and pressure gradients of water across the membrane. The concentration in the membrane is averaged by the algebraic mean of the concentration of water at the membrane-electrode interface of the anode and cathode side [32].

The concentration of water can be expressed in terms of water content \( \lambda \), that is the amount of water molecules per mole of sulfonic groups in the membrane [33]:

\[
c_{H_2O,m} = \frac{\rho_m}{M_m} \cdot \lambda \tag{3.15}
\]

where \( \rho_m \) and \( M_m \) are the dry density and the dry equivalent weight of the membrane.
The coefficients for drag and diffusion both depend on the water content in the membrane $\lambda$. The water content of Nafion membranes has been measured by Hinatsu et al. [44] and Zawodzinski et al. [26, 45, 46] with similar results. Generally, an empirical relationship between water content and water activity $a$ in the form of Eq. 3.16 is put forward.

$$\lambda = k_0 + k_1 a + k_2 a^2 + k_3 a^3$$ \hspace{1cm} (3.16)

The coefficients $k$ are dependent on the water activity and on the system temperature. The values given in Table 3-1 are taken from Dannenberg et al. [40], who adapted the data from the references [26, 33, 34] and [44].

<table>
<thead>
<tr>
<th>activity $a$</th>
<th>$T_{fe}$</th>
<th>$k_0$</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a \leq 1$</td>
<td>30</td>
<td>0.043</td>
<td>17.81</td>
<td>-39.85</td>
<td>36.00</td>
</tr>
<tr>
<td>$a \leq 1$</td>
<td>80</td>
<td>0.30</td>
<td>10.80</td>
<td>-16.00</td>
<td>14.10</td>
</tr>
<tr>
<td>$1 &lt; a \leq 2.5$</td>
<td>30</td>
<td>-9.1776</td>
<td>37.276</td>
<td>-15.877</td>
<td>2.255</td>
</tr>
<tr>
<td>$1 &lt; a \leq 2.5$</td>
<td>80</td>
<td>-30.412</td>
<td>61.978</td>
<td>-25.960</td>
<td>3.7008</td>
</tr>
<tr>
<td>$a &gt; 2.5$</td>
<td>30</td>
<td>$\lambda = 20$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a &gt; 2.5$</td>
<td>80</td>
<td>$\lambda = 20$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3-1: Coefficients $k$ for the calculation of the water content $\lambda$.

The water activity is calculated by the Eq. 3.17:

$$a = x_{H_2O} \frac{P_{tot}}{P_{H_2O}^{sat}}$$ \hspace{1cm} (3.17)

where $x_{H_2O}$ is the mole fraction of water at membrane-electrode interface.
The drag coefficient, $n_d$, is calculated using the model developed by Springer et al. [33, 34]. It postulates a value for $n_d$ of 2.5 for a Nafion 117 membrane equilibrated with liquid water ($\lambda = 22$).

$$n_d = 2.5 \times \frac{\lambda}{22}$$

(3.18)

Several expression for the diffusion coefficient, $D_w$, have been proposed in literature (see Motupally et al. [47] for an overview). Here the expression given by Springer et al. [33, 34] is used. It is based on fitted data from Zawodzinski et al. [45] for Nafion 117 membranes at 30°C and is valid for $\lambda > 4$.

$$D_w = D_0 \exp\left[2416\left(\frac{1}{303} - \frac{1}{T_f c}\right)\right](2.563 - 0.33\lambda + 0.0264\lambda^2 - 0.000671\lambda^3)$$

(3.19)

where in this model $D_0$ is a coefficient to be defined from experimental data (see Chapter 4).

Iterative solution

The water content of the membrane cannot be defined explicitly, but has to be found by iteration. First, a value for $\alpha$ is guessed and the fluxes are calculated using Eq. 3.1 to 3.8. With the fluxes known the water concentration (Eq. 3.11 and 3.12) is calculated. Then the water content (Eq. 3.16) and the drag coefficient (Eq. 3.18) as well as the diffusion coefficient (Eq. 3.19) are computed. Finally, the real value of $\alpha$ is determined form Eq. 3.14. The procedure is repeated until the values for $\alpha$ converge.

In the following an estimation of the convergence behavior is given. First, Eq. 3.11 is integrated and the resulting expression for the water concentration at the membrane-anode interface substituted in Eq. 3.17 yielding the water activity. Through substitution of this expression in Eq. 3.16 the water content at the anode side is obtained. This expression is then applied in Eq. 3.14. Here the effect of the convection may be neglected, since the contribution is small.
Furthermore, the dependence of $D_w$ on the water content is disregarded, because the influence is minor. Finally, the resulting expression for $\alpha$ is differentiated. Applying typical values for the other operating parameters (pressure, temperature and current density) it can then be shown that the convergence criteria $|f'(\alpha)| < 1$ is fulfilled for $\alpha \in [-5, 5]$.

**Pressure drop in flow channel**

Eq. 3.20 was presented by Argyropoulos et al. [48] to describe the relationship between pressure drop and flow rate of a homogeneous two-phase flow.

\[
\Delta p_{fc} = \int_0^l G^2(z) \left( \frac{2zf(z) + K}{d_H} \right) \times \left( 1 + \frac{x_g(z)v_{fg}(z)}{2v_g(z)} \right) \, dz \tag{3.20}
\]

where $G$ is the mass velocity, $z$ the axial co-ordinate, $f$ the friction factor, $K$ the hydraulic resistance, $v_g$ the specific volume of the gas phase, $v_{fg}$ the difference in specific volume between the gas and liquid phases, $x_g$ the gas phase quality ($x_g = m_g/(m_g + m_{liq})$) and $d_H$ the hydraulic diameter of the flow channel. In Eq. 3.20 the acceleration pressure drop and the gravitational head, which are included in the original equation given by Argyropoulos et al. [48], have been neglected, since their contribution is small.

The trapezoidal rule is used to solve Eq. 3.20 while continuously checking if two-phase conditions apply. In case of a single-phase flow, the second term on the right-hand side of Eq. 3.20 is zero.

Once the pressure drop in the flow channels is known the total system pressure for the one-dimensional model is calculated from the algebraic mean of the inlet and outlet pressures.
3.1.2 Electrochemistry

Membrane resistance

With the membrane water content \( \lambda \) being determined, the membrane resistance and the Ohmic voltage drop can be calculated. The proton conductivity \( \sigma_m \) of Nafion 117 was measured by Springer et al. [33, 34] for different water contents. Using two parameters \( \sigma_{m1} \) and \( \sigma_{m2} \), which describe the dependence of the conductivity on the membrane water content, they derived the following expression:

\[
G_m(\lambda) = \exp \left[ 1268 \left( \frac{1}{303} - \frac{1}{T_{fc}} \right) \right] (\sigma_{m1} \cdot \lambda - \sigma_{m2})
\]  

(3.21)

In this model the numerical values of the parameters \( \sigma_{m1} \) and \( \sigma_{m2} \) are determined from measurement data (see Chapter 4).

Since the water content varies through the membrane, the resistance of the membrane is obtained by integrating Eq. 3.21 over its thickness, \( t_m \) [33, 40]:

\[
R_{ohm} = \int_0^{t_m} \frac{1}{\sigma_m(\lambda)} \, dy = \frac{t_m}{\sigma_m(\bar{\lambda})}
\]  

(3.22)

Using the algebraic mean value of the water content at the anode and cathode, \( \bar{\lambda} \), (see assumption 10) the integral is simplified to the expression on the right hand side of Eq. 3.22.

Cathodic polarization loss

The Butler-Volmer equation describes the dependence between the electrode potential, \( U_D \), and the combined current density of the forward and backwards reaction.

\[
i_{fc} = i_0 \left[ \exp \left( \frac{(1 - \alpha_c)nFU_D}{RT_{fc}} \right) - \exp \left( -\frac{\alpha_c nFU_D}{RT_{fc}} \right) \right]
\]  

(3.23)
where $\alpha_c$ is the transfer coefficient for the cathodic reaction and $n$ the number of electron participating in the reaction. The exchange current density $i_0$ is dependent on pressure and temperature and is determined at a defined reference pressure and temperature. Assumption 12 allows the simplification of the Butler-Volmer equation by neglecting the current density of the backwards reaction. After transforming the equation into a logarithmic form, the Tafel equation is obtained [5]:

$$U_D \left|_{p_{O_2}^{ref}} = -2.3 \frac{R T_{fc}}{\alpha_c n F} \log \left( \frac{i_{fc}}{i_0(T)} \right) \right.$$  \hspace{1cm} (3.24)

Eq. 3.24 has to be extended to consider deviation from the reference pressure $p_{O_2}^{ref}$:

$$U_D = -2.3 \frac{R T_{fc}}{\alpha_c n F} \log \left( \frac{i_{fc}}{i_0(T)} \right) + 2.3 \frac{R T_{fc}}{\alpha_c n F} \log \left( \frac{p_{O_2}}{p_{O_2}^{ref}} \right)$$  \hspace{1cm} (3.25)

From the experimental data of Parthasarathy et al. [49], the dependence of the cathodic exchange current density on the temperature can be described with an equation of the form $i_0 = i_{01} \exp(i_{02} T_{fc} - T_{ref})$ [50]. In this work the equation is expanded to take into account the flooding of the electrodes:

$$i_0(T) = \left( 1 - A_r \cdot x_{H_2O,C}^{liq} \right) \cdot i_{01} \exp[i_{02} \cdot T_{fc} - T_{ref}]$$  \hspace{1cm} (3.26)

where $x_{H_2O,C}^{liq}$ is the concentration of liquid water at the membrane-electrode interface at the cathode side. The first term in brackets on the right-hand side of Eq. 3.26 has been introduced to consider the decrease of the catalytic surface area with a rising content of liquid water due to flooding. In this work the numerical value of the parameters $A_r$, $i_{01}$ and $i_{02}$ are determined from measurement data (see Chapter 4).
Tafel plots reported in the literature \([51, 52]\) show two distinct slopes with the break occurring at a potential of 0.75-0.8 V. The low Tafel slope observed at potential above the threshold value corresponds to a potential regime where the oxygen reduction proceeds on Pt-oxide covered surface. The high Tafel slope observed at potentials below the threshold voltage indicates that the oxygen reduction proceeds on Platinum free from oxide. To account for this phenomenon, different values for the transfer coefficient are used dependent on whether the cell voltage is larger or smaller than the threshold voltage. The numerical values of the parameters \(\alpha_{c1}\) and \(\alpha_{c2}\) are determined from measurement data (see Chapter 4). The threshold voltage is set to 0.775 V. The build up of the Pt-oxide layer is investigated with more detail in Chapter 5.3.

**Open-circuit potential (OCV)**

Usually the Nernst equation defined in Eq. 1.7 is used to calculate the open-circuit voltage. However, using the standard values for the Nernst equation results in much higher voltages than the experimentally observed open-circuit voltages. Therefore, the parameters \(k_{oc1}\) and \(k_{oc2}\) are introduced to take this deviation into account:

\[
U_{oc} = \left( k_{oc1} - k_{oc2} \cdot x_{H_2O,C}^{liq} \right) \cdot \\
\left[ E^0 + \frac{\Delta S}{nF} (T_f c - T^0) + \frac{2.3RT_f c}{2F} \log \left( \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \right) \right] \quad (3.27)
\]

The parameters \(k_{oc2}\) is used to consider the variable degree of flooding at the cathode. The numerical value of the parameters \(k_{oc1}\) and \(k_{oc2}\) are determined from measurement data (see Chapter 4).

Finally the cell voltage is calculated from Eq. 3.28:

\[
U_{cell} = U_{oc} - U_D - i_c R_{ohm} \quad (3.28)
\]
Figure 3-2: General structure of stack model.
The cell voltage is found by iteration of Eq. 3.22, 3.25, 3.27 and 3.28. Using similar considerations as in the previous section, the convergence criteria is found to be fulfilled in the relevant voltage range. The general structure of the model is given in Figure 3-2.

The fundamental structure of the model outlined in this chapter shows some similarities to those of one-dimensional models found in the literature [33, 40], which are typically used for small single cells. However, the approach used in this model, which takes into account the dependence of the exchange current density (Eq. 3.26) and the open-circuit voltage (Eq. 3.27) on the liquid water concentration at the cathode-side is new. Furthermore, to the authors knowledge, this is the first time that a one-dimensional model is used to accurately reproduce the data of large PEM fuel cell stack. Compared to other models [61] the number of parameters that need to be identified is significantly smaller and the procedure for determining them is simplified. In the Chapter 4 the simulation data is compared to the measurement data.

