Doctoral Thesis

Mass and charge transfer on various relevant scales in polymer electrolyte fuel cells

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Mass and Charge Transfer on Various Relevant Scales in Polymer Electrolyte Fuel Cells

A dissertation submitted to
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZÜRICH

for the degree of
Doctor of Sciences

presented by
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2007
Seite Leer / Blank leaf
To my parents
Meinen Eltern
Acknowledgements

Although only my name appears on the cover of this thesis, this work would not have been possible without the help of a number of people. First and foremost I want to express my gratitude to my supervisors during the years of my doctoral work, Prof. Alexander Wokaun, Günther Schiesser, and Felix Büchi, for giving me the chance to work towards my Ph.D. at ETHZ and PSI. I particularly thank the head of the fuel cell systems group, Felix Büchi, for continuous encouragement and support, for creating a lively working environment, and for giving me freedom in work topics. Furthermore, I acknowledge Philip Dietrich for taking me into the INTEGRAL 1 team. I also thank Prof. Dimos Poulakakos for accepting to be co-examiner of my thesis.

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Stefan Freunberger
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Zusammenfassung


bestimmen, während bei hoher Last Massentransportlimitierungen die Stromproduktion unter dem Steg behindern.


Abstract

This dissertation is concerned with the development, experimental diagnostics and mathematical modelling and simulation of polymer electrolyte fuel cells (PEFC). The central themes throughout this thesis are the closely interlinked phenomena of mass and charge transfer. In the face of developing a PEFC system for vehicle propulsion these phenomena are scrutinized on a broad range of relevant scales. Starting from the material related level of the membrane and the gas diffusion layer (GDL) we turn to length scales, where structural features of the cell additionally come into play. These are the scale of flow channels and ribs, the single cell and the cell stack followed by the cell, stack, and system development for an automotive power train.

In Chapter 3 selected fundamental material models and properties, respectively, are explored that are crucial for the mathematical modelling and simulation of PEFC, as needed in some succeeding parts of this work. First, established mathematical models for mass and charge transfer in the membrane are compared within the framework of the membrane electrode assembly (MEA), which represents the electrochemical unit. Second, reliable values for effective diffusivities in the GDLs which are vital for the simulation of gaseous mass transport are measured. Therefore, a method is developed that allows measuring this quantity both as a function of compression and direction as this is a prerequisite of sophisticated more-dimensional numerical PEFC-models.

Besides the cross section of the catalyst layer (CL) mass transfer under channels and ribs is considered as a major source of losses in particular under high load operation. As up to now there have been solely non-validated theoretical investigations, in Chapter 4 an experimental method is developed that is for the first time capable of resolving the current density distribution on the this scale. For this, the electron conductors in the cell are considered as 2-dimensional shunt resistors and the current distribution is obtained from Laplace's equation with the measured potential at the reaction layer vs. current collector as boundary condition. First results show that electrical and ionic resistances govern the current distribution at low current regimes, whereas mass transport limitations locally hamper the current production at high loads.

For the examination of phenomena on the single cell level in Chapter 5 both an efficient numerical model and a cell of technical size that is capable of employing various advanced
in-situ diagnostic methods is developed. As gradients on this scale occur essentially in along-the-channel direction the model is formulated in a $1+1D$ manner, i.e. local transport phenomena are treated $1D$ in through-plane direction and coupled in-plane by convective transport in gas and coolant channels. In terms of experimental diagnostics we apply localized current density measurement, electrochemical impedance spectroscopy, and liquid water detection by neutron radiography to a large scale PEFC.

With combinations of this sophisticated repertoire we investigate the following aspects in Chapter 6: (i) The theoretical prediction of the efficiency of the cell internal humidification device of the process air. (ii) Co and counter flow regimes are investigated on the influence of operating conditions both isothermally and under the influence of temperature gradients by limited cooling. Current density measurements are employed to validate the model in either case and to further explore non-isothermal operation. (iii) Capable of identifying voltage loss mechanisms, the model is used to explain the influence of in-plane catalyst gradients on current distribution and power. (iv) Oxygen concentration oscillations in the gas channels as the origin of low frequency capacitive arcs in spectra of H$_2$/air PEFC could be proved and mechanistically explained. (v) Mass transport phenomena under different loads are investigated by simultaneously measuring the current density distribution, the high frequency resistance, localized impedance spectra, and the liquid distribution using neutron radiography.

In Chapter 7 electrical cell interaction phenomena that arise from inequalities between adjacent cells in a stack are investigated in detail experimentally and theoretically. For this, a specialized 2-cell stack with advanced localized diagnostics was developed. The mechanism and effect of coupling as a reaction on practically relevant variations in reactant feed flow is analyzed and overall and local power changes due to the arising non-uniform polarization are scrutinized. A 2D model based on a commercial CFD-code is used to back and extend the experimental findings to more general cases. Furthermore, the experimental setup allowed for the first time to perform simultaneous localized electrochemical impedance spectroscopy beyond the single cell level.

The final Chapter 8 gives an overview of the contributions of this work on the cell, stack and system development for the automotive propulsion system of HY-LIGHT, a collaborative project between Conception et Développement Michelin SA, Michelin’s research center in Givisiez, Switzerland, and PSI’s Electrochemistry Laboratory. HY-LIGHT is a car with pure electric power train comprising a H$_2$/O$_2$ FC system hybridized with a electrochemical double layer capacitor (super capacitor, SC) unit.
Notations