3.2 Air Supply System

In Chapter 5.2 the effect of different air supply strategies on the response of the fuel cell stack voltage is investigated. This requires the exact knowledge of the inlet and outlet pressure and of the reactant flow rates through the stack. Pressure sensors are mounted at the inlet and outlet of the fuel cell in the air as well as the hydrogen stream. Furthermore, a hydrogen mass flow sensor is placed adjacent to the stack inlet. However, the air mass flow sensor is positioned in front of the compressor (to avoid contact to liquid water) and thus cannot supply any accurate data on the air mass flow in the stack during transients. To gain information about the transient flow in the stack, a dynamic model of the air supply system is required. The development of this model is outlined in the following.

Figure 3-3 shows the layout of the air supply system. It consists of a twin-screw compressor, a water injection device, a vessel, which is filled with porous material (to increase the water-air contact surface, thereby enhancing the evaporation of water), a water separator in front of the fuel cell (to avoid
Figure 3-3: Basic schema of air supply system, consisting of a twin-screw compressor, a humidification device, a 100 cell PEM fuel cell stack and a control valve. The indices of mass flow \( m \) and pressure \( p \) are explained in this section.

The air supply model structure is shown in Figure 3-4 along with the major input/output signals. Only the dynamic effects with a time constant in the range of \( 10^{-2} \) s to \( 10^{1} \) s are taken into account. Typically, manifold filling/emptying dynamics and the compressor/electric-motor have time constants in the relevant time range [53]. The electrochemical effects are several orders of magnitude faster than the flow processes considered in this system model and thus are treated statically. In conjunction with assumption 1 for the fuel cell stack, steady state conditions are assumed for the temperature.

In the following, the model of the compressor/electric-motor unit and the manifold filling/emptying model are described.
The compressor flow is determined on the basis of a compressor flow map, which is dependent on the compressor speed and the pressure ratio. As twin-screw compressors have a linear speed-flow relationship over a wide speed range, this approach is considered suitable even for dynamic system simulations. The compressor speed is calculated as shown in Eq. 3.29 [54].

\[ \theta \cdot \dot{\omega}_{em}(t) = T_{q_{em}}(t) - i \cdot T_{q_{cmp}}(t) \]  \hspace{1cm} (3.29)

\[ T_{q_{cmp}}(t) = f(\Pi(t), n_{cmp}(t)) \]  \hspace{1cm} (3.30)
3.2 Air Supply System

\[ T_{q_{em}}(t) = (c_1 \cdot n_{em}(t) + c_2) \cdot u_{em} + c_3 \cdot n_{em}(t) + c_4 \]  

(3.31)

where \( \theta \) denotes the combined inertias of the compressor (subscript \( cmp \)) and the electric motor (subscript \( em \)), \( \omega = 2\pi \cdot n \) the speed, \( T_q \) the torque, \( i \) the transmission ratio between motor and compressor, \( u_{em} \) the input to the controller of the motor and \( \Pi \) the pressure ratio across the compressor. The parameters \( c_1 \) to \( c_4 \) are fitting parameters.

The compressor torque \( T_{q_{cmp}} \) is interpolated from measurement data obtained by varying the compressor speed and the pressure ratio. With this approach all losses due to deviations from the isentropic compression, friction and belt slip are included. The torque of the electric motor \( T_{q_{em}} \) is calculated by means of a linear relationship between torque and input signal as well as motor speed.

The flow through the fuel cell is dependent on the electric current and on the pressure loss across the stack. In accordance with assumption 9 from Chapter 3.1.1 an uniform reaction rate is assumed in z-direction. The mass flow distribution along the channel is then given by the following equation:

\[
\dot{m}_{fc}(z, t) = \dot{m}_{fc}^{in}(t) \cdot \frac{z}{l_{fc}} \cdot \dot{m}_{cons}(t) + \frac{l_{fc} - z}{l_{fc}} \cdot \dot{m}_{prod}(t)
\]

(3.32)

where \( \dot{m}_{fc}^{in} \) is the inlet mass flow, \( z \) the co-ordinate along the channel, \( l_{fc} \) the channel length, \( \dot{m}_{cons} \) the consumed oxygen mass flow and \( \dot{m}_{prod} \) the mass flow due to the production of water [53].

Due to the large share of the nitrogen flow in the total mass flow, the first term on the right-hand side in Eq. 3.32 exceeds by far the value of the second and third terms combined. Hence, for this investigation the effects of oxygen consumption and water production on the total mass flow are neglected. Therefore, the total air mass flow is considered not to vary along the channel. Eq. 3.32 is thus rewritten to:

\[
\dot{m}_{fc}(z, t) = \dot{m}_{fc}(t) = \dot{m}_{fc}^{in}(t) = \dot{m}_{fc}^{out}(t)
\]

(3.33)
Since the channel cross section is very small (<1 mm²), the flow in the channels is well below the critical Reynolds number and fully developed, thus laminar. But the presence of water droplets in the flow channels requires the calculation of the pressure drop for two-phase flows. This pressure drop is found by iteration of Eq. 3.20. The resulting relationship between pressure loss and mass flow rate is well approximated by the following equation:

\[ \dot{m}_{fc}(t) = a_1 \cdot (\Delta p_{fc}(t))^{a_2} \quad \text{with} \quad \Delta p_{fc}(t) = p_{om}(t) - p_{im}(t) \quad (3.34) \]

where \( a_1 \) and \( a_2 \) are fitting parameters.

The flow through the valve is calculated assuming isentropic expansion [55]:

\[ \dot{m}_{valve}(t) = A_{eff} \frac{p_{om}(t)}{\sqrt{RT_{valve}}} \Psi(\Pi(t)) \quad (3.35) \]

with

\[ \Psi(\Pi, t) = \sqrt{\frac{2\kappa}{\kappa - 1}} \left[ \frac{2}{\Pi(t)^\kappa} - \frac{\kappa + 1}{\kappa} \right] \quad \text{with} \quad \Pi(t) = \frac{p_{amb}(t)}{p_{om}(t)} \quad (3.36) \]

where \( \kappa \) is the ratio of the specific heat capacities and \( A_{eff} \) is the effective opening area of the nozzle, i.e., the valve. \( p_{amb} \) is the ambient pressure downstream of the valve. Eq. 3.36 has to be modified for choked flows:

\[ \Psi_{max}(\Pi) = \left( \frac{2}{\kappa + 1} \right)^{-\frac{1}{\kappa - 1}} \sqrt{\frac{2\kappa}{\kappa + 1}} \quad \Pi < \left( \frac{2}{\kappa + 1} \right)^{-\frac{\kappa}{\kappa - 1}} \quad (3.37) \]

The volumes between compressor, fuel cell stack, and valve are represented by manifold models. The inlet manifold contains the lumped volume between compressor and stack, whereas the outlet manifold contains the lumped volume between stack and valve. The manifolds are made up mainly from
3.2 Air Supply System

piping. In the inlet manifold the piping has a length of 5 m, in the outlet manifold 2.5 m. The Biot number $Bi$ provides a measure for the validity of the lumped capacitance method and thus for the validity of the assumption of a uniform temperature distribution in the manifolds. $Bi$ is much larger than one in the manifolds investigated here. Hence, no isothermal conditions can be applied [56]. The pressure in the manifolds is then calculated by applying the energy conservation principle [57, 58].

$$\frac{dp_{im}(t)}{dt} = \frac{\kappa R_{air}}{V_{im}} (T_{cmp} \cdot m_{cmp}(t) - T_{fc}^{in} \cdot m_{fc}^{in}(t) - Q_{im})$$  \hspace{1cm} (3.38)

$$\frac{dp_{om}(t)}{dt} = \frac{\kappa R_{air}}{V_{om}} (T_{fc}^{out} \cdot m_{fc}^{out}(t) - T_{valve} \cdot m_{valve}(t) - Q_{om})$$  \hspace{1cm} (3.39)

where $p$ is the pressure in the manifold, $R_{air}$ the gas constant of air, $\kappa$ the ratio of specific heat capacities, $T$ the temperature, $V$ the lumped volume of the manifold and $m$ the mass flow. The subscripts $im$, $om$, $cmp$, $valve$, $fc$ denote the inlet manifold, the outlet manifold, the compressor, the valve and the fuel cell, respectively. The terms $Q_{im}$ and $Q_{om}$ take into account the heat dissipation through the piping walls and the evaporation heat in the inlet manifold. The determination of these values is difficult since it requires knowledge about the amount of liquid water inside the manifolds and about the heat transfer coefficients. The terms $Q_{im}$ and $Q_{om}$ are therefore together with $T_{cmp}$ and $T_{valve}$ approximated from measurement data:

$$Q_{im} = \frac{m_{cmp}^{in} + m_{fc}^{in}}{2} \cdot (T_{cmp} - T_{fc}^{in}) \hspace{1cm} T_{cmp} = T_{fc}^{in} + 40 \text{ K}$$

$$Q_{om} = \frac{m_{fc}^{out} + m_{valve}}{2} \cdot (T_{fc}^{out} - T_{valve}) \hspace{1cm} T_{valve} = T_{fc}^{out} - 10 \text{ K}$$

(3.40)
As can be seen from Eq. 3.38 the inlet manifold is governed by the compressor flow (inlet flow) and the flow into the fuel cell (outlet flow). Similarly, the outlet manifold is governed by the flow out of the stack (inlet flow) and the flow through the valve (outlet flow).

The filling/emptying model of the inlet manifold is expanded to include inertial effects beside the capacitive effects. Cipollone et al. [59, 60] presented a model to describe the transient flow in engine manifolds. Adapting their first-order solution the pressure at the compressor outlet $p_{cmp}^{out}$ is calculated as follows:

$$\frac{d}{dt} p_{cmp}^{out}(t) = \frac{p_{cmp}^{out}(t) - p_{cmp}^{out}(t)}{\tau}$$

(3.41)

where $p_{cmp}^{inf}$ is the steady state pressure at the compressor outlet. The time constant $\tau$ is dependent on the pipe length and on the wave propagation speed [59, 60].

The stationary pressure is defined as [59, 60]:

$$p_{cmp}^{inf}(t) = k_{\Delta p} \cdot \dot{m}_{cmp}(t) + p_{fc}^{in}(t)$$

(3.42)

where $k_{\Delta p}$ is a flow parameter. The first term on the right hand side of Eq. 3.42 describes the pressure loss in the piping and in the vessel with the porous material.

The air supply model thus is described by four states, namely the inlet manifold pressure, the outlet manifold pressure, the pressure at the compressor outlet and the compressor speed.
CHAPTER 4

EXPERIMENTAL INVESTIGATION
STEADY STATE CONDITIONS

4.1 Reproducibility and Error of Measurement

The experiments described in the following have been repeated several times in course of this work. Thereby a good reproducibility of the current-voltage relationship was found. Figure 4-1 shows the fine reproducibility for the base case. The deviation of the open-circuit voltage was less than 0.5%. At full load \( I_{fc} = 70 \) A) the deviation of the stack voltage was approx. 1.5% or 1 V. Through the application of a standard testing procedure (the details are described in the next chapter) the conditions prior to the recording of the current-voltage relationship do not deviate much between the different runs. Hence, the fine reproducibility is also obtained at other operating conditions.

The stack voltage is the most important quantity measured in this work. The measuring chain is put together by a voltage transducer, an A/D converter and a CAN transmission. Using an accurate voltage source (HP 3245A) the measurement error was found to be less than 1% over the total voltage range (see Figure 4-2). This value agrees well with the data supplied by the manufacturer of the voltage transducer and the A/D converter (0.8% at \( U_{fc} = 100 \) V). The difference between measurement and manufacturer data results from the manufacturing tolerance of the apparent Ohmic resistance required for the voltage measurement.
Chapter 4  Experimental Investigation Steady State Conditions

Base Case:
- $p_{\text{air}} = 2.0 \text{ bar}_{\text{abs}}$
- $p_{\text{H}_2} = 2.2 \text{ bar}_{\text{abs}}$
- $\lambda = 2.2$
- $T_{\text{air}} = 60 \degree \text{C}$
- $T_{t_{\text{air}}} = 45 \degree \text{C}$

**Figure 4-1:** Variation of the current-voltage relationship for base case for different runs.

**Figure 4-2:** Measurement error of stack voltage obtained with accurate power source. An error of 0.8% is expected from manufacturer data sheets of the voltage transducer and the A/D converter.
The accuracy of the pressure transmitter is given by the manufacturer as <1%, those of the air flow sensor as 2%. Similar values were obtained using a pressure and a flow calibration device.

4.2 Stack Model

This chapter provides a discussion of features of this particular stack observed under steady state conditions and simultaneously a comparison between measurement and simulation data. Characteristics specific to this stack are pointed out and their origins investigated.

4.2.1 Test Procedure

To compare the effects of different parameter settings (such as stack temperature, system pressure or stoichiometry) current-voltage curves are recorded. On the test bench the electric load applied on the fuel cell stack is current controlled, i.e., the current is set by the operator and the fuel cell voltages settles to a value specific to the operating conditions. To obtain a current-voltage curve (often called polarization curve) the current is increased in small steps from zero current to the maximum current and at the same time the voltage is recorded. The voltage should not be biased by dynamic effects. Therefore, enough time has to be allowed after each current step for the voltage to settle down to a steady state value.

Figure 4-3 shows exemplary the procedure to record the current-voltage curve for the base case (stack temperature $T_{fc} = 60 \, ^\circ C$, air inlet pressure $p_{air} = 2.0 \, \text{bar}_{abs}$, hydrogen inlet pressure $p_{H2} = 2.2 \, \text{bar}_{abs}$, air stoichiometry $\lambda_{air} = 2.2$). In Figure 4-4 the polarization curves obtained thereby are plotted. The measurement points have been fitted with the following equation:

$$U_{fc} = E^0 - b \log i_{fc} - R i_{fc}$$

(4.1)

where $U_{fc}$ is the cell voltage, $b$ is the Tafel slope, $i_{fc}$ is the current density, $R$ is the Ohmic resistance, and $E^0$ is the reversible potential.
Figure 4.3: Outline of typical test procedure.

Figure 4.4: Polarization Curves recorded during the measurement outlined in Figure 4.3. Curve C is used for further investigations. $T_f = 60$ °C, $P_{air} = 2.0$ bar$_{abs}$, $P_{H_2} = 2.2$ bar$_{abs}$, $\lambda_{air} = 2.2$. 
First, the current is set to 30 A and the stack is warmed up. Once the desired temperature is reached two current-voltage curves are recorded. The first curve (curve A in Figure 4-4) is obtained by increasing the current in steps of 5 A from zero current to 70 A. After each step the current is kept constant for 20 s. This is followed by the second curve (curve B in Figure 4-4) where the current is reduced in steps of again 5 A from 70 A back to zero current. These two curves are not used for data analysis but are employed to activate the cell. Hereafter the cell is operated at 30 A for 30 min to allow the fuel cell to reach steady state conditions. Finally, two more current-voltage curves are recorded applying the procedure described above (curves C and D in Figure 4-4). Typically the duration of the procedure is 80 min depending on time required to heat the stack to the desired temperature. Curve C is used in the following chapters to discuss the effect of different operating parameters.

The slight degradation observed between sets A/B and C/D is believed to result from changes in the hydration state of the membrane and/or from the formation of an oxide layer at the cathode. These phenomena are discussed in more detail in Chapter 5, together with the origin of the hysteresis between the upward and downward slopes.

From current-voltage curves at best conclusion on the steady-state behavior can be drawn. No conclusion at all is possible on the dynamic behavior of the fuel cell. However, the effect of different parameter settings on the overall fuel cell performance can be investigated. The cause for these effects cannot be investigated with current-voltage curves alone. Diametrically opposed phenomena, such as flooding and membrane dehydration, often alter the current-voltage curve in a similar way. Nevertheless, current-voltage curves are readily obtainable and above all have a high reproducibility. Furthermore, they facilitate a fairly simple comparison between measurement and simulation data.

4.2.2 Parameters of Reactants

*Hydrogen Stoichiometry:*

The hydrogen mass flow is not directly controllable on this test bench. On the contrary, the mass flow from the H₂-tank adjusts itself to the amount of hydrogen consumed in the electrochemical reaction. Without any recirculation
the flow would settle to a value equivalent to a stoichiometry of one. By means of an ejector excess hydrogen is recirculated, resulting in a flow of excess hydrogen ($\lambda_{H2} > 1$). The exhaust from the pump that generates the vacuum needed for the low pressure pulses increases the hydrogen mass flow further (compare description in Chapter 2.2). Figure 4-5 shows the mass flow over time for an arbitrarily chosen span of time. Clearly visible is the dynamic flow condition resulting from the pressure pulsing. The first peak of the two distinct peaks corresponds to the high pressure pulse, whereas the second peak results from the low pressure pulse. Since the hydrogen mass flow sensor is positioned at the stack inlet the magnitude from the low pressure pulses is weakened, because these pulses primarily result in an increased mass flow at the stack outlet.

In Figure 4-6A the mass flow was averaged over 20 s at different fuel cell currents. Also given is the (calculated) mass flow that refers to a stoichiometry of one. As can be seen the surplus hydrogen is independent from the applied load. The mean hydrogen mass flow is about 20 l/min larger than that required for a $\lambda_{H2} = 1$. Hence, at low current a high stoichiometry is achieved (compare Figure 4-6B). The stoichiometry then decays and asymptotically approaches one as the current density increases. At the maximum current achievable on the testbench (70 A) the hydrogen stoichiometry is about 1.4.

**Air Stoichiometry:**

The air mass flow is controlled, thus a stoichiometry can be demanded. However, the mass flow cannot be reduced below 4 kg/h. If the mass flow is lower than this threshold, several cells are not properly supplied with oxygen. This causes the reaction to break down. This phenomenon is believed to result from liquid water droplets blocking the channel. A minimum air velocity is necessary to remove these droplets from the supply channels.

As a consequence of this minimum flow requirement it is not possible to operate the fuel cell at low current with the specified stoichiometry. Rather will the stoichiometry increase towards infinity at zero current. The grey highlighted area in Figure 4-7 depicts the region where the stoichiometry cannot be controlled. It is obvious, that a stoichiometry of two can only be specified above 14 A.
Figure 4-5: Shape of hydrogen flow at the fuel cell stack inlet at $i_{fc} = 30$ A, $T_{fc} = 60$ °C. The grey line corresponds to a flow at a stoichiometry of one at the specified current.

Figure 4-6: Top: Measured hydrogen mass flow at different currents. Data has been mean averaged over 20 s. Grey line shows mass flow with $\lambda_{H2} = 1$. Bottom: The corresponding stoichiometry of hydrogen at different currents.
Chapter 4 Experimental Investigation Steady State Conditions

The air inlet humidity is 100% for all parameter settings as a result of the injection of water into the hot air that leaves the compressor. The water injection reduces the temperature and saturates the air flow. The dew point at the air inlet is invariant to the stack temperature but varies slightly with the system pressure (38/40/45/48 °C at 1.6/1.8/2.0/2.2 bar$_{abs}$). The large thermal capacity of the piping in the inlet manifold and the injection of water averts larger variations of the inlet conditions.

Due to the recirculation of excess hydrogen, the hydrogen inlet temperature is influenced by the stack temperature, though the influence is minor (see Table 4-1). When the stack temperature is increased from 40 °C to 70 °C, the hydrogen inlet temperature rises from 36 °C to 42 °C unaffected by the applied load. The inlet humidity of hydrogen, however, is dependent on the stack temperature and the applied load. At 40 °C stack temperature the inlet
relative humidity is 80%, 45% and 25% at loads of 0 A, 30 A and 70 A, respectively. These values increase to 100%, 65% and 35% at a stack temperature of 70 °C.

<table>
<thead>
<tr>
<th>$T_{fc}$</th>
<th>$T_{H2,in}$</th>
<th>RH$_{H2}$ @ 0 A</th>
<th>RH$_{H2}$ @ 30 A</th>
<th>RH$_{H2}$ @ 70 A</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 °C</td>
<td>36 °C</td>
<td>80%</td>
<td>45%</td>
<td>25%</td>
</tr>
<tr>
<td>50 °C</td>
<td>37 °C</td>
<td>80%</td>
<td>50%</td>
<td>25%</td>
</tr>
<tr>
<td>60 °C</td>
<td>41 °C</td>
<td>90%</td>
<td>55%</td>
<td>30%</td>
</tr>
<tr>
<td>70 °C</td>
<td>42 °C</td>
<td>100%</td>
<td>65%</td>
<td>35%</td>
</tr>
</tbody>
</table>

Table 4-1: Hydrogen inlet temperature and humidity at different stack temperatures.

These values can be interpreted as follows. The inlet hydrogen stream is put together from dry hydrogen leaving the H$_2$-tank and from recirculated hydrogen. The latter has picked up water while passing through the stack. At low loads the inlet hydrogen is well humidified since the hydrogen stream consists mostly of recirculated and thus humid hydrogen. The higher the stack temperature, the more water is picked up (the hydrogen stream reaches the stack temperature instantaneously upon entering the stack - see assumption 2) and the higher is the inlet humidity. The amount of recirculated hydrogen is constant over the relevant current range. Hence, the portion of recirculated and thus humidified hydrogen in the inlet stream decreases when the load is increased since the total inlet flow is increased to match the hydrogen consumption. This causes the inlet humidity to decrease towards higher loads.

4.2.3 Polarization Curves

Measurement data of variations in system pressure and stack temperature was employed for the identification of the modeling parameters mentioned in Chapter 3. The steady state stack model contains 10 numerical parameters that need to be identified:

- Diffusion parameter $D_0$ - Eq. 3.19
- Conductivity parameters $\sigma_{m1}$ and $\sigma_{m2}$ - Eq. 3.21
• Cathodic transfer coefficient $\alpha_{c1}$ and $\alpha_{c2}$ - Eq. 3.24
• Exchange current density parameters $A_r$, $i_{01}$ and $i_{02}$ - Eq. 3.26
• Open-circuit voltage parameters $k_{oc1}$ and $k_{oc2}$ - Eq. 3.27

The values of these parameters are found by applying a least-square minimization function on the error between the measured and simulated fuel cell voltage. The values found thereby are in the order of magnitude as those values reported in the literature, with the exception of the conductivity parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>this work</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_0$ [cm$^2$/s]</td>
<td>5.3e-7</td>
<td>5.5e-7 [31] &lt;br&gt; 1e-6 [33, 34]</td>
</tr>
<tr>
<td>$\sigma_{m1}$ [-]</td>
<td>6.32e-4</td>
<td>0.005139 [33]</td>
</tr>
<tr>
<td>$\sigma_{m2}$ [-]</td>
<td>-0.0046</td>
<td>0.00326 [33]</td>
</tr>
<tr>
<td>$\alpha_{c1}$ [-]</td>
<td>0.712</td>
<td>0.6~1 [5, 35]</td>
</tr>
<tr>
<td>$\alpha_{c2}$ [-]</td>
<td>0.722</td>
<td>0.6~1 [5, 35]</td>
</tr>
<tr>
<td>$A_r$ [-]</td>
<td>0.303</td>
<td>-</td>
</tr>
<tr>
<td>$i_{01}$ [A/cm$^2$]</td>
<td>0.0055</td>
<td>0.005 [5]</td>
</tr>
<tr>
<td>$i_{02}$ [-]</td>
<td>0.0143</td>
<td>0.014189 [5]</td>
</tr>
<tr>
<td>$k_{oc1}$ [-]</td>
<td>0.857</td>
<td>0.7927 [61]</td>
</tr>
<tr>
<td>$k_{oc2}$ [-]</td>
<td>0.336</td>
<td>0.755 [61]</td>
</tr>
</tbody>
</table>

**Table 4-2:** Comparison of values of simulation parameters used in this work and found in literature.

In this chapter the comparison between measurement and simulation data is made only for steady state conditions. Dynamic conditions are investigated in Chapter 5.
Both the stack temperature and pressure of operation significantly influence the fuel cell performance [62]. These influences are discussed in the following.

**Dependence on temperature**

The effect of the temperature on the performance is illustrated in Figure 4-8 for four temperatures from 40 °C to 70 °C at an air/hydrogen pressure of 2.0/2.2 bar\textsubscript{abs}. The influence of the temperature on the current-voltage characteristic is twofold. On the one hand, the exchange current density \(i_0\) increases with the cell temperature as the activation losses are reduced. Furthermore, according to Eq. 3.21, the membrane conductivity also increases with temperature when the water content is kept unchanged [63]. On the other hand, at higher temperatures, the membrane keeps less water, and this decrease in water content causes a lower conductivity. These two phenomena influence the fuel cell performance simultaneously [40].

As stated at the beginning of this chapter the air stream at the stack entrance has a temperature of 45 °C and a relative humidity of 100%. However, the air stream takes on the stack temperature immediately upon entering the flow channels [23, 41], thereby affecting the relative humidity. If the stack temperature is below 45 °C, water condenses and may flood the gas diffusion electrodes. Contrary, if the stack temperature exceeds 45 °C the air stream is not saturated at the stack inlet and takes up water from the MEA. In Figure 4-9 the water vapor uptake capability of the air stream is compared to the water production from the electrochemical reaction. For the calculation of this data it was assumed that all water is removed in the air stream. The air stream takes up water until the partial pressure of water reaches the saturation pressure. Consequently, the dryer the incoming air stream, the more water is taken up and the more water is removed from the cell in vapor form. In the low current region the water uptake capability exceeds the water production as a consequence of the surplus air (see Chapter 4.2). In this region thus the membrane is severely dehydrated in the long run [64]. At middle and high currents more water is produced than is removed in the vapor form. This surplus water is partly removed in liquid form if the air velocity is high enough or otherwise accumulates in the cell. However, the air stream picks up water only gradually over the total channel length. Hence at the stack entrance
Figure 4-8: Measured (symbols) and computed (lines) polarization curves for different stack temperatures. $p_{air} = 2.0 \text{ bar}_{abs}, p_{H2} = 2.2 \text{ bar}_{abs}, \lambda_{air} = 2.2$.