\[
\begin{align*}
A & \quad \text{area, } m^2 \\
A_i & \quad \text{model fitting parameters (Sec. 3.1)} \\
\alpha_i & \quad \text{activity of species } i \\
\textbf{B} & \quad \text{body force, } m/s^2 \\
c & \quad \text{concentration, } mol/m^3 \\
c_t & \quad \text{concentration of pore fluid (Sec. 3.1), } mol/m^3 \\
C & \quad \text{merged expression (Sec. 3.1)} \\
C_p & \quad \text{heat capacity at constant pressure, } J/K \text{ mol} \\
C_{ij} & \quad \text{transport coefficient (Sec. 3.1), } m^2/s \\
d & \quad \text{thickness, } m \\
D & \quad \text{diffusion coefficient, } m^2/s \\
\textbf{D} & \quad \text{stiffness matrix} \\
E & \quad \text{Young's modulus, } Pa \\
E^0 & \quad \text{equilibrium potential, } V \\
f & \quad \text{factor for dry medium effective diffusivity } V \\
\text{F} & \quad \text{Faraday constant, } C/mol \\
\Delta H_{vd} & \quad \text{enthalpy of vaporization, } J/mol \\
h & \quad \text{mixture enthalpy, } J/kg \\
h_i & \quad i\text{-th species enthalpy, } J/kg \\
i & \quad \text{current, } A \\
\bar{i} & \quad \text{current density, } A/m^2 \\
\bar{j} & \quad \text{exchange current density, } A/m^2 \\
\bar{j}_i & \quad \text{limiting current density, } A/m^2 \\
J & \quad \text{current density, } A/m^3 \\
\textbf{J}_i & \quad i\text{-th species diffusive flux, } kg/m^2s \\
k & \quad \text{thermal conductivity, } W/m-K \\
k & \quad \text{permeability (Sec. 3.1) } W/m^2K \\
L & \quad \text{characteristic length, } m \\
\text{L} & \quad \text{channel length, } m \\
m_{cw} & \quad \text{cooling water flow, } kg/s \\
m & \quad \text{empirical constant} \\
M & \quad \text{molecular weight, } kg/mol \\
n & \quad \text{molar flux, } mol/m^2s
\end{align*}
\]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_{a/c}$</td>
<td>water molar flux in a or c channel, mol/s</td>
</tr>
<tr>
<td>$n_d$</td>
<td>drag coefficient</td>
</tr>
<tr>
<td>$N$</td>
<td>flow density, mol/m²s</td>
</tr>
<tr>
<td>$p$</td>
<td>total pressure, Pa</td>
</tr>
<tr>
<td>$p_i$</td>
<td>partial pressure of species i, Pa</td>
</tr>
<tr>
<td>$p_l$</td>
<td>liquid pressure, Pa</td>
</tr>
<tr>
<td>$P$</td>
<td>power density, W/m²</td>
</tr>
<tr>
<td>$q_{ev}$</td>
<td>evaporation heat flux, J/m³s</td>
</tr>
<tr>
<td>$Q$</td>
<td>heat flux, J/m³s</td>
</tr>
<tr>
<td>$r_c$</td>
<td>contact resistance, Ωm²</td>
</tr>
<tr>
<td>$r$</td>
<td>BPP resistivity, Ω/m</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant, J/K mol</td>
</tr>
<tr>
<td>$R_0$</td>
<td>electrochemical resistance, Ωm²</td>
</tr>
<tr>
<td>$s$</td>
<td>diffusion coefficient exponent (Sec. 3.1)</td>
</tr>
<tr>
<td>$s$</td>
<td>saturation</td>
</tr>
<tr>
<td>$S$</td>
<td>source term in conservation equation</td>
</tr>
<tr>
<td>$S_a$</td>
<td>catalyst specific area per unit volume, m²/m³</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>entropy, J/K·mol</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature, K</td>
</tr>
<tr>
<td>$u$</td>
<td>displacement vector, m</td>
</tr>
<tr>
<td>$u$</td>
<td>bulk fluid velocity, m/s</td>
</tr>
<tr>
<td>$U$</td>
<td>voltage, V</td>
</tr>
<tr>
<td>$U_c$</td>
<td>concentration induced voltage (Sec. 6.5), V</td>
</tr>
<tr>
<td>$U_i$</td>
<td>current induced voltage (Sec. 6.5), V</td>
</tr>
<tr>
<td>$U_{mod}$</td>
<td>modulation voltage (Sec. 6.5), V</td>
</tr>
<tr>
<td>$v$</td>
<td>velocity, m/s</td>
</tr>
<tr>
<td>$V$</td>
<td>molar volume, m³/mol</td>
</tr>
<tr>
<td>$x$</td>
<td>coordinate, m</td>
</tr>
<tr>
<td>$x$</td>
<td>mole fraction</td>
</tr>
<tr>
<td>$x_{a/c}$</td>
<td>water mole fraction at interface a or c</td>
</tr>
<tr>
<td>$y$</td>
<td>coordinate, m</td>
</tr>
<tr>
<td>$Y_i$</td>
<td>$i$-th species mass fraction, kg/m²s</td>
</tr>
<tr>
<td>$z$</td>
<td>coordinate, m</td>
</tr>
<tr>
<td>$z$</td>
<td>number of electrons</td>
</tr>
</tbody>
</table>

**Greek**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>heat transfer coefficient, W/m²·K</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>transfer coefficient</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>concentration exponent in Butler-Volmer Eq.</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>shearing strain</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>general transport coefficient</td>
</tr>
<tr>
<td>$\delta$</td>
<td>thickness, m</td>
</tr>
</tbody>
</table>
\(\epsilon\)  normal strain
\(\varepsilon\)  volume fraction or porosity
\(\eta\)  overpotential, V
\(\kappa\)  liquid permeability, \(\text{mol}^2\text{s}/\text{m}^3\text{kg}\)
\(\lambda\)  membrane water content \(\text{H}_2\text{O}/\text{SO}_3^-\)
\(\lambda\)  fccd stoichiometry
\(\mu\)  friction coefficient
\(\mu\)  chemical stoichiometry, J/mol
\(\mu\)  dynamic viscosity, \(\text{kg}/\text{m}\cdot\text{s}\)
\(\nu\)  Poisson’s ratio
\(\phi\)  electric potential, V
\(\phi_m\)  membrane phase potential, V
\(\phi_s\)  solid phase potential, V
\(\varphi\)  relative humidity
\(\varphi\)  phase angle, \(^\circ\)
\(\Phi\)  general quantity
\(\rho\)  density, \(\text{kg}/\text{m}^3\)
\(\sigma\)  normal stress, Pa
\(\sigma\)  electric conductivity, S/in
\(\tau\)  shearing stress, Pa
\(\tau\)  shearing stress vector, Pa
\(\tau\)  tortuosity
\(\sigma\)  stress vector, Pa
\(\phi\)  electric potential, V
\(\omega_{pw}\)  number of waters in hydrated complex (Sec. 3.1)

**Subscripts**

\(+\)  proton
\(a\)  anode channel or anodic
\(b\)  backward
\(ct\)  charge transfer
\(am\)  anode GDL-membrane interface
\(c\)  cathodic (Chapter 2)
\(c\)  contact (Chapter 4)
\(c\)  carbon, cathode channel (Sec. 5.1)
\(c\)  concentration (Sec. 6.5)
\(cl\)  GDL-catalyst layer interface or catalyst layer
\(clm\)  catalyst layer - membrane interface
\(cm\)  cathode GDL membrane interface
\(conc\)  concentration
\(e\)  east face of control volume
\(f\)  fluid
\( f \)  
foreward

gl  
gas liquid phase change

h  
hydrogen or enthalpy

\( i, j \)  
species or index

\( i \)  
current induced (Sec. 6.5)

l  
limiting, liquid

m  
membrane or membrane phase

meas  
measured

mod  
modulation

n  
nitrogen

o  
oxygen

p  
product (Sec. 5.1)

p  
porc volume or percolation limit (Chapter 3)

r  
relative

R  
olmic

s  
solid

u  
velocity

w  
water or west face of control volume

x  
in-plane direction

y  
through-plane direction

Superscripts

eff  
effective

ref  
reference value

sat  
saturation

(\(^{'}\))  
deformed space

0  
standard, uncompressed, equilibrium

Abbreviations

BFM  
binary friction model

BFCM  
binary friction conductivity model

CL  
catalyst layer

CFD  
computational fluid dynamics

EIS  
electrochemical impedance spectroscopy

FC  
fuel cell

GDL  
gas diffusion layer

LEIS  
localized EIS

LHV  
lower heating value

MEA  
membrane electrode assembly

MPL  
microporous layer

PEFC  
polymer electrolyte fuel cell

RHS  
right hand side of an equation
Chapter 1

Motivation & Structure of the Thesis

"My advice is to go for the messes — that’s where the action is."


This work scrutinizes aspects of charge and mass transfer on a broad range of relevant scales. In order to provide a framework for the particular selection of the chosen topics in Chapters 3 to 8 the following gives an overview on challenges regarding charge and mass transfer and on the undertaken research performed in this work.