Figure 4-9: Simulated data on water vapor uptake capability of air stream at different stack temperatures and water production from the electrochemical reaction. The air stream has stack temperature and dew-point of 45 °C. $p_{air} = 2.0 \text{ bar}_{abs}, p_{H2} = 2.2 \text{ bar}_{abs}, \lambda_{air} = 2.2$. 
dry conditions will prevail, even if the section closest to the exit is flooded. At some point along the channel the condition changes from dry to wet. The exact determination of this point requires a two-dimensional model, but Figure 4-9 gives a qualitative solution. The closer the line of the water uptake capability is to the water production line, the more water is taken up and the further is the point from the stack entrance where the conditions change from dry to wet. At 50 °C stack temperature most of the channel is in wet condition, whereas at 70 °C the channel is mostly in dry conditions.

In this setup the hydrogen stream is considered not to have a major impact on the temperature dependence of the fuel cell performance since the hydrogen flow is small compared to the air flow. The amount of water transported in the hydrogen flow is therefore considerably less than in the air stream.

The dehydration of the membrane over large parts of the cell surface increases with the temperature. Thus the decrease of the activation losses with increasing temperatures is gradually neutralized. At temperature above 60 °C the improvements in the kinetics are outweighed by the increase of the membrane resistance caused by the dehydration. Therefore, the cell performance is reduced and the cell voltage drops. At 40 °C the cell performance is inhibited by the sluggish kinetics due to the low temperature as well as by the existence of large quantities of liquid water which block the transport of the reactants to the catalyst sites. The transport hindrance due to liquid water is less pronounced at high currents since the air velocity is sufficiently high to remove water droplets.

Simulation and measurement data agree very well except for the case of 40 °C stack temperature, where the effects due to the presence of liquid water are not predicted by the simulation.

*Dependence on pressure*

Figure 4-10 shows the pressure dependence of the fuel cell performance for four different air pressures ranging from 1.6 bar\textsubscript{abs} to 2.2 bar\textsubscript{abs}. The hydrogen pressure is in all cases 0.2 bar higher than the air pressure. The current-voltage curve is affected by changes in pressure over the total current range, starting
with the open-circuit voltage. The overall cell performance improves by around 50 mV per cell at full load when increasing the pressure from 1.6 to 2.2 bar$_{abs}$.

Generally a higher system pressure leads to higher partial pressures of the reactants. Thereby the activation losses are reduced (Eq. 3.24) and the open-circuit voltage is increased (Eq. 3.27). However, the pressure also affects the water balance of the fuel cell stack. Figure 4-11 shows the water uptake capability at a stack temperature of 60 °C for different system pressures. Clearly the variation is not as large as for different temperatures. This indicates that effects resulting from water removal and membrane dehydration play only a minor role in forming the pressure dependence of the fuel cell performance.

The simulated current-voltage curves match those from measurement very well, as can be seen in Figure 4-10. Only the open-circuit voltage is overestimated in all cases. The open-circuit voltage is reduced in the experiment by the formation of Pt oxides, from the build-up of impurities on the catalytic surface or by hydrogen crossover. These effects are not considered in the simulation.

**Dependence on air stoichiometry**

In Figure 4-12 measured and simulated current-voltage curves for different air stoichiometries are presented. The curves form a narrow band and almost no variations between the curves are distinguishable. On the one hand, the partial pressure of oxygen increases with an increase of the air stoichiometry and thus the activation losses are reduced. On the other hand, large quantities of excess air facilitate the removal of water, thus causing the membrane to dry out and the Ohmic resistance to increase. In this setup these two effects seem to cancel each other out in the investigated current density range.

Similar to the pressure and temperature data the agreement between simulation and measurement data is good. Nevertheless, two discrepancies between simulation and measurement data exist. At large current densities the simulated curves fan out. This effect is not visible in the measurement data. The model predicts that at high stoichiometric values the membrane water content decreases and the Ohmic resistance increases. The measurement data
4.2 Stack Model

**Figure 4-10:** Measured (symbols) and computed (lines) polarization curves for different pressure. $T_{fc} = 60^\circ$C, $\lambda_{\text{air}} = 2.2$, $p_{H2} = p_{\text{air}} + 0.2$ bar$_{\text{abs}}$.

**Figure 4-11:** Comparison of water vapor uptake capability of air stream at different system pressures to water production from the electrochemical reaction. $T_{fc} = 60^\circ$C, $\lambda_{\text{air}} = 2.2$, $p_{H2} = p_{\text{air}} + 0.2$ bar$_{\text{abs}}$. 
was obtained with a waiting time of 20 s at every measurement point. As will be discussed in Chapter 5.1 this span of time is not sufficient for the water household to reach steady state. In Chapter 5.1 the model is extended to include dynamic effects of water removal.

The second discrepancy occurs at low stoichiometric values and medium current densities. In this region liquid water droplets are difficult to remove since the amount of excess air and the flow velocity are small. These droplets block part of the channels and/or flood the gas diffusion electrode thereby hindering the supply of reactants to the reaction site and causing the voltage to drop. At even lower current densities the stoichiometry is increased in order to satisfy the minimum air flow requirement. Even though the flow velocity remains unchanged, the water production decreases and fewer droplets accumulate. Therefore, the effect is not visible at very low current densities. This behavior cannot be mirrored by the simulation, since no specific model is implemented to describe the removal of water droplets. Moreover, it is assumed that the droplets are in a dispersed state and are removed instantaneously in the air exhaust.
4.2.4 Validation

The stack model was also applied to simulate operating conditions that were not used for the parameter identification. In Figure 4-13 the simulated and measured stack voltage are compared for a parameter set, in which system pressure, stack temperature and air stoichiometry are varied from the base case. A good agreement of the data is achieved. Furthermore, the stoichiometry data given in Figure 4-12 and the temperature data of 40 °C have neither been used for model identification.

![Figure 4-13: Comparison of simulated (line) and measured voltage (symbol) of parameter set not used for parameter identification (square symbol) and the base case (circle symbol).](image)

These comparisons demonstrate that the stack model accurately describes the steady state behavior of the fuel cell stack, even with the applied simplifications discussed in Chapter 3.1. The model thus provides a basis for investigations of the dynamic behavior of the fuel cell given in Chapter 5.
Pressure loss

In Figure 4-14 the measured pressure drops in the cathode flow channels are shown for different current densities. No obvious distinction between the different sets is recognizable, confirming the assumption that the production and consumption of gases can be neglected when calculating the pressure drop. This is in line with the observations of Wilkinson and Vanderleeden [65] who reported that the pressure drop is influenced by the electrochemical reaction rate only to a small extent. The simulated pressure drop (Eq. 3.20) is plotted for comparison. In the simulation the fuel cell current has no large effect, as the consumed oxygen is replaced by the product water. Thus the total mass flow is not significantly affected by the electric current.

4.3 System Model

In Figure 4-15 the simulation and measurement data of the fuel cell system are compared. Figure 4-16 and Figure 4-17 show details of the pressure and mass flow trace for better visualization. The sequence of the compressor and

![Figure 4-14: Measured pressure drops in cathode flow channels for different current density values. Line shows simulation results using Eq. 3.20 with a hydraulic resistance $K$ of 1.71.](image)
4.4 Cell Voltage

valve input signals were recorded from measurement and used as inputs for the system model. The parameters $p_{amb}$ (Eq. 3.30 and 3.35), $\theta$ (Eq. 3.29), $V_{im}$ (Eq. 3.38), $V_{om}$ (Eq. 3.39), $A_{eff}$ (Eq. 3.35) and $\tau$ (Eq. 3.41) have been fitted from the measurement data by applying a least square minimization function on the error.

In the first part of the sequence, the compressor input signal was kept constant and the valve input signal was varied (first 120 s). Then in the second part the valve input signal was fixed and the compressor input signal was altered. The agreement between simulation and measurement in the second part is excellent. The deviations in the first part, visible in the pressure as well as the mass flow trace are attributed to a hysteresis in the valve.

In Figure 4-16 and Figure 4-17 the traces computed by a linearized model are given. The linearization was performed at the operating point with $p_{air} = 2.0$ bar and $m_{air} = 8.8$ kg/h. The linearized model is used to develop a model-based controller for the air supply, the performance of which is discussed in Chapter 5.2. The mass flow and pressure traces of the non-linear and linearized model agree well. Only at elevated pressure (> 2.1 bar) the results of the linearized model deviates from the non-linear model. This deviation is considered acceptable, since it is observed only outside the operating pressure range and is fairly small (< 2%).

4.4 Cell Voltage

In this chapter the voltage variation between the cells is investigated. The actual cell voltages may differ from the stack mean cell voltage (i.e., the stack voltage divided by the number of cells). The data presented in the following visualize the challenge to simulate the three-dimensional stack, where the conditions not only vary along the channel but also from cell to cell, with an one-dimensional model.

The variation of the cell voltage is the cumulative result of at least four factors:

- Uneven flow distribution of reactant gases.
Figure 4-15: Comparison of dynamic response of inlet pressure and mass flow in measurement (black line) and simulation (grey line).
Figure 4-16: Comparison of dynamic response of inlet pressure in measurement and simulation - detail of Figure 4-15.

Figure 4-17: Comparison of dynamic response of mass flow in measurement and simulation - detail of Figure 4-15.
Chapter 4  Experimental Investigation Steady State Conditions

- Non-uniform temperature field in the stack.
- Different stages in the ageing process.
- Defects or tolerance of fabrication in particular cells.

Since all flow channels are fed in parallel, the pressure loss across all cells is the same. Therefore, the flow in each channel will vary with the flow resistance, which is primarily influenced by restrictions in the cross section of the flow channels. These may be caused by variations in the flow channel depth and width due to fabrication tolerances, the intrusion of the gas diffusion electrode, or an accumulation of liquid water.

The second set of factors causing variations in the cell voltages relates to the temperature distribution inside the fuel cell, which has an important effect on nearly all transport phenomena. A non-uniform temperature distribution may arise from varying flow resistance in the flow channel of the cooling media, air pockets in the channel, or variations in the membrane resistance and a resulting variation in local heat generation. Furthermore, cells located in the middle of the stack are typically warmer than those at the edges due to the less efficient head convection [6].

The third set of factors deals with differences in the ageing process. St.-Pierre et al. [66] have shown that longtime exposure to excess water facilitates the poisoning of the active layer of the electrode due to impurities washed into the fuel cell. Thereby the ageing process is accelerated. Especially the cells closest to the inlet are at risk of being exposed to excess water. Not only during operation but also after the shutdown any water which might have condensed in the piping will most probably pass through the flow channels of these cells assisted by the gravitational force.

The final set of factors relates to variations in the material or defects which occurred during the assembly of the stack. These may include weak points in the membrane, fault in the bipolar plates, uneven distribution of the catalyst on the electrode, or insufficient contact between electrode and membrane. All these factors lead to additional deviations, thereby altering the voltage.
In Figure 4-18 the distribution density curves of the cell voltages across the stack are presented for different currents. The cell voltages are plotted assuming a gamma distribution, since this distribution yielded good results compared to other distributions. In the top part of Figure 4-18 the distributions are plotted around the respective stack mean voltage, whereas in the bottom part a normalized representation is given. The distribution is exemplified by the voltage histogram at 10 A in Figure 4-18A. Except for currents below 10 A the cell voltage distribution widens with an increasing current. In the region below 10 A the voltage is very sensitive to current variations, since the polarization curve is very steep here. Hence even small deviations in the current, which are otherwise insignificant compared to the total current, can cause changes in the voltage. These deviations in current are believed to result from short circuit currents caused by extensive local stress on the membrane due to the electrode roughness.

Figure 4-19 shows the evolvement of the standard deviations of the cell voltages over the current density range for different values of air stoichiometry. The shape of the evolvement is very similar in all cases. The standard deviation drops from zero current to a minimum at around 10 A and then increases again. The deviations are larger for low stoichiometric values. The increase of the standard deviations with decreasing stoichiometric values is expected since less excess oxygen is available and the effects resulting from uneven flow distribution are intensified.

Also given in Figure 4-19 is the deviation of the minimal cell voltage (i.e., the voltage of the cell with the lowest performance) from the stack mean voltage. The shape of the evolvement over the current density is very similar to that of the standard deviation, although the deviations are one order of magnitude larger for this particular stack.

In Figure 4-20 and Figure 4-21 the evolvement of the standard deviation and of the deviation of the minimum cell voltage are given for different system pressures and different stack temperatures, respectively. The shape here resembles those of different stoichiometric values. At a system pressure of 2.0 and 2.2 bar the curves are similar. Towards lower pressures the deviation increase substantially. In case of different stack temperatures the shape at
Figure 4-18: Distribution of density curve of cell voltages for base case at different current. \( T_{fc} = 60 \, ^{\circ}\text{C}, \ p_{air} = 2.0 \, \text{bar}_{abs}, \ p_{H_2} = 2.2 \, \text{bar}_{abs}, \ \lambda_{air} = 2.2 \) : Distribution at the respective voltage. B. Distribution aligned at stack mean voltage.
Figure 4-19: Top: Standard deviation for different air stoichiometries at different currents. Bottom: Deviation of minimal voltage from mean voltage for different air stoichiometries at different currents.
Figure 4-20: Top: Standard deviation for different air pressures at different currents. Bottom: Deviation of minimal voltage from mean voltage for different air pressures at different currents.
Figure 4-21: Top: Standard deviation for different stack temperatures at different currents. Bottom: Deviation of minimal voltage from mean voltage for different stack temperatures at different currents.
70 °C is out of line, as the deviation is significantly higher. The small spike observed at $T_{fc} = 40$ °C and 15 A is believed to result from the blockade of individual flow channels due to the accumulation of water droplets. At even lower currents the flow velocity does not decrease due to the minimal flow requirement, but the water production decreases, thus the droplets are less likely to form here and the spike appears only at 15 A.

In a fuel cell stack the cell with the poorest performance, i.e. with the lowest voltage determines the maximum power output of the stack. Although the influence of this cell on the overall characteristic of the fuel cell stack is not significant as its power contribution is low, care has to be taken that no cell reaches negative voltage to avoid permanent damage to the cell. Naturally, the cells with poor performance are the first to reach this critical point. Typically, none of the cells should be operated below a threshold level of 0.5 to 0.6 V to have a proper margin of safety. To protect the fuel cell stack from irreversible damages a watchdog is installed that generates an alarm when any cell voltage drops below 0.5 or 0.6 V. However, a fixed threshold of this kind does not detect any complications in the low to medium current density range. Therefore, the threshold value should be adjusted according to the actual current.

The measurement results shown in Figure 4-19, 4-20 and 4-21 provide an appropriate measure to define a control method for cell voltage monitoring. At low current densities the threshold value should be close to the mean cell voltage, whereas at high current densities larger deviations from the mean voltage should be allowed. This would facilitate the establishment of a relationship between the current and voltage with an allowable operating range. The variation of the cell voltage is well approximated by Eq. 4.2:

$$U_{std} = 0.0145 + 10^{-5}\left(1.35 + \frac{1.84}{\lambda_A} + \frac{1.79}{P_{tot, c}} + \frac{1.14}{\lambda_{air}}\right) \cdot I_{fc}^2$$  (4.2)

where $U_{std}$ is the standard deviation of the cell voltage, $\lambda_A$ the membrane water content at the anode, $P_C$ the total pressure at the cathode and $\lambda_{air}$ the air stoichiometry factor. The membrane water content is calculated using the fuel cell stack model.
The resulting error between measurement and simulation is, with the exception of the pressure dependence, less than 10%. In case of the pressure dependence an error of up to 20% is obtained. Nevertheless, Eq. 4.2 defines a relationship between the cell voltage deviation across the stack and the operating parameters. Using an appropriate margin of safety an allowable voltage range is formulated. If any voltage drops outside of this band an alarm should be generated and the fuel cell load should be reduced to avoid any serious damage to the cell.

The proposed cell monitoring procedure still requires the measuring of the voltage of all cells. But in contrast to a watchdog function with a fixed threshold, with the proposed monitoring procedure any complication is detected early and not only at high current densities where the scope of the damage is much larger than at low current densities.
CHAPTER 5

EXPERIMENTAL INVESTIGATION DYNAMICS

5.1 Step in air stoichiometry

The simulation data about the effect of the air stoichiometry on the polarization curve in Chapter 4.2.3 predicted a decrease of the voltage at high stoichiometries (>2) and high currents (>50 A) due to excessive drying of the membrane. However, this phenomenon was not observed in the measurements. This discrepancy was attributed to the insufficient waiting time while recording the polarization curve and the large time constant of the hydration and dehydration processes of the fuel cell stack. In this chapter the hydration/dehydration process is investigated.

The visualization of fuel cell hydration/dehydration phenomena ideally requires the abrupt changing of the humidification of the fuel cell stack. However, on the test bench the humidification of neither the cathode nor the anode facilitates such changes. Therefore, to modify the water balance of the fuel cell the water removal at the cathode is manipulated. This is accomplished by changing the air stoichiometry. Since the water production remains unchanged the water removed in vapor form from the stack is governed by the air flow through the stack. Provided that the stack temperature is higher than the air inlet dew point the water removal increases with an increasing air stoichiometry.
In Figure 5-1 the relative channel position at which water condensation is expected to set on is given in function of the air stoichiometry for different stack temperatures. For these calculations it was assumed that water is removed only in the air stream. In reality quantities of water are also removed in the fuel stream, especially since the hydrogen is not externally humidified. Thus the onset of water condensation is likely to be further away from the entrance. Nevertheless, the data in Figure 5-1 allows to make a qualitative comparison. It can be seen that at a stack temperature of 60 °C and an air stoichiometry of 1.65 liquid water starts to form after around 30% of the total channel length, whereas at $\lambda_{air} = 3.3$ water condensates only in approximately the last 40% of the channel. In case of a stack temperature of 70 °C and a stoichiometry of 3.3 no water condensation is expected at all. Therefore, by changing the air stoichiometry from low values to high values the humidification condition is substantially altered. A step in stoichiometry thus facilitates the investigation of the hydration/dehydration process of the fuel cell stack.
A series of measurements was conducted in which the stack was first operated with an air stoichiometry of 1.65. After 20 min the stoichiometry was doubled to 3.3. 20 more minutes later the stoichiometry was reduced again to 1.65. In course of the measurements the fuel cell current was kept constant at 30 A. Hence, the doubling of the air mass flow during the first step represents a change of the humidification condition from mostly wet to mostly dry, whereas in the second step when the air stoichiometry is halved the condition is changed from mostly dry to mostly wet.

Figure 5-2 shows the voltage response to the described air stoichiometry variation. For better visualization of the long term trends the data was fitted by an equation of the form given below:

\[
U_{fc} = C_1 + C_2 \cdot \exp[-C_3(t-t_0)] - C_4(t-t_0)
\]  

(5.1)

where \(C_1\) to \(C_4\) are fitting parameters, \(t\) is the time and \(t_0\) the time of the respective air stoichiometry step.
The linear term on the right-hand side was included as it helped to reduce the residual of the curve fitting, especially in case of the measurement data with \( T_{fc} = 70 \, ^\circ C \). The motivation to include a linear term can be derived from the data in Figure 5-3 where two measurements are compared. One curve shows the \( T_{fc} = 60 \, ^\circ C \) case from Figure 5-2 where the air stoichiometry is varied in course of the experiment. The other curve shows the voltage trace when the air stoichiometry is kept constant for one hour. In latter case the voltage is not constant but seems to drop linearly with time after a small initial increase. The reason for this slow decay of the voltage with time is not clear. The effect is reversible as the voltage recovers after every system shutdown. Thus any degradation due to ageing can be ruled out. One possible explanation is the gradual flooding of the electrodes with liquid water. The presence of liquid water in the diffusion layer blocks the diffusive pathways of the reactants and thus causes the mass resistance to increase. Furthermore, liquid water at the reactive interfaces covers the active sites for the electrochemical reaction [35, 27]. In either way flooding results in a lower voltage.
Another possibility is extensive dehydration of the membrane at the air inlet causing its Ohmic resistance to rise and the voltage to drop. In either case the slope of the voltage decrease should vary for different stack temperatures, since the effects are expected to scale with the stack temperature (see Chapter 4.2.3). However, this is not the case. Moreover, the voltage decreases at a rate of 1.55 V/h ± 0.1 V/h regardless of the stack temperature. A combination of the two effects might result in a similar decrease at all investigated temperatures (at low stack temperatures the flooding is heavy and the dehydration is minor, whereas at high stack temperatures the flooding is minor and the dehydration is extensive). However, this seems unlikely since the variation of the decrease between the different temperatures would be expected to be larger. In Chapter 5.3 the formation of Pt-oxides at the cathode as well as the accumulation of impurities on the catalyst are discussed. These oxides/impurities cause a reduction of the active catalyst sites and hence are expected to influence the cell performance negatively. The discussion on possible sources for the linear voltage decrease is therefore continued in Chapter 5.3.

In response to the doubling of the air mass flow rate the voltage increases for all stack temperatures (see Figure 5-2). This initial steep and very quick rise ($\tau \sim 1$ s) is followed by a slow decay ($\tau > 5$ min) to a new equilibrium voltage. The effect of the higher stoichiometry on the cell performance is twofold (see Figure 5-4). On the one hand, the oxygen partial pressure rises and the kinetic at the cathode is improved. On the other hand, the dehydration of the fuel cell stack is accelerated, leading to a decreased ionic conductivity and an increased Ohmic resistance. The voltage traces suggests that the cathode kinetic adjusts quickly, whereas the Ohmic resistance responds more slowly. Similarly, the reduction of the air stoichiometry leads to a initial steep drop in voltage followed by a slow rise. Again, the kinetics seems to react swiftly to the change of the oxygen partial pressure while the Ohmic resistance reaches the new equilibrium slowly.

At a stack temperature of 50 °C the humidification conditions are not substantially altered, even when the air stoichiometry is doubled from 1.65 to 3.3. The data in Figure 5-1 shows that the relative channel position at which liquid water starts to form is barely shifted. This is very much in contrast to
the case of 70 °C stack temperature. At $\lambda_{\text{air}} = 1.65$ more water is produced by the electrochemical reaction than is removed in vapor form by the air stream. This water surplus in the fuel cell has tipped over into a water deficit at $\lambda_{\text{air}} = 3.3$. Now more water can be removed by the air stream than is produced. The magnitude of the disturbance therefore differs between the investigated cases and increases as the stack temperature is moved away from the air inlet dew point (45 °C). As expected the settling time at 50 °C is much shorter compared to that at 70 °C. Furthermore, the difference between the voltage immediately after the step and the new equilibrium voltage is larger for the higher stack temperature.

These remarks are supported by the data on the pressure loss in the air flow channels. Liquid water can accumulate either in the form of water droplets or by forming a film on the channel surface [67]. Water droplets are removed by the momentum of the gas, thus the larger the flow velocity the more droplets are removed. At very low velocities the removal of droplets may be inhibited due to the insufficient momentum causing individual channels to be blocked. Water films decrease the channel cross section, which in turn translates into a
5.1 Step in air stoichiometry

higher flow velocity and thus an increased pressure loss. The build-up or the removal of these films is dependent on the condition of the adjacent gas stream and proceeds only gradually. A low velocity and a well humidified air stream should tendentiously support the accumulation of water and result in a higher pressure loss.

Figure 5-5 presents the total pressure loss in the air flow channels. The increase/decrease of the mass flow rate results in a steep increase/decrease of the pressure loss. This initial transition is followed by a much slower alteration to a new equilibrium value. It is obvious that the pressure loss at $T_{fc} = 50^\circ C$ is throughout the experiment higher than that at a stack temperature of $70^\circ C$. In agreement with the previous discussion this indicates that more water accumulates at the low stack temperature. The data also supports the assumption that at $T_{fc} = 70^\circ C$ the humidification condition substantially changes when the air stoichiometry is doubled from 1.65 to 3.3. In case of the $70^\circ C$ stack temperature (and thus in case of a poorly humidified air stream) the step in air stoichiometry at $t = 20$ min results in a steep initial steep increase of the pressure drop which is followed by slow decrease,

Figure 5-5: Evolvement of pressure drop in cathode flow channels with different humidification properties of the air stream. $I_{fc} = 30$ A.
indicating that the amount of accumulated water is reduced. In contrast at a stack temperature of 50 °C the pressure drop remains almost unchanged (after the steep initial increase), implying that the water film is more or less stationary. At t = 40 min the air stoichiometry is reduced again to λ_{air} = 1.65 and the pressure drop at T_{fc} = 70 °C increases gradually (after the steep initial decrease), reaching its initial value after 10 min. The water film thus increases until an equilibrium level is reached at which the water removal and production are in balance. At T_{fc} = 50 °C the pressure loss again changes only marginally after the second step, as a result of the similar humidification conditions at λ_{air} = 1.65 and 3.3.

A higher partial oxygen pressure at the higher stoichiometry leads to a smaller activation overvoltage and a higher reversible cell potential. The gains predicted by the simulation due to the doubling of the air mass flow rate amount to 0.8/0.8/1.0 V at a stack temperature of 50/60/70 °C. This is substantially less than observed in the measurements, here the gains are approximately 1.8/2.0/3.5 V. This unexpectedly high voltage increase indicates that other factors beside the improved kinetics are modified by the step in air stoichiometry. In the following two hypotheses are given to explain this deviation between measurement and simulation data.