In PEFCs charge and mass transport and the intimately connected heat and current density distribution on all scales is of high interest for improving power density, which is associated to performance and costs. Despite considerable improvements, the major voltage losses in PEFCs arise from poor oxygen reduction kinetics, mass transport limitations and a high resistance of dehydrated ionomer. Catalyst activity and membrane conductivity are material specific properties. However, associated mass transport limitations and the hydration level of the ionomer are highly influenced by structural properties of the gas distributors. This is the morphology of the catalyst layer, mass transport properties of the micro porous layer (MPL) and the gas diffusion layer (GDL), and the flow field geometry. In terms of flow field geometry both the geometry of channels and ribs, the layout of the channels over the cell area, and the relative flow direction of the reactants come into play.

Convective and diffusive mass transport phenomena together with depletion of reactants and formation of product water cause inhomogeneous reaction rates on all scales in the fuel cell. These scales include first the cross section of the catalyst layer (CL). Second, the repetitive unit of channels and ribs in the flow field. Third, the current distribution on the full cell level, where gradients occur essentially in along-the-channel direction.

The integral characteristic of a PEFC results from the interaction of the local characteristics on all of those scales. The phenomena on these scales have to be analyzed in order to develop a detailed understanding of the integral characteristics. Insight can be
gained from both theoretical and experimental work. In the fuel cell literature there is
the tendency that localized investigations tend to be more on the experimental side when
dimensions become large, whereas phenomena on small scales, namely smaller than a few
millimeters, are investigated locally resolved, mostly theoretically.

This work seeks to fill some gaps in the understanding of the aforementioned phenomena
on most of the mentioned scales by using both theoretical and experimental approaches
and combinations thereof.

1.1 Transport in Electrolyte and Gas Diffusion Layer

An earlier at the University of Victoria, Canada, developed mathematical model for mass
and charge transfer in the membrane based on the binary friction model was implemented
for use in a general purpose computational fluid dynamics (CFD) solver during a stay
there. This model is compared in Section 3.1 to other established mathematical models
within the framework of the membrane electrode assembly.

Although being vital for the simulation of gaseous mass transport, very limited reliable
data for effective diffusivities in gas diffusion media are available. Therefore, a method
that allows measuring this quantity both as a function of compression and direction is
developed in collaboration with KRAMER and FLÜCKIGER in Section 3.2.

1.2 In-depth Understanding of the Channel and Rib
Scale

In Chapter 4 a novel method, developed in close collaboration with REUM, for measuring
for the first time the current density distribution in PEFC with unique spatial resolution
smaller than the channel/rib scale of the flow field is introduced. The electron conductors
in a plane perpendicular to the channel direction are considered as two-dimensional resis¬
tors. Hence, the current density is obtained from the solution of Laplace’s equation with
the potentials at current collector and reaction layer as boundary conditions. Using ohmic
drop for calculating the local current, detailed knowledge of all resistances involved is of
prime importance. In particular, the contact resistance between gas diffusion layer (GDL)
and flow field rib, as well as GDL bulk conductivity, are strongly dependent on clamping
pressure. They represent a substantial amount of the total ohmic drop and therefore
require careful consideration. The method is applied successfully to a cell operated on
pure O₂ and air up to high current densities. The results show that electrical and ionic
resistances govern the current distribution at low current regimes, whereas mass transport
limitations locally hamper the current production at high loads. The method was devel-
oped in a joint effort with Reum with emphasis on the concept and data evaluation in this work.

1.3 Inhomogeneities on the Single Cell Level

At the single cell level, gradients occur essentially in the along-the-channel direction. Changing flow compositions along the flow path in technical fuel cells occur due to reactant consumption, product water formation, exchange of water between anode and cathode through the MEA, and heating of the coolant. Hence, inhomogeneous current production over the active area is very likely to occur. Other than at smaller scales phenomena due to the forced convective transport in the channels have to be taken into account. By this, the arrangement of fuel and oxidant streams in either co or counter flow becomes a major determinant.

System efficiency concerns limit the energetically costly gas humidification to an extent well below cell operation temperature and allow only for stoichiometric ratios that are not capable of completely removing product water as vapor. Liquid water is prone to impede the transport of the educts through the porous GDLs to the reaction layers and therefore to limit performance. Low air stoichiometrics in turn cause substantial current deterioration towards the air outlet. Along-the-channel coupling via the gas streams causes the local characteristics to superpose to yield the integral characteristics of the PEFC. Therefore, to gain a detailed understanding of the integral characteristics refined insight into local phenomena in the context of the entire cell is required. This can be attained both by modeling and experimental locally resolved mapping of cell properties, e.g. current density, resistances, gas composition, liquid content, to name the most important ones.

Both approaches feature their individual strength yet offer the most comprehension in conjunction. Models yield the distribution of properties in range and spatial resolution, which are experimentally difficult or currently not accessible. However, theory cannot substitute experimental diagnostics to the most comprehensive extent. Hence, this work develops and employs both modeling and experimental tools as well as combinations thereof for localized characterization of PEFC on the single cell level. Those tools are described in detail in Chapter 5. Detailed results of their application are given in Chapter 6.

Modelling and diagnostic methods on the single cell level.— A quasi-two-dimensional along-the-channel mass and heat transfer model for a proton exchange membrane fuel cell (PEFC) is described and validated against experimental current distribution data in Section 5.1. The model is formulated in a 1 + 1 dimensional manner, i.e. local transport phenomena are treated one-dimensional in through-plane direction and coupled in-plane by convective transport in the gas and coolant channels. Thus, a two-dimensional
slice running through the repetitive unit of a cell from the anode channel via membrane-electrode assembly (MEA) and cathode channel to the coolant channel and from inlet to outlet is modeled. Arbitrary flow arrangements of fuel, oxidant and coolant stream directions can be described. The model is used throughout most part of Chapter 6 for a variety of tasks.

For the experimental investigation of phenomena on the single cell level a cell of technical size that is capable of employing various advanced in-situ diagnostic methods is developed in Section 5.2. Applicable experimental diagnostics methods are localized current density measurement and in collaboration electrochemical impedance spectroscopy (with SCHNEIDER) and liquid water detection by neutron radiography (with KRAMER).

**Isothermal and non-isothermal cell operation.**— Sections 6.2 and 6.3 investigate the basic flow arrangements of co and counter flowing reactants. The influence of operating conditions such as feed gas humidities and stoichiometric ratios on the along-the-channel current density distribution is elucidated and the distinct underlying voltage loss mechanisms are identified. Furthermore, a complicated technical flow field is modeled by a combination of co- and counter-flow sub domains and compared with experimental current densities. Section 6.3 address the implications of in-plane temperature gradients that additionally occur in realistic operation due to limited coolant flow. Possibilities to beneficially counteract local drying at gas inlets and flooding in downstream regions by means of temperature inhomogeneities caused by cooling strategy are explored. Due to the serious impact of temperature on all processes in the PEFC both the relative direction of the coolant stream to the gas streams and its mass flow turns out to significantly affect the cell performance.

**Low frequency behaviour of air fed PEFC during EIS.**— In Section 6.5 the physical processes behind the evolution of low frequency features in electrochemical impedance spectra of air-fed PEFC are elucidated in a joint effort with SCHNEIDER. Oxygen concentration oscillations in the channels caused by local current perturbations are proved. They affect further on both subsequent local spectra downstream and the integral spectrum. Therewith, finite diffusion as commonly assumed in the literature could be disproved and the formation of both positive and negative resistive low frequency arcs comprehensively explained based on the uncovered physical processes.