The reasoning of the first hypothesis is as follows: Increasing the air stoichiometry leads to an increased air mass flow and thus an increased flow velocity. The higher velocity accelerates the removal of water droplets from the flow channels and the diffusion layer. These droplets hinder the transport of oxygen to the catalysts or may even block the flow channel. Hence, the removal of the droplets is accompanied with a thrust of oxygen to the membrane-electrode interface. The presence of liquid water is not taken into account in the model developed in Chapter 3.1. Therefore, the simulations cannot depict any related effects. However, the observation that the rise of the voltage is greatest at 70 °C stack temperature seems to contradict this argument. From the data in Figure 5-1 it can be seen that at 70 °C far less droplets should form compared to 50 °C, therefore the voltage step should be more pronounced at 50 °C.
Here the second hypothesis sets in. A prerequisite for this hypothesis is the existence of liquid water in the electrode pores even at the air inlet where dry conditions are assumed to prevail. A possible source of these droplets is the water transported from the anode through the membrane to the cathode. From the flow field layout in Figure 2-4 it can be seen that even though the layout forms a combination of co-, counter- and cross-flow areas, the counter-flow area dominates. The hydrogen stream thus carries water from the wet air outlet to the dry air inlet and thereby acts as an internal humidification. This indicates that the water is much more evenly distributed across the cell surface than suggested by Figure 5-1. This reasoning is supported by the localized impedance measurements along a single channel by Brett et al. [68], who observed no significant variation of the membrane resistance along the channel, even when the local current density varied substantially. They suggested that external factors such as the drying effect of the reactant flow only affect the membrane in a uniform manner along the channel.

It is assumed that the force of the increase in mass flow rate deflects the diffusion layer at the cathode and causes the water droplets that were stuck in the pores to move [69]. At 70 °C stack temperature the capability of the air stream to remove water is higher, hence more of these droplets are removed and the gain in voltage is larger in this case compared to the lower stack temperatures.

Both hypotheses - a) removal of liquid water that hinders the oxygen flow and b) a uniform water distribution across the cell - have their drawbacks and their advantages. The data about the stack voltage alone does not facilitate a definitive decision, localized current density measurements are required. However, neither hypothesis conflicts with the conclusion that a considerable time elapses before an equilibrium is retained between the humidification conditions in the flow channel and membrane-electrode interface. Mench et al. [70] observed that the flooding process when liquid water gradually accumulates in the electrodes can take minutes to hours, which is confirmed for a large fuel cell stack with the data of this work. The time interval until steady state is reached in case of a membrane dehydration is found to be of a similar dimension. Furthermore, this discussion can be concluded with the remark that the initial conditions decisively form the dynamic response of the voltage.
In the following an equation is proposed to describe the behavior over time of the amount of water accumulated in the cell, \( V_{\text{liq}} \):

\[
\frac{\partial V_{\text{liq}}}{\partial t} = i_{fc} \left( a_f (v_{\text{air}}, b - v_{\text{air}}) + \frac{T_{t,\text{air}} - T_{fc}}{\tau_f} \right)
\]  

(5.2)

where \( v_{\text{air}} \) is the air flow velocity, \( v_{\text{air}, b} \) the threshold velocity below which the air droplets in the channels remain stationary, \( T_{fc} \) the stack temperature, \( T_{t,\text{air}} \) the air inlet dew point. The parameter \( a_f \) links \( V_{\text{liq}} \) to the cell current and \( \tau_f \) is the time constant related to the build up of a water film. The first term on the right-hand side of Eq. 5.2 describes the accumulation of water droplets in the channel, whereas the right term considers the build up of the water film.

In Eq. 3.26 the parameter \( A_r \) was introduced to consider the obstruction of the electrochemical reaction by liquid water covering the active catalyst sites. This parameter is suggested to be proportional to \( V_{\text{liq}} \). Between the membrane water content, \( \lambda \), and the amount of accumulated water a affine relationship is proposed. This implies that on the one hand the presence of liquid water helps the hydration of the membrane. On the other hand liquid water impedes the electrochemical reaction through coverage of the reaction sites.

### 5.2 Current step

In automotive applications a short response time to load changes is desired, especially when the fuel cell is operated in a load-following mode without any buffer between the fuel cell and the electric drive. The response of the fuel cell power output is set to a large extent by the response of the reactant supplies and the controllers used. The experimental results demonstrate the superiority of a model-based controller over PI controllers. In this chapter first the experimental data on load changes are discussed. This analysis is followed by an attempt to explain the measurement data with the models developed in the previous chapters.
5.2 Current step

5.2.1 Experimental

The test bench setup of this work does not allow the hydrogen mass flow to be controlled (see Chapter 2.2) and thus cannot be used to shape the voltage response. Therefore, the response of the fuel cell voltage and hence the power output is influenced mainly by the dynamics of the air supply and the quality of the controllers within.

The voltage response of the fuel stack has been measured for different air supply strategies. Measurement results are compared between (a) a Linear Quadratic Gaussian (LQG) controller, (b) a set of PI controllers and (c) a constant air mass flow rate. The LQG approach of case (a) is a model-based design approach that produces output feedback controllers which are obtained as the solution of two optimization problems. A trade off between control input and error output signal energy may be obtained in this way [71]. The model on which the LQG controller is based, is outlined in Chapter 3.2. The relevant equations are Eq. 3.29 to 3.42. A comparison of the performance between the non-linear and the linearized model is given in Figure 4-16 and Figure 4-17. Case (b) is put together from two independent control loops. The first loop is used to control the mass flow and consists of the compressor and the mass flow sensor. The other loop regulates the pressure using the control valve and the pressure sensor in front of the stack. The controller parameters have been found by manual tuning with focus on fast setpoint following ($\tau < 1$ s) and small overshoot/undershoot ($< 10\%$). The PI controllers are equipped with an anti-windup. For the signal transmission a CAN-Bus is used with a sample time of 20 ms. Both controller approaches have been implemented in the control algorithms using Matlab/Simulink. In case of (c) the mass flow rate is set to 11.6 kg/h which corresponds to a stoichiometric value of 2/4 at 40/20 A. For the experimental data shown in Figure 5-6 the current was doubled from 20 to 40 A, whereas in Figure 5-7 the current was halved from 40 to 20 A.

In all experiments the pressure pulses on the air side as well as on the hydrogen side were turned off in order to record a clean voltage signal not influenced by other effects. The pump otherwise used to create the vacuum needed for the low pressure pulses on the hydrogen side is used to recirculate
Figure 5-6: Voltage response to a step in current from 20 to 40 A for LQG controller (a), PI controllers (b) and a constant air mass flow of 11.6 kg/h (c) which corresponds to a stoichiometric value of 2 at 40 A.

Figure 5-7: Voltage response to a step in current from 40 to 20 A for LQG controller (a), PI controllers (b) and a constant air mass flow of 11.6 kg/h (c) which corresponds to a stoichiometric value of 4 at 20 A.
hydrogen. Thereby a stoichiometry of 3/5 at 40/20 A is achieved. These stoichiometries are high enough for any transport delays on the anode side to be negligible. To facilitate a better comparison in the figures, the steady state value at which the voltage settles after the step, $U_\infty$, has been subtracted from the voltage traces.

The following discussion focuses on the step in which the current is doubled, since it is more critical. The voltage responses to the load changes are faster than 50 ms, which is the sampling time of the data acquisition system. The different supply strategies have distinctive responses. In case of the constant mass flow (c) no undershoot is observed and after an initial steep drop the voltage asymptotically approaches the steady state voltage. The measurement data confirms the assumption that the diffusion lag in the anode is very small and may even be neglected altogether, since any lag has to result in a undershoot of the voltage in response to a doubling of the current in case (c), where due to the constant high air flow rate enough oxygen is available at any time. However, no undershoot is observed in Figure 5-6. The slight voltage improvement after the asymptotic approach is believed to result from a better humidification of the membrane and thus a decrease of the Ohmic resistance (see Chapter 5.1).

Both the LQG controller (a) and the PI controllers (b) cause the voltage to drop below the steady state voltage, though in case (b) the undershoot is more heavy, even resulting in an oscillating behavior of the voltage. The voltage stabilizes only after four to five seconds, whereas in (a) the voltage stabilizes in one to two seconds. These undershoots are caused by oxygen depletion at the electrode-membrane interface [72]. The voltage response may be divided into three characteristic zones. First, immediately after the current step the voltage drops within 50ms to a new value marked A in Figure 5-6. Hereafter the voltage decays with a constant gradient to the minimal voltage observed in course of the response (marked B). Finally, the voltage recovers and increases to its steady state value. Here the voltage may overshoot, but the magnitude is small.

The differences between the air supply strategies observed in the voltage responses are the result of transient phenomena of the oxygen supply to the membrane-electrode interface. Figure 5-8 and Figure 5-9 show the mass flow...
trace corresponding to the upward step of current for the LQG controller and for the set of PI controllers, respectively. With the LQG controller a shorter settling time is achieved compared to the PI controllers. The system model has been used to simulate these mass flow traces by applying the respective controller on the model. As can be seen from the figures, the mass flow traces at the compressor are reproduced well by the model. The system model has been further employed to calculate the mass flow at the stack inlet. In case of the PI controllers the mass flow traces at the compressor, at the stack inlet and outlet do not differ much. In contrast, when the LQG controller is employed the traces deviate. Here the rise of the mass flow at the stack inlet is less steep compared to that of the compressor flow. Furthermore, the mass flow trace has a plateau, which appears when the compressor flow temporarily decreases. The supply of “fresh” oxygen to the stack is therefore slower than the compressor flow signal suggests, due to the extended inlet manifold volume. Nevertheless, the 60% response time with the LQG controller (200 ms) is substantially faster than that of the PI controllers (1 s).

**Magnitude of Step**

The effect of the magnitude of the current step on the voltage response is presented in Figure 5-10 for the LQG controller and in Figure 5-11 for the PI controllers. The data in Figure 5-10 demonstrates the high performance of the LQG controller. The current can be ramped up from zero to almost full load in less than 50 ms nearly without any major undershoot of the voltage (compared to the PI controllers). The measured undershoot amounts to only 1% of the steady state voltage after the step. This steady state voltage is achieved in around one second.

The results are relativized to some extent by the fact that the mass flow is not increased from zero flow but from the minimum flow of 4 kg/h. Therefore, prior to the step large quantities of excess air are available. This also explains the asymptotic behavior in case of the 0 to 20 A step, since enough oxygen facilitates a smooth transition. Nevertheless, for the step from 0 to 60 A the mass flow has to be increased more than fourfold.
5.2 Current step

Figure 5-8: Case (a): Mass flow trace corresponding to current step from 20 to 40 A. Measurement data of flow at compressor and simulation data of flow at compressor and at stack inlet are given.

Figure 5-9: Case (b): Mass flow trace corresponding to current step from 20 to 40 A. Measurement data of flow at compressor and simulation data of flow at compressor and at stack inlet are given.
Figure 5-10: Case (a): Measured voltage response to step in current for three different magnitudes. Operating conditions: $p_{\text{air}}/p_{\text{H2}} = 2.0/2.2$ bar$_{\text{abs}}$; $\lambda_{\text{air}} = 2.2$; $T_f = 60$ °C.

Figure 5-11: Case (b): Measured voltage response to step in current for three different magnitudes. Operating conditions: $p_{\text{air}}/p_{\text{H2}} = 2.0/2.2$ bar$_{\text{abs}}$; $\lambda_{\text{air}} = 2.2$; $T_f = 60$ °C.
Some interesting effects in Figure 5-10 and Figure 5-11 require mentioning. First, the position of A is not influenced by magnitude of the step. Second, the gradient between A and B decreases (to more negative values) with an increase in step magnitude. Finally, the time interval between A and B decreases when the step magnitude is increased.

The quality of the LQG controller is even better revealed by the data shown in Figure 5-12. For these measurements the current was instantaneously increased from 15 to 70 A. The starting value of 15 A was chosen, because it is the lowest current at which the stack can be operated with an air stoichiometry of 2.2. At this current no benefit can be drawn from the large amounts of excess air at the starting current as seen in the steps from 0 to 60 A. Although in case of the LQG controller the undershoot amounts to 5 V or nearly 10% of the steady state value, the voltage stabilizes within 1 s. In contrast, with the PI controllers the current step from 15 to 70 A causes the voltage to decrease heavily and after 0.55 s the emergency controller reduces the current to prevent a complete breakdown of the reaction.
Air Stoichiometry

To investigate the effect of the amount of excess air on the voltage response, the current step was performed with different air stoichiometries. Figure 5-13 and Figure 5-14 show the results for the LQG controller and the PI controllers, respectively. Generally, the undershoots with the LQG controller are only half the size of those with the PI controllers, again demonstrating the superiority of the LQG controller.