**The impact of cell current on water management.**— Motivated by results in Section 6.2 issues of drying and liquid water formation in an air-fed PEFC in co flow mode at different current densities are addressed in Section 6.6. Therefore, current density measurement is simultaneously applied with localized electrochemical impedance spectroscopy and neutron radiography in cooperation with SCHNEIDER and KRAMER. To get deeper
1.4 Operation of PEFCs in Stacks

In Chapter 7 cell interaction phenomena in PEFC stacks that arise from inequalities between adjacent cells are investigated in detail experimentally and theoretically. For that, a specialized cell developed in Chapter 5 with advanced localized diagnostics was extended to a 2-cell stack. It was used to analyze the mechanism and effect of cell-to-cell coupling as a reaction on practically relevant variations in reactant feed flow and temperature. Contributions to overall and local voltage changes with respect to uniformly operated cells are scrutinized. A 2D model based on a commercial CFD-code, developed jointly with Sui (University of Victoria), was used to back and extend the experimental findings to more general cases. Furthermore, the experimental setup allowed for the first time to perform simultaneous localized electrochemical impedance spectroscopy beyond the single cell level, which was performed jointly with SCHNEIDER. Results show that virtually equal operation of the cells is essential to obtain meaningful integral spectra.
Seite Leer / Blank leaf
Chapter 2

Introduction

During the last one and a half decades fuel cells (FCs) have encountered a tremendous rise in the interest of research, industry, and society. The working principle is yet not a recent discovery but was found independently almost at the same time already in 1839 by Schönbein and Grove. However, with the invention of the electric generator by Jedlik and Siemens and the internal combustion engine by Otto and Diesel cheaper and technologically easier energy conversion technologies and energy carriers entered the market. Therefore, the further development of FCs with their need for sophisticated materials and high amounts of noble metal as a catalyst was abandoned.

In the 1960ies the FC gained again attention in space applications, where cost factors play a secondary role but relatively light weight, efficiency, and lack of emissions were more important. Since then continuous effort in the understanding of the electrochemical reaction, in material research, and in engineering aspects has been undertaken. This led to different kinds of FCs which are discriminated by the used electrolyte, fuel, or the range of operation temperature [1]. All FCs have in common that the chemical energy of fuel and oxidant is directly converted into electrical energy. Contrary to batteries and similar to internal combustion engines reactor and fuel storage are separated from each other. Unlike in thermal engines the efficiency of FCs is not limited by the Carnot factor. A further advantage is the scalability from μW to MW.

The intensified FC research since the early 1990ies has ecological reasons. Decreasing resources in fossil fuels and growing energy demand due to growing population call for new energy sources. At the same time awareness of pollution and growing CO₂ content of the atmosphere associated with the use of fossil energy carriers fostered the search for sustainable primary energy sources and less-polluting energy carriers and conversion technologies with high efficiencies along the entire pathway. Hydrogen is hereby considered to play a central role. This is because it is considered to producible from various renewable sources and to be converted efficiently and nearly pollution-free. Hydrogen production in a sustainable way may be either performed by electrolysis from CO₂ neutral electricity or
from biomass, to name just two. However, hydrogen is contrary to established liquid fossil fuels relatively costly to handle and to transport. High pressure storage or liquefaction require high energy amounts and elaborate transport. As an alternative the chemical bonding of hydrogen in liquids, e.g. in methanol, is under consideration which would allow for the use of existing infrastructure for its distribution and storage.

In addition to providing a sustainable energy carrier an efficient conversion technology is required. Fuel cells meet both the requirement for efficient and non-polluting conversion better than other established technologies. Particularly the polymer electrolyte fuel cell (PEFC) is well suited for transportation applications because of its low operation temperature and therefore quick start up. However, obstacles for commercialization from the early days are still not entirely solved. These are mainly the issues of cost, durability, and power density. To solve this material research as well as engineering, both supported by experimental diagnostics, is required.

2.1 Working Principle of the PEFC

The PEFC is alike all batteries an electrochemical reactor, which converts the chemical energy of the reactants directly into electrical energy\(^1\). Unlike other types of batteries, which combine reactor and educt/product reservoir the fuel cell serves only as the reactor with continuous supply of educts and removal of products. A schematic of setup and working principle the fuel cell is given in Fig. 2.1.

![Figure 2.1: Schematic of the fuel cell working principle and setup. H\(_2\) and air or oxygen are supplied through porous GDLs to the CL. Right: magnifications of the carbon/catalyst/ionomer agglomerates and the gas/electrolyte/catalyst interface, where the FC reactions are taking place.](image)

The main part of the PEFC is the membrane electrode assembly (MEA), which comprises of a proton conducting polymer electrolyte with porous electrodes attached to either side

\(^1\)The electrochemical fundamentals outlined in this section can also be found in textbooks concerning electrochemistry [2, 3, 4].
and adjacent electron conducting gas diffusion layers (GDLs) that serve as porous gas and water distributors and current conductors. Supply of educts as well as removal of product water and electrical connection of the GDLs is accomplished by flow field plates (FFP) comprising both flow channels for media transport and ribs for electrical contact and application of clamping force. Besides serving as proton conductor between anode and cathode the membrane is also electronic insulator and separator of the gases.

The electrochemical reactions take place in the porous electrodes (catalyst layers, CLs) where gas phase, electron conductors, and proton conductors are in close contact. This CL consists typically of a mixture of a highly dispersed precious metal catalyst supported on high surface area carbon and ionomer as binder. The two half-cell reactions are the anodic hydrogen oxidation reaction (IIOR)

$$\text{H}_2 \rightarrow 2 \text{H}^+ + 2e^- \quad (2.1)$$

and the cathodic oxygen reduction reaction (ORR)

$$\frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \quad (2.2)$$

yielding the total reaction

$$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} \quad (2.3)$$

Protons are transported through the membrane from anode to cathode, whereas electrons flow through the current drain and outer circuit.

**Reaction mechanisms.**— There are two mechanism of the HOR under discussion in the literature:

<table>
<thead>
<tr>
<th>TAFEL–VOLMER mechanism</th>
<th>HEYROVSKI–VOLMER mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}<em>2 \rightarrow 2 \text{H}</em>{\text{ads}}$</td>
<td>$\text{H}<em>2 \rightarrow \text{H}</em>{\text{ads}} + \text{H}^+ + e^-$</td>
</tr>
<tr>
<td>$2 \text{H}_{\text{ads}} \rightarrow 2 \text{H}^+ + 2e^-$</td>
<td>$\text{H}_{\text{ads}} \rightarrow \text{H}^+ + e^-$</td>
</tr>
</tbody>
</table>

With the TAFEL–VOLMER mechanism two adjacent coordination sites are required at a time at the Pt-surface, where the H$_2$ is dissociatively adsorbed. In the second step, the Volmer reaction, charge is transferred between H-atom and Pt. This is in contrast to the HEYROVSKI–VOLMER mechanism, where only one active Pt-site is involved. The two H-atoms are oxidized one after another. Which mechanism actually takes place with the HOR in the PEFC is still not clearly clarified.

The reduction of O$_2$ on Pt in acidic environments has been subject of research over decades. An overview of proposed reaction pathways is given in Fig. 2.2 (MARKOVIC et al. [5]).

The reduction of adsorbed O$_2$ may yield directly H$_2$O in a 4 electron step as given in Eq. 2.2. Alternatively adsorbed H$_2$O$_2$ may form as an intermediate species, which is
further oxidized to $\text{H}_2\text{O}$

$$
\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \longrightarrow \text{H}_2\text{O}_2 \quad (2.4)
$$

$$
\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \longrightarrow 2 \text{H}_2\text{O} \quad (2.5)
$$

These pathways stem from different adsorption mechanisms [3]. A possible reaction mechanism is given in Eq. 2.6, where the rate limiting step (denoted by *) is caused by the necessity for two adjacent active Pt-sites [6].

$$
\text{O}_2 + \text{Pt} \longrightarrow \text{Pt-O}_2 \quad (2.6)
$$

$$
\text{Pt-O}_2 + \text{H}^+ + \text{e}^- \longrightarrow \text{Pt-HO}_2
$$

$$
\text{Pt-HO}_2 + \text{Pt} \quad * \longrightarrow \text{Pt-OH + Pt-O}
$$

$$
\text{Pt-OH + Pt-O + 3 H + 3 e}^- \longrightarrow 2 \text{Pt} + 2 \text{H}_2\text{O}
$$

### 2.2 Thermodynamics

The energy change during a reversible electrochemical reaction, i.e. an infinitely small driving force is applied, is given by the change of Gibbs free energy, which is the charge passed ($nF$) times the reversible potential difference $E^0$

$$
\Delta G = -nFE^0 = \Delta H - T\Delta S \quad (2.7)
$$

with the superscript 0 denoting the equilibrium. Thermodynamic data for the fuel cell reactions at standard conditions are given in Table 2.1.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H^0$ [kJ mol$^{-1}$]</th>
<th>$\Delta S^0$ [J K$^{-1}$ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2$</td>
<td>0</td>
<td>130.68</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>0</td>
<td>205.14</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_f$</td>
<td>-285.83</td>
<td>69.91</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_g$</td>
<td>-241.82</td>
<td>188.83</td>
</tr>
</tbody>
</table>
The contact of the electrode with the electrolyte in presence of an electroactive species leads to the formation of an electrochemical double layer with a potential difference between the two phases. By convention the half cell potential difference is given by the difference of solid phase and electrolyte phase potential

\[ \Delta \phi^0 = \phi_s^0 - \phi_m^0 \]  

Therefrom, the equilibrium cell potential is obtained from

\[ E^0 = \Delta \phi_c^0 - \Delta \phi_e^0 \]  

The electrolyte phase potential \( \phi_m^0 \) is not measurable since every measuring device would include a solid/electrolyte interface. Furthermore, the absolute value of the potentials is not defined.

When the system is not under standard conditions the reversible cell potential is changing as the free energy \( \Delta G \) is both a function of temperature and reactant activity. It changes with temperature according to

\[ \frac{\partial E^0}{\partial T} = \frac{\Delta S}{zF} \quad \text{or} \quad E^0(T) = E^0(0) + \frac{1}{zF} \int_{T_0}^{T} \Delta S \, dT \]  

For the \( \text{H}_2/\text{O}_2 \) cell we get \( \frac{\partial E^0}{\partial T} = -0.85 \text{ mV/K} \). Its change with reactant partial pressure is given by

\[ \frac{\partial E^0}{\partial p} = -\frac{\Delta V}{zF} \quad \text{or} \quad E^0(p_i) = E^{0,\text{ref}} + \frac{RT}{zF} \ln \prod_i \left( \frac{p_i}{p^0} \right)^{\nu_i} \]  

with the exponent \( \nu_i = 1 \) for \( \text{H}_2 \) and \( \nu_i = 1/2 \) for \( \text{O}_2 \). The actually measurable open circuit voltage (OCV) of a fuel cell is due to reactant cross over lower than the value of \( \sim 1.23 \text{ V} \) as calculated with Eq. 2.10 and 2.11.

### 2.3 Kinetics

The relations given in the previous section were derived for the equilibrium state of the system with no net current flowing. Current results from the application of a driving force to the system, which is called overpotential or polarization

\[ \eta = U - E^0 \quad \text{or generally} \quad \eta = \phi - \phi^0 \]  

in the case of an electrochemical system. Herein \( U \) is the measurable voltage of the electrochemical cell. As there are several processes involved in the flow of current in a fuel cell, the overall needed driving force is a sum of different contributions

\[ U = E^0 + \eta_R - \eta_{\text{d.a}} + \eta_{\text{d.c}} \]
\( \eta_R \) is the ohmic drop in electron and proton conductors. The biggest contributions to this voltage drop are due to ionomer resistance in the membrane and the CLs, particularly the anodic one, where dehydration is likely to occur due to electro-osmotic drag at high current operation. The energetic barrier involved in the charge transfer between catalyst and electroactive species (cf. Eq. 2.1 to 2.6) is overcome by anodic and cathodic charge transfer polarization \( \eta_{ct,a} \) and \( \eta_{ct,c} \). Because of Eq. 2.8 \( \eta_{ct,a} \) and \( \eta_{ct,c} \) are positive and negative, respectively. An overview of the above potentials and overpotentials as well as on the associated current generation in the CL is given in Fig. 2.3.

**Figure 2.3:** Schematic of potentials, overpotentials and current densities in the PEFC. a) Solid phase potential \( \phi_s \) and membrane phase potential \( \phi_m \) on the cross section of the cell for open circuit (---, superscript 0) and loaded (—) conditions referenced vs. NHE. b) Cumulative overpotentials along the cross section. c) Local \( \eta_{kt} \) and transition between electronic and ionic current in the anodic CL.

Derived from the basic case of flat electrodes with a potential step between solid and ionomer phase the porous electrodes in PEFCs cause these two potentials to be coexistent in representative volumes of the CL (cf. Fig. 2.3a+b). Due to ohmic drop both in the solid and ionomer the local driving force \( \eta_{kt,local} \) is a function of position in the CL. Consequently, we define a volumetric current density \( J \) (unit \( \text{A/m}^3 \)) that balances electronic and protonic current source and sink, respectively.

\[
J = \nabla(\sigma_s \nabla \phi_s) = -\nabla(\sigma_m \nabla \phi_m) \quad \text{or} \quad \nabla(\sigma \nabla \phi) = 0 \quad (2.14)
\]

This implies charge conservation in the CL (cf. Fig. 2.3c). It is linked to superficial current density \( j \) by \( J = \sigma_s \nabla j_s \). In the following the most widely used model for the current-overpotential characteristic is described.

**The Butler-Volmer model for electrode kinetics.**— Consider an electrochemical half cell reaction

\[
\text{Ox} + ze^{-} \overset{k_f}{\underset{k_h}{\rightleftharpoons}} \text{Red} \quad (2.15)
\]

with both elementary reactions active at all times and the rates of the reactions being given by rate constant \( k \) times educt concentration. The rate constants are potential dependent.
The change of energy barrier for forward and backward reaction with potential change is interlinked by the transfer coefficient \( \alpha \) yielding

\[
\frac{\dot{k}_f}{k_f} = k^0 \exp\left((1 - \alpha)zF\eta_{ct}/RT\right)
\]

\[
\frac{\dot{k}_b}{k_b} = k^0 \exp\left(-\alpha zF\eta_{ct}/RT\right)
\]

The standard rate constant \( k^0 \) is the rate constant at equilibrium potential and is potential independent. It governs the balanced elementary reaction rates at equilibrium, which is expressed in terms of exchange current \( \dot{i}_0 \). By setting \( f = F/RT \) the effective current flowing outside equilibrium is given by the current-overpotential characteristic

\[
j = j_f - j_b = j^0 \left[ \frac{C_{Ox}}{C_{Ox}^0} e^{-\alpha f_{net}} - \frac{C_{Red}}{C_{Red}^0} e^{(1-\alpha)f_{net}} \right]
\]

which is also known as the BUTLER–VOLMER equation\(^2\). For large values of \( |\eta_{ct}| \gg \frac{RT}{zF} \), one of the bracketed terms in Eq. 2.18 becomes negligible. Large negative overpotentials give for example

\[
j = j^0 e^{-\alpha f_{net}} \quad \text{or} \quad \eta_{ct} = \frac{RT}{\alpha F} \ln j^0 - \frac{RT}{\alpha F} \ln j
\]

when additionally the surface concentration remains virtually unchanged. This approximate form of Eq. 2.18 is known as the TAFEL equation, which is particularly useful for determining \( j^0 \) and \( \alpha \) from a semilogarithmic plot.