The settling time is substantially shorter with the LQG controller. However, in both cases the settling time increases with a decreasing air stoichiometry. The longer settling time mainly results from the increased time required for the voltage to recover from the minimal voltage, since the time interval between A and B is not visibly influenced by the stoichiometry. By decreasing the air stoichiometry the voltage of point A is shifted to lower levels. Furthermore, the gradient between A and B decreases (to more negative values) with a decreasing stoichiometry. These effects are discussed in the following chapter.

5.2.2 Discussion

The mass flow trace at the stack inlet calculated with the system model, is used to simulate the voltage response in the stack model. The thereby obtained voltage differs substantially from the measurement data. The magnitude of the undershoot due to the current increase is severely underestimated (not shown). Here the limitations of the model presented in Chapter 3 are exposed. Especially the following assumptions restrict the capability of the model to predict the dynamic response of the voltage. First, the reactant flow channels have been reduced to a single point, thereby neglecting the spatial extension of the reaction zone and any transport delay along the channel. Second, steady state conditions are assumed for the diffusion in the electrode. Therefore, any diffusion lag in the gas-diffusion-electrodes is not reproduced by the model. Furthermore, a uniform current density distribution across the active area of the cell has been assumed. Finally, the double layer capacitance was disregarded. To circumvent the first three limitations requires either the development of a two-dimensional model or the solving of partial differential equations, which is in contrast to the desire to develop a fast and fairly simple simulation tool.
5.2 Current step

Figure 5-13: Case (a): Measured voltage response to step in current from 20 to 40 A with different air stoichiometries. Operating conditions: \( p_{\text{air}}/p_{\text{H}_2} = 2.0/2.2 \) bar\(_{\text{abs}}\); \( T_{\text{fc}} = 60 \) °C.

Figure 5-14: Case (b): Measured voltage response to step in current from 20 to 40 A with different air stoichiometries. Operating conditions: \( p_{\text{air}}/p_{\text{H}_2} = 2.0/2.2 \) bar\(_{\text{abs}}\); \( T_{\text{fc}} = 60 \) °C.
The voltage response in case (a) and (b) is explained in the following. The interpretation is deprived from current interruption experiments where a steady state current is suddenly interrupted, and the voltage response is measured. Here the instantaneous jump is associated with Ohmic losses, whereas the subsequent rise represents the non-Ohmic losses of the system [73]. Applying this line of thought on the data yields that the initial voltage drop to point A represents the increase of the Ohmic voltage loss due to the increased current. The initial decay is similar in all traces of the air stoichiometry variation, but not identical (see Table 5-1). The larger decay at low stoichiometries can be explained by the partial coverage of active sites with liquid water and resulting higher local current density in the regions not impaired by the water.

<table>
<thead>
<tr>
<th>$\lambda_{\text{air}}$</th>
<th>PI</th>
<th>LQG</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6</td>
<td>9.1 V</td>
<td>9.2 V</td>
</tr>
<tr>
<td>1.8</td>
<td>8.2 V</td>
<td>8.3 V</td>
</tr>
<tr>
<td>2.0</td>
<td>7.5 V</td>
<td>6.8 V</td>
</tr>
<tr>
<td>2.2</td>
<td>7.6 V</td>
<td>7.5 V</td>
</tr>
</tbody>
</table>

Table 5-1: Initial voltage drop after current step from 20 to 40 A for different air stoichiometries. $p_{\text{air}}/p_{\text{H}_2} = 2.0/2.2$ bar$_{\text{abs}}$; $T_{\text{fc}} = 60$ °C.

The observation that point A is lower than the steady state voltage in some cases points to a relaxation process. It is believed to result from the removal of liquid water and thus from the increase of active sites as the flow rate is increased.

Between point A and point B the reaction is assumed to be diffusion controlled. The consumption of oxygen at the reaction sites thus proceeds faster than oxygen diffuses through the gas diffusion electrode. Consequently, the reaction starts to breakdown due to oxygen starvation and the voltage decreases. Especially towards the end of the air flow channels the reaction suffers from oxygen starvation. The decrease rate is set by the oxygen flux.
through the gas diffusion electrode, which in turn is dependent on the oxygen content in the flow channels. During this interval the oxygen reduction reaction relies on the oxygen capacity of the flow channels [74]. Hence the lower the air stoichiometry is, the smaller the flux and the steeper the voltage drop is. At point B the air supply from the compressor has been increased high enough for the oxygen content in the channels to increase. From this point onward the oxygen flux slowly increases to the new equilibrium level.

The asymptotic approach observed in case (c) is believed to result from the charging/discharging of the double-layer capacitance [75]. In the other cases the charging/discharging effect is covered by the stronger effect of the diffusion lag.

Brett et al. [68] investigated the response to air introduction in a fuel cell initially flooded with nitrogen. They found that the current restoration along the channel is slower than the average flow velocity by a factor of 2.3. They related this delay to the time required for the fresh reactant to flow through the diffusion layer. A similar delay is obtained in this work when the simulated mass flow data at the stack inlet is compared to the voltage response data. If instead the mass flow signal is used for this investigation the results may be distorted as a significant time delay may exist between the flow at the sensor location and at the relevant stack inlet.

The investigations in this chapter demonstrated that with a fast controller based on modeling data an almost instantaneous response of the fuel cell to load changes is feasible. A large oxygen excess ratio helps to smooth the transient response but is not essential for a stable operation.

5.3 Current spike

In this chapter the linear and reversible decrease with time of the cell performance (Chapter 5.1) and the hysteresis of the polarization curve (Chapter 4.2.3) are investigated in more detail. In Figure 5-15 the voltage traces at three different stack currents are compared. The other operating parameters ($p_{air}/p_{H2} = 2.0/2.2$ bar, $\lambda_{air} = 2.2$; $T_f = 60 \degree C$) are identical in all cases. The assumption of a linear decrease seems justified for all currents.
Figure 5-15: Decrease of cell voltage for different stack currents. In the inlet the mean voltage averaged over the 25 min shown and the average gradient is given. $p_{air}/p_{H2} = 2.0/2.2\text{ bar}_{\text{abs}}; \lambda_{air} = 2.2; T_{fc} = 60^{\circ}\text{C}$

The slope of the gradient, the values of which are presented in the legend decreases towards the higher currents. This decrease in cell performance can occur from a variety of source, which are discussed in the following.

- (i) Partial dehydration of the membrane.
- (ii) Partial flooding of the cathode/anode.
- (iii) Build-up of a Pt-oxide layer at the cathode.
- (iv) Accumulation of impurities on the catalyst at the cathode/anode.

If a cell is operated for long periods of time at low current densities, the catalyst layer and the membrane may dry out, since only little water is generated [76]. This drying effect is eased as more water is produced at higher currents. The humidification with product water is very effective, since the water is generated directly at the membrane-electrode interface and has not to diffuse through the electrode backing layer to reach the membrane. The backing layer is typically hydrophobic and thus may form a barrier to water
diffusion and consequently to hydration of the membrane in the case of the standard humidification procedure. The product water therefore assists the humidification of the membrane and delays the membrane dehydration.

During the discussion of the polarization curves in Chapter 4 it was found that the reactant flow channels are prone to be blocked by water droplets at low flow velocities. Applying this finding to the data in Figure 5-15 yields that the high degradation rate at 15 A is a result of the low flow velocity and the thus larger amounts of accumulated water compared to the higher currents.

Performance decreases of cells operating at low current densities have also been observed by Uribe and Zawodzinski [76] who attributed these observations to a deteriorated hydration or to changes of the Pt catalyst particle surface. Partial oxide coverage of the active Pt surface reduces the rate of the oxygen reduction reaction at the cathode. These oxides have been found by many other researchers [77, 78, 79]. The oxide coverage is a function of the voltage and at a given potential it is also a function of time. Studies by Damjanovic et al. [77] found that these oxygenated species are reduced below a critical voltage, which is in the range of 0.75 to 0.8 V. Hence the higher the cell current and the lower the cell voltage, the smaller is the surface oxides layer and the smaller is the performance degradation due to oxides coverage.

Cells contaminated with impurities, such as alkali metals, alkaline earths, transition elements and ammonium derivatives exhibit a decreased cell performance [80, 81]. The foreign cations enter the membrane and displace H\(^+\) ions and therefore decrease its conductivity. These impurities often result from corrosion processes in the piping leading to the fuel cell or in the humidification circuit [82].

Furthermore, CO adsorbs strongly on the catalyst surface at the anode, thereby blocking the adsorption sites for hydrogen and hindering the hydrogen oxidation reaction. The adsorption and desorption of CO is dependent on the cell voltage, i.e., high anode potentials lead to the oxidation of the CO layer [83]. Therefore, at low current densities and high voltages the performance reduction due to CO adsorption is more pronounced.
These hypotheses also facilitate an explanation of the hysteresis observed while recording the polarization curves (see Figure 4-4). The downward slope (70 A to 0 A) exhibited a higher voltage throughout the investigated current range compared to the upward slope (0 A to 70 A). Employing hypothesis (i) the hydration of the cell is gradually improved as the current is increased. Therefore, the cell has to struggle against the low conductivity while the current is raised and it profits from the better hydrated membrane during the downward slope [84]. In case (ii) the droplets are removed while the current and thus the velocity is high. Hence in the downward slope (70 A to 0 A) the reactants feed is not inhibited by water droplets blocking the transport pathway. According to hypotheses (iii) and (iv) during the upward slope the reaction proceeds on at catalyst surface covered by oxides or impurities. These are gradually removed as the current is increased. During the downward slope the catalyst is free from oxides and impurities and thus the performance is higher. In the literature the hysteresis is commonly attributed to the presence of Pt oxide on the electrode surface in one potential range and its reduction in the other [77, 78, 85]. The lower reaction rate on the oxide-covered surface is due to a lower probability for electron tunneling through the oxide film [77], or due to a structure-sensitive adsorption of OH⁻ [78, 86].

Uribe and Zawodzinski [76] operated a small air/H₂ fuel cell with short excursions to low cell voltages. These voltage pulses yielded significant increases of the current density. They argued that the excursions to low voltages provide the catalyst layer with conditions more favorable for the oxygen reduction reaction. The improvements were attributed to a better hydration of the catalyst layer due to the high currents or to the removal of oxygenated species from the Pt-catalysts.

In case of fuel cells fed with reformat several groups found beneficial effects resulting from the alteration of the anode potential. In Ref. [87] a method is described by which a fuel cell is periodically starved at the anode side. These momentary fuel starvation conditions are believed to cause the anode potential to increase, resulting in the oxidation and removal of poisons from the anode catalyst surface and an improved cell performance. Similarly Carrette et al. [81] impose a rectangular current pulse on the fuel cell that is fed with
Figure 5.3 Current spike

**Figure 5-16:** Improvement of cell performance at $I_{fe} = 15$ A by imposing a short pulse of high current on the cell. $p_{\text{air}}/p_{H2} = 2.0/2.2$ bar, $\lambda_{\text{air}} = 2.2$; $T_{fe} = 60$ °C. The mean voltage was averaged over the 25 min shown, the gradient assumes a linear decrease.

different amounts of CO. Thereby the anode potential is increased and the cathode potential is decreased. The positive alteration of the anode potential leads to the desired effect of the oxidation of the CO layer.

Wilson et al. [88] observed a 10 to 30% performance decrease over the duration of life tests with air/H$_2$ fuel cells. The injection of small amounts of oxygen into the fuel stream led to a recovery of all but 10% of the initial air/H$_2$ power density. They reasoned that the oxygen removes anode contaminants. The residual loss of performance was suspected to be caused by water accumulation in the cathode gas diffusion layer.

In this work the beneficial effect of current pulses is confirmed for a large-scale fuel cell stack. In Figure 5-16 the cell performance with a constant current of 15 A is compared to that when a current pulse is imposed thereon. During the pulse the current was increased to 35 A for 2 s. The pulse was applied every 60 s. The pulse current is taken back, if the stack voltage drops below 58 V. At this voltage several cells are close or even below 0 V, thus any extended exposure to this low voltage must be avoided. The comparison in
Figure 5-17: Improvement of cell performance at $I_{fc} = 30$ A by imposing a short pulse of high current on the cell. $p_{air}/p_{H2} = 2.0/2.2$ bar$_{abs}$; $\lambda_{air} = 2.2$; $T_{fe} = 60 \degree$C. The mean voltage was averaged over the 25 min shown, the gradient assumes a linear decrease.

case of a base current of 30 A is shown in Figure 5-17, where the magnitude of the current pulse was 60 A. The air flow was not adjusted during the pulses, resulting in a depletion of oxygen. After the initial drop in voltage due to the larger current, the voltage settles at a value which is higher than that prior to the current pulse. From this value the voltage then decays exponentially. In both cases, 15 A and 30 A, the cell performance is improved by the application of the current pulses. The mean voltage is shifted to higher values and the degradation is lessened. The improvements are larger in case of the 15 A base current and thus the higher cell voltage. The mean voltage is increased by more than 2% and the gradient is reduced to one third of the former value.

Figure 5-18 shows the polarization curves recorded after the fuel cell was constantly operated at 15 A for 30 min with (a) no pulses and (b) with pulses of 35 A and a duration of 2 s at a waiting time of 58 s. The upward slope (0 to
5.3 Current spike

Figure 5-18: Comparison of polarization curves recorded after the stack was operated at 15 A/0.075 A/cm$^2$ for 30 min with and without current pulsing. The current is first increased from 0 to 70 A/0.34 A/cm$^2$ (upward slope) and then decreased back to 0 A (downward slope). $P_{\text{air}}/P_{\text{H}_2} = 2.0/2.2 \text{ bar abs}$; $\lambda_{\text{air}} = 2.2$; $T_{\text{fc}} = 60 ^\circ\text{C}$; $T_{\text{t,air}} = 45 ^\circ\text{C}$.

70 A) is represented by the star symbol and the downward slope (70 to 0 A) by the diamond symbol. The respective sets are fitted with the following equation:

\[
U_{fc} = E_0 - b \log i_{fc} - R i_{fc}
\]

\[
E_0 = E_r + b \log i_0
\]  

(5.3)

where $U_{fc}$ is the cell voltage, $b$ and $i_0$ are the Tafel slope and the exchange current density, respectively, $i_{fc}$ is the current density, $R$ is the Ohmic resistance, and $E_r$ is the reversible potential.

By applying current pulses to the fuel cell, the voltage in the upward slope (when the current is changed from 0 to 70 A) was increased, especially in the low to medium current density range. The fitted Tafel slope coefficient $b$ in the low current density region ($E > 0.75 \text{ V}$) is 59 mV/dec for the upward slope of case (a) with no pulses and 56 mV/dec for the upward slope of case (b) with pulses. This change indicates that current pulses improve the oxygen
reduction reaction rate. For the downward slope a fitted value for $b$ of $53 \pm 0.5 \text{ mV/dec}$ is obtained in the low current density region for both cases, indicating that similar kinetic conditions exist in both cases. Thus the voltage in the downward slope is not influenced by the operational condition prior to recording of the polarization curve.

The current pulse causes the cathode potential to shift to more negative values. Thereby, applying the reasoning from hypothesis (iii) any oxides are removed from the cathode. In accordance with hypothesis (iv) the potential shift further facilitates the oxidation of impurities from the cathode catalyst. Both arguments require that the catalyst activation by either the oxide removal or the oxidation of impurities is substantially faster that the subsequent deactivation. Simultaneously the current pulses move the anode potential to more positive values. Hence the application of the current pulse also removes any impurities from the anode. The beneficial effect of the oxidation of impurities at the anode is, however, considered to be small, since the anode catalytic activity is much higher compared to that of the cathode [33].

The pulse is inherent with a higher current and consequently a larger water production. Although the enhanced water production is small due to the limited pulse length, the water is produced directly at the membrane-electrode interface at the cathode side. According to hypothesis (i) this internal humidification is very effective and might explain the higher voltages in the downward slope. Hypothesis (ii) is weakened by the current pulse experiment, since the air flow is not increased in course thereby. However, the depletion of the reactants is followed by a momentarily increased flux through the diffusion layer, which might be sufficient to move part of the droplets. The hydrogen mass flow trace at the stack inlet exhibits such an increased flux, but the increase is only small ($\sim 10\%$).

In course of this work the fuel cell stack was operated for more than 300 h and over 1000 duty cycles were performed. During this time a slight but consistent irreversible degradation in voltage was detected. The experiments corresponding to the data in Figure 5-15 were repeated 200 h of operating later, the results of which are shown in Figure 5-19. The performance decreased in course of the 200 h slightly. The previously obtained voltage levels at the different currents could not be achieved (reduction of stack
5.3 Current spike

Figure 5-19: Decrease of cell voltage for different stack currents. $p_{\text{air}}/p_{\text{H}_2} = 2.0/2.2 \text{ bar}_{\text{abs}}$; $\lambda_{\text{air}} = 2.2$; $T_{\text{fc}} = 60 \, ^\circ\text{C}$. Experiment performed approximately 200 h of operating time after those in Figure 5-15.

Voltage by 0.3/0.8/0.8% at 15/30/50 A) and the gradient of the reversible voltage decrease is steeper (-3/-88/-335% at 15/30/50 A). The degradation is much more pronounced at higher currents, whereas at 15 A the degradation is small. Similarly the current pulsing experiments were repeated after 200 h (see Figure 5-20 and Figure 5-21). The benefit previously obtained through the current pulsing is reduced, but still existent. The improvement in voltage is reduced from 2.2% to 1.8% at 15 A, and from 1.7% to 1.1% at 30 A. The reduction of the voltage gradient decreased from 63% to 39% at 15 A, and from 51% to 48% at 30 A.

The investigation of the origin of this permanent degradation is not part of this work. The sources are numerous, such as membrane degradation [80], catalyst decomposition and/or ripening [88] or alteration of electrode properties [89]. Since the ageing is more pronounced at higher currents where the water production is larger, it is believed that the degradation results from heavier flooding in the parts of the cell that are continuously exposed to liquid
Figure 5-20: Improvement of cell performance at $I_{fc} = 15\, \text{A}$ by imposing a current pulse on the cell current. $p_{air}/p_{H2} = 2.0/2.2\, \text{bar}_{abs}$; $\lambda_{air} = 2.2$; $T_{fc} = 60\, ^\circ\text{C}$. Experiment performed approximately 200 h after those in Figure 5-16.

Figure 5-21: Improvement of cell performance at $I_{fc} = 30\, \text{A}$ by imposing a current pulse on the cell current. $p_{air}/p_{H2} = 2.0/2.2\, \text{bar}_{abs}$; $\lambda_{air} = 2.2$; $T_{fc} = 60\, ^\circ\text{C}$. Experiment performed approximately 200 h after those in Figure 5-17.
water. The heavier flooding in turn is believed to be caused by an electrode that is increasingly becoming hydrophil. A proof for this assumption is however still outstanding.

To obtain further indications about the source of the reversible voltage decrease observed at constant current, the current pulsing experiment was modified. Instead of periodically applying a current pulse, the air flow is temporarily reduced below a stoichiometry of one. The thereby generated voltage response is comparable to that of the current pulsing as Figure 5-22 shows. The voltage drops due to the oxygen starvation, followed by a sharp rise in voltage and a slow decay. The mean voltage and the gradient of the linear decrease are very similar in both cases.

The starvation of the fuel cell from oxygen causes the cathode potential to drop, whereas the anode potential should remain unchanged since the hydrogen supply is not interrupted. Therefore, the oxidation of impurities at the anode in hypothesis (iv) may be ruled out, as it requires an increase of the anode potential. The fact that the current is not increased in this experiment
and thus the water generation is not enhanced seems to counter hypothesis (i). However, the reduction of the air flow rate in turn results in a reduced water removal rate. In Chapter 5.1 it was reasoned that the disturbance of the water balance due to change in air stoichiometry might be sufficient to improve the hydration of the catalyst layer and membrane. The set in of the hydration effect in case of the stoichiometry step was very swift. Therefore, the impeded water removal during the reduction of the air flow might be enough to achieve an improved hydration state. Hence, hypothesis (i) cannot be ruled out with the results from the oxygen starvation experiment.

In conclusion, the slow performance degradation and the hysteresis between the upward and downward slope of the polarization curve may result either from the formation of Pt oxide at high cathode potentials, from the build-up of impurities on the cathode catalytic surface, from partial dehydration of the membrane due to limited water generation at high cathode potentials or from the partial blockage of the reactant transport pathway due to water droplets. Most likely a combination of the effects above is responsible for the decrease of the voltage with time at constant currents. Short excursions to lower potentials by current pulses effectively lessen the voltage decrease and the hysteresis. However, the decrease is not totally eliminated by the current pulses, suggesting that electrode flooding also affects the cell performance.
CHAPTER 6

CONCLUSIONS

In this thesis the dynamic behavior of a large size fuel cell stack operated in an environment typical for automotive applications has been investigated. It was found that the hydration/dehydration process of the MEA, the quality of the air supply control and the operative conditions of the applied load greatly influence the performance of the fuel cell.

The experimental investigations have demonstrated that the time constant of the hydration/dehydration process is dependent on the size of the disturbance. It ranges from several minutes to more than half an hour. Until the new steady state conditions are reached the cell voltage may change by more than 5%. This finding has major consequences for the interpretation of polarization curves. These are assumed to represent the cell performance under steady state conditions. However, the large time constant of the hydration/dehydration process together with the often observed hysteresis suggests that this is not the case. The voltage of the polarization curve with positive current increments (current is increased) is lower compared to that with negative current increments (current is decreased). Although other phenomena such as the oxidation of Pt oxide and impurities also affect the shape of the hysteresis the improved humidification of the membrane at high currents is considered to have a major effect. When the current is increased the performance suffers from poor hydration, whereas when the current is decreased the performance is enhanced by the lower Ohmic resistance due to the water production at high currents. Hence the polarization curves are biased by dynamic effects that have to be considered.
In this thesis a model based controller has been used for the air supply system. With this controller excellent performance has been achieved with regard to response time. Experiments show that the load on the fuel cell can be ramped up from zero to full load in less than 50 ms. Furthermore, the air mass flow and pressure are successfully decoupled and the under-/overshoots of the mass flow are reduced. These results suggest that the transient performance restrictions of the Hy.Power vehicle could have been eased to a considerable extent if this model based controlled had been used. The proposed control would further facilitate the operation of the fuel cell in a load-following mode without the need for any electric buffer.

The experimental results on the constant operation at low current densities have shown a slight but continuous deterioration of the voltage. This short-term deterioration was found to be reversible ruling out any ageing or degradation processes. There are several indications that the voltage decrease is the cumulated result of several effects. Namely, of the flooding of the gas diffusion electrode, of the formation of Pt oxide as well as of the accumulation of impurities at the cathode. The accumulation of impurities at the anode was shown to have no effect on the voltage deterioration. No final conclusion on the origin of this voltage decrease could be formulated. However, experimental investigations showed that by imposing short pulses of high currents on the fuel cell the voltage decrease is effectively reduced and the overall voltage level is increased by approx. 2%.

In course of this work a one-dimensional model was developed in order to simulate the performance of a large scale PEM fuel cell stack and facilitate the investigations. In this model the relevant dimension is orthogonal to the membrane surface. The model considers the transport of reactants (oxygen and hydrogen) and that of water through the gas diffusion electrode. The transport of water in the membrane is modeled by considering the electro-osmotic drag, the back-diffusion and the convection. The gas concentration in the flow channels is averaged by assuming a uniform current distribution across the cell. The cell voltage is found by subtracting the activation polarization and the Ohmic losses from of the reversible cell potential. Here the effect of flooding (partial coverage of the active sites by liquid water) and the change of the Tafel slope during the transition from high to low cell voltage are taken into account.
Finally, the variation of the cell voltage across the stack was explained. A model was derived from the measurement data. Using this model a cell monitoring procedure was proposed which allows to detect any complications even at low current densities. Thereby the risk of any serious and irreversible damage to the cells is minimized.

This thesis gives valuable insight into the transient operation of a large fuel cell system. However, several effects could not be quantitatively dissolved. Data on the current distribution across the cell would allow to distinguish between such diametrical different effects as flooding and extensive drying. Therefore, the equipping of at least several cells with current distribution measurement systems is suggested.

Furthermore, with the lack of a proper humidification the membrane could not be fully hydrated. However, for further investigations on the origin of the hysteresis and the deteriorating voltage (short-term) a fully hydrated membrane is essential in order to exclude the effect of increased humidification at high currents. Finally, the development of humidification control is considered to be a challenging and demanding task.
REFERENCES


[14] O. Garcia: DC/DC-Wandler für die Leistungsverteilung in einem Elektrofahrzeug mit Brennstoffzellen und Superkondensatoren, Diss. ETH Zürich Nr. 14859, 2002


CURRICULUM VITAE

Name: Rodatz
First names: Paul Hendrik
Date of birth: 18. September 1973
Place of birth: Tokyo, Japan

Education

1979-1993 Deutsche Schule Tokyo, Japan
1993-1996 Studies in mechanical engineering,
Technische Universität Hamburg-Harburg
1996-1999 Studies in mechanical engineering,
Swiss Federal Institute of Technology (ETH), Zurich
1999 Diploma in mechanical engineering
Swiss Federal Institute of Technology (ETH), Zurich
1999-2003 Doctoral student and research assistant at the
Institute of Energy Technology and the
Measurement and Control Laboratory,
Swiss Federal Institute of Technology (ETH), Zurich