The actual concentration \( C \) of the reactant at the reaction site is current dependent. Diffusive transport gives \( j \propto D/\delta(C^0 - C) \) with \( \delta \) being the diffusion layer thickness. By introducing a limiting current \( j_l \), where the reactant concentration at the reaction site is vanishing we arrive at

\[
\frac{j}{j^0} = \left(1 - \frac{j}{j_l}\right) e^{-\alpha f_{net}} \quad \text{or} \quad \eta_{ct} = \frac{RT}{\alpha zF} \ln \frac{j^0}{j_l} + \frac{RT}{\alpha F} \ln \frac{j_l - j}{j}
\]

in the TAFEL region.

The exchange current density \( j^0 \) is a measure for the electrochemical activity of the catalyst towards a reaction. On Pt, \( j^0 \approx 1 \times 10^{-3} \) A/cm\(^2\) for the HOR and \( j^0 \approx 1 \times 10^{-9} \) A/cm\(^2\) for the ORR. In the FC the cathode contributes therefore the main part of voltage losses. However, drying of the ionomer may also cause the anode to contribute a significant part of total polarization.

\(^2\)This description is usually used in terms of current per active catalyst surface \( j \). However, it may also be turned into superficial current density \( j = \dot{j}A_V/V_S \), where \( A_V \) is active surface per volume and \( V_S \) is CL volume per cell area.
Chapter 3

Mass Transfer in the Electrolyte and the Gas Diffusion Layer

Simulation is widely recognized in engineering to be an essential tool for improving technical devices by understanding the essential transport and transition phenomena and their interactions. One prerequisite for that are robust and efficient numerical tools for the solution of the encountered coupled systems of partial differential equations. The most important one, however, is the availability of physical and mathematical models for all processes involved. An excellent review on such models for transport phenomena in PEFCs is given by Weber and Newman [8]. Djilali provides an overview on challenges and opportunities with particular computational simulation [9]. A more general overview on the potential improvements to be gained by theory was given by Eikerling and coworkers [10]. The general consensus of these reviews is that for truly predictive simulations several challenges have to be tackled: (i) General models for transport in the membrane, (ii) two phase transport, (iii), models for the catalyst layer, and (iv) data for transport coefficients and for the validation of simulations with linked transport phenomena.

In this Chapter the issues of a membrane transport model (Section 3.1) and of the measurement of effective gas transport properties in GDL materials (Section 3.2) are addressed.

3.1 The Binary Friction Conductivity Model for Mass Transport in the Membrane

Fimrite and coworkers [11, 12] have developed a transport model for water and protons in ion exchange membranes based on the Binary Friction Model (BFM) described earlier by Kerkhof [13] for general mutually coupled transport of multiple species. The unknown parameters are obtained using a simplified form of the BFM for per-fluoro sul-
fonated membranes, termed the *Binary Friction Conductivity Model* (BFCM). The BFCM has shown to fit measured conductivity data more consistently over the entire range of water contents and temperatures than other conductivity models[12]. In this work the model was implemented for use in PEFC models based on a general purpose CFD-solver. Furthermore, the predicted transport characteristics of the BFCM are compared to other models available in the literature.

### 3.1.1 The Model and its implementation

The application of the Stefan-Maxwell equation on the mixture of immobile membrane backbone and mobile water and protons yields

$$ -\frac{1}{RT} (\nabla \mu_i)_{T} = \sum_{j=1}^{n} \frac{x_j}{D_{ij}} \left( \frac{N_i}{c_i} - \frac{N_j}{c_j} \right) + \frac{1}{D_{im}} \left( \frac{N_i}{c_i} \right). $$

The first term on the RHS describes the interaction between the movable species and the second one their additional resistance against motion due to the interaction between them and the membrane backbone. Thus, in the BFCM the membrane is considered as a fixed dust species that provides additional friction force on the species being transported.

In Eq. 3.1 $\mu_i$ is the electrochemical potential of species $i$, $D_{ij}$ are the Stefan-Maxwell diffusion coefficients and $D_{im}$ an inverse friction coefficient between the membrane and a given species. Figure 3.1 provides an overview on the related interactions and driving forces.

![Figure 3.1: Schematic representation of driving forces and friction coefficients acting between hydrated proton and water and between them and the membrane backbone.](image)

The electrochemical potential

$$ (\nabla \mu_i)_{T} = RT \left( \ln \frac{x_i}{x_{eq}} + \ln \gamma_{i} \right) + V_i \nabla p + z_i F \nabla \phi_m $$

serves as driving force for the transport of species $i$. Herein, $x_i$ are the mole fractions of the species and $\phi_m$ the membrane phase potential. By neglecting the gradients in the activity coefficient $\gamma$ and the pressure $p$ the transport equations for water and protons may be rewritten in the form

$$ -C \left[ \begin{array}{c} \nabla x_p + \frac{F}{RT} \nabla \phi_m \\ \nabla x_w \end{array} \right] = \left[ \begin{array}{ccc} x_w & 1 & -x_p \\ \frac{x_w}{D_{12}} & \frac{1}{D_{1m}} & \frac{x_p}{D_{12}} \\ \frac{1}{D_{12}} & \frac{x_w}{D_{12}} + \frac{1}{D_{2m}} \end{array} \right] \left[ \begin{array}{c} N_p \\ N_w \end{array} \right] $$

(3.3)
The conservation equations yield with \(-\nabla N_i = S_i = 0\) as

\[
-\nabla \cdot C \begin{bmatrix} D_{pp} & D_{pw} \\ D_{wp} & D_{ww} \end{bmatrix} \begin{bmatrix} \nabla \phi_m \\ \nabla \lambda \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}
\]

(3.4)

The transport coefficients \(C \cdot D\) are given in Table 3.1 (p. 20). They are obtained by substituting the \(x_i\) by their dependence on the water content \(\lambda\). In Fig. 3.2a the \(C \cdot D\) plotted against \(\lambda\).

The parameters \(D_{12}, D_{1m}, \text{ and } D_{2m}\) cannot be obtained from the literature and are therefore subject to fitting to experimental data. Membrane conductivity as a function of water content and temperature is the most thoroughly investigated transport process in the membrane and is therefore used to fit these values using

\[
\sigma = F \cdot C \cdot D_{pp}
\]

(3.5)

That is, the coefficient \(C \cdot D_{pp}\) governs proton transport without humidity gradients. As all other coefficients \(C \cdot D\) are also functions of these fitted parameters water transport as well as the associated change are described by parameters fitted on pure proton transport. The membrane conductivity \(\sigma\) calculated from \(D_{pp}\) (Eq. 3.5) with the fitted parameters is drawn for different temperatures in Fig. 3.2b.

The conservation equation Eq. 3.4 is solved using the user programmable capabilities of the commercial CFD-package CFD-ACE' (CFD Research Company, Huntsville, USA). Besides solving predefined conservation equations (momentum, enthalpy, mass, ...) the generic conservation equation

\[
\frac{\partial \rho \Phi}{\partial t} + \nabla \rho \mathbf{u} \Phi = \nabla (\Gamma \nabla \Phi) + S_{\Phi}
\]

(3.6)

for the quantity \(\Phi\) may be solved and coupled to the other quantities. For modelling the fuel cell Eq. 3.6 is applied for the ionic potential \(\phi_m\), the electronic potential \(\phi_e\), and the membrane water content \(\lambda\). The transient and convective term is in either case zero.

![Figure 3.2: (a) Dependence of the transport coefficients \(C \cdot D_{ij}\) on the membrane humidity at 343 K and (b) the conductivity as defined by Eq. 3.5 as a function of humidity for various temperatures.](image-url)
Table 3.1: Parameters of the BFCM and relations for coupled transport phenomena in the MEA.

<table>
<thead>
<tr>
<th>Parameters of the membrane model</th>
<th>Value</th>
<th>Other relations</th>
<th>Value</th>
</tr>
</thead>
</table>
| \( c_i \) | \( 1/V_2 \) | \( \lambda \sum_{i=0}^{3} k_i \cdot a_i^{L_i}; k_i = a_i \cdot \exp \left[ b_i \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right] \) | \[
\begin{pmatrix}
0.043 \\
17.8 \\
-39.9 \\
36.0
\end{pmatrix}
\begin{pmatrix}
3382 \\
-616 \\
-1024 \\
-1046
\end{pmatrix}
\] |
| \( D_{30}^{\text{ref}} \) | \( 6.5 \times 10^{-9} \) | | \( V_m \) | \( 537 \times 10^{-6} \) |
| \( D_{1m}^{\text{ref}} \) | \( D_{30}^{\text{ref}} \cdot \exp \left( 1196 \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right) \) | | \( V_w \) | \( 18 \times 10^{-6} \) |
| \( D_{2m}^{\text{ref}} \) | \( A_1^{\lambda/4} \cdot D_{1m}^{\text{ref}} \) | | \( q \) | \( 1.5 \) |
| \( D_{3m}^{\text{ref}} \) | \( A_2^{\lambda/4} \cdot D_{2m}^{\text{ref}} \) | | \( s \) | \( 1.2 \) |
| \( D_{12} \) | \( A_3^{\lambda/4} \cdot D_{1m}^{\text{ref}} \) | | \( C \) | \( 30000 \) |
| \( c_i (\varepsilon - \varepsilon_0) \) | \( \frac{1}{1 + A \cdot w_{\text{pw}}} \) | | \( \tau \) | \( 7 \) |
| | \( \frac{1}{D_{12} D_{1m}} + \frac{\lambda - \omega_{\text{pw}}}{D_{12} D_{2m}} + \frac{1 + \lambda - \omega_{\text{pw}}}{D_{1m} D_{2m}} \) | | \( \xi \) | \( 1 \) |
| \( D_{pp} \) | \( \frac{F}{RT} \left( \frac{1}{D_{12}} + \frac{1 + \lambda - \omega_{\text{pw}}}{D_{2m}} \right) \) | | \( D_{\text{ref}} \) | \( D_{\text{ref}}^{-\frac{\lambda}{\tau}} \) |
| \( D_{pw} \) | \( \frac{-1}{D_{2m}} \) | | \( d_a \) | \( 3 \times 10^{-4} \) |
| \( D_{wp} \) | \( \frac{F \cdot \lambda - \omega_{\text{pw}}}{RT \cdot D_{12}} \) | | \( d_c \) | \( 3 \times 10^{-1} \) |
| \( D_{wmc} \) | \( \frac{1}{D_{1m}} \) | | \( d_m \) | \( 6 \times 10^{-5} \) |
| \( \varepsilon \) | \( \lambda \cdot \left( \frac{V_m}{V_w} + \lambda \right)^{-1} \) | | \( \lambda_{\text{min}} \) | \( 1.65 \) |
| \( \varepsilon_0 \) | \( \lambda_{\text{min}} \cdot \left( \frac{V_m}{V_w} + \lambda_{\text{min}} \right)^{-1} \) | | \( j_n \) | \( 0.0216 \cdot \exp \left[ 8895 \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right] \) |
| \( \lambda_{\text{min}} \) | \( 1.65 \) | | \( j_i \) | \( 7.2 \times 10^4 \) |
| \( T_{\text{ref}} \) | \( 303 \) | | \( k_c \) | \( 5 \) |
| | | | \( p_{\text{ref}} \) | \( 1.0 \times 10^5 \) |
3.1. The Binary Friction Conductivity Model for Mass Transport in the Membrane

coupling terms in the membrane transport model associated with the off-diagonal terms in Eq. 3.4 are treated as source terms for the respective conserved quantity. Since coefficients $C \cdot D_{pw}$ and $C \cdot D_{wp}$ are both humidity and temperature dependent their partial derivatives have to be incorporated according to

$$
\nabla (D_{pp} \nabla \lambda) = C \cdot D_{pw} \nabla^2 \lambda + \left( \frac{\partial (C \cdot D_{pw})}{\partial \lambda} \nabla \lambda + \frac{\partial (C \cdot D_{pw})}{\partial T} \nabla T \right) \nabla \lambda 
$$

$$
\nabla (D_{ww} \nabla \phi_m) = C \cdot D_{wp} \nabla^2 \phi_m + \left( \frac{\partial (C \cdot D_{wp})}{\partial \lambda} \nabla \lambda + \frac{\partial (C \cdot D_{wp})}{\partial T} \nabla T \right) \nabla \phi_m
$$

where the RHS corresponds to $S_B$ in Eq. 3.6.

Fig. 3.3 shows the solution of the two quantities and the contributions of the two components on the total flow for given boundary conditions of potential and humidity. As Eq. 3.4 is source free in the membrane the total flux is uniform throughout the membrane thickness. The solution of the coupled transport equations behaves like a convection-diffusion equation. This becomes clearer in Fig. 3.4, where the humidity profiles in Nafion 112 and 117 are given for constant humidity boundaries and different proton currents are given.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3_3.png}
\caption{Solutions for (a) $\phi_m$ and (b) $\lambda$ in a pure membrane with fixed Dirichlet-type boundary conditions and the partial fluxes in the potential and humidity gradient for (c) protons and (d) water.}
\end{figure}

3.1.2 Application of the BFCM to the electrochemical unit

Proton and water flux are constant throughout the membrane (cf. Fig. 3.3). However, charge and mass conservation in catalyst layer ($- \sum \nabla N_i = 0$) imposes the proton flux
to be transformed into electron flux by the electrochemical reaction and the water flux in the membrane to be transformed into vapor or liquid flux in the void. In either case the driving force for the exchange is the non equilibrium of the species between the two involved phases. The exchange flux appears as source term in the respective conservation equation.

Charge transfer is governed by the Butler Volmer equation with the charge transfer over-voltage η_{ct} = φ_s - φ_m as driving force regarding to

\[ S_p \propto φ_s - φ_m \]  \hspace{1cm} (3.9)

Exchange of water takes place due to differences in the equilibrium membrane humidification λ(x_w, T) given by the sorption isotherm (cf. Table 3.1) and the actual membrane humidity λ_m.

\[ S_w \propto λ(x_w, T) - λ \]  \hspace{1cm} (3.10)

In order to keep the membrane in quasi-equilibrium with the adjoining gas phase a sufficiently big proportionality coefficient is used. The source terms for the quantities that are coupled with the species in the membrane (electron transport, diffusion of the gas species H_2, O_2, N_2, H_2O, continuity, enthalpy) are obtained from Eq. 3.9 and 3.10 with the appropriate signs and by considering the stoichiometrics. Heat sources are the Joule heating and the reversible and irreversible contributions in the electrochemical reaction. The properties of the reaction layer in terms of active surface and phase compositions are obtained from a percolation type model [14].

The coupling is tested in a 2D along-the-channel model as schematically shown in Fig. 3.5. Figure 3.6 shows results for fully humidified air and partly humidified H_2 and a total polarization of -0.2 V on the cross section of the domain in Fig. 3.5. Similar to Fig. 3.3 the solution for φ_m, φ_s, and λ in the catalyst layers and the membrane and the respective partial fluxes are drawn.

Inside the catalyst layers the fluxes transform from one phase into the other (N_p ⇔ N_e and N_{w,m} ⇔ N_{w,v}). For better clarity this is only drawn for charges in Fig. 3.6c. Note that
Figure 3.5: Schematic of the 2D test geometry for coupling the membrane model to the other transport phenomena in the MEA and the flow field channels. Channel length is 1 cm and compressed in this figure, whereas the thicknesses of the layers are in scale.

for the case of the potentials only overpotentials due to charge transport in conductors and charge transfer in the electrochemical reaction arc drawn, but not absolute potentials.

Figure 3.6: Solution for (a) $\phi_m$ and $\phi_s$ and (b) $\lambda$ in the entire cross section of the MEA. (c) Total and partial charge flux and (d) total and partial water flux. Total fluxes are composed of contributions driven by $\nabla\phi_m$ and $\nabla\lambda$.

Comparison with other Membrane Models in the Literature

The structure of the conservation equation Eq. 3.4 is also found in other membrane models in the literature [15, 16, 17]. With the implemented code for solving the BFCM Eq. 3.4 transport models of the form

$$
\begin{bmatrix}
N_1 \\
N_2
\end{bmatrix}
= 
\begin{bmatrix}
-\Gamma_{11} & -\Gamma_{12} \\
-\Gamma_{21} & -\Gamma_{22}
\end{bmatrix}
\begin{bmatrix}
\nabla\Phi_1 \\
\nabla\Phi_2
\end{bmatrix}
$$

(3.11)
may be solved without substantial changes in the code. Same examples for such models in comparison with the BFCM are given in Table 3.2.

Table 3.2: Comparison of the general form of the transport coefficients between BFCM and some membrane models in the literature. All coefficients refer to molar fluxes.

<table>
<thead>
<tr>
<th>Model</th>
<th>( \Phi_1, \Phi_2 )</th>
<th>( \Gamma_{11} )</th>
<th>( \Gamma_{12} )</th>
<th>( \Gamma_{21} )</th>
<th>( \Gamma_{22} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFCM</td>
<td>( \phi_m, \lambda )</td>
<td>( c \cdot D_{pp} )</td>
<td>( c \cdot D_{pw} )</td>
<td>( c \cdot D_{wp} )</td>
<td>( c \cdot D_{ww} )</td>
</tr>
<tr>
<td>Weber [15]</td>
<td>( \phi_m, \mu_w )</td>
<td>( \sigma/F )</td>
<td>( \sigma \cdot n_d/F^2 )</td>
<td>( \sigma \cdot n_d/F )</td>
<td>( \alpha + \sigma \cdot n_d^2/F^2 )</td>
</tr>
<tr>
<td>Eikerling [16]</td>
<td>( \phi_m, \rho' )</td>
<td>( \sigma/F )</td>
<td>( \sigma \cdot n_d/F )</td>
<td>( \sigma \cdot n_d/F )</td>
<td>( c_w \cdot k/\mu )</td>
</tr>
<tr>
<td>Springer [17]</td>
<td>( \phi_m, \lambda )</td>
<td>( \sigma/F )</td>
<td>( \sigma \cdot n_d/F )</td>
<td>( \rho \cdot D/M_w )</td>
<td>( )</td>
</tr>
</tbody>
</table>

All those models have in common to describe electro-osmosis, whereas water transport is captured using different mechanisms and therefore driving forces. The transport coefficients are obtained from various mechanistic considerations and are fitted to experiments. In particular the first two approaches are due to the mechanistic derivation both applicable to membranes in equilibrium with liquid water and vapour. Weber's model incorporates already the transition between these two extrema within the membrane by blending the respective applicable coefficients. This is not yet realized for the BFCM.

Transport coefficients from BFCM are compared with the most widely used model by Springer et al. [17] in Fig. 3.7. The BFCM has revealed to fit experimentally observed conductivities remarkably well both as function of humidity and temperature [12]. Significant differences occur with predicted electro-osmotic drag coefficients \( n_d \) (Fig. 3.7b) and the water transport coefficient \( D_{ww} \) (Fig. 3.7c).

![Figure 3.7: Comparison of transport coefficients \( \sigma \), \( n_d \), and \( D_{ww} \) predicted by the BFCM and by Springer's model at 343K.](image)

With the differences in transport coefficients considerable differences in terms of the associated transport phenomena predicted by the models are found as shown in Fig. 3.8. This figure compares voltage loss, water flux, and effective drag calculated with the two models. The higher values for \( n_d \) and \( D_{ww} \) in the BFCM result in increased positive water flux (towards cathode) with high anode humidity and even slightly negative flux at low
anode humidity as compared to the Springer model (Fig. 3.8a). Correspondingly, the associated voltage drop shows differences due to differing humidity profile in the membrane and conductivities (Fig. 3.7a). Effective drag results from the superposition of osmotic and diffusive transport. Higher $D_{w}$ in the BFCM results in more negative fluxes at low currents, whereas higher positive fluxes are predicted at high current due to the higher value for $n_{d}$.

**Figure 3.8:** Comparison of the BFCM and Springer's model. (a) Voltage loss at 10000 $\Lambda$/m$^2$ and water flux with a constant humidity of $\lambda = 14$ at the cathode side and variable anodic humidity. (b) The effective drag coefficient as a function of current density with a constant cathode humidity of $\lambda = 14$ and either $\lambda = 10$ or $\lambda = 4$ at the anode. $T = 343$ K.
3.2 Gas Transport Properties of Gas Diffusion Layer Materials

One key parameter for fuel cell models is the effective diffusivity $D_{\text{eff}}$ of porous transport media when they are treated as macroscopically homogeneous materials. That is, the length scale of the pores is well below the resolution of the model. Although being vital for the simulation of gaseous mass transport, no measured data for $D_{\text{eff}}$ in gas diffusion media in PEFC are available. Available relations between $D_{\text{eff}}$ and porosity were theoretically derived for packed spheres, multi-length scale particles, and random fibrous media [19, 20]. Parameters of those models were fit against $D_{\text{eff}}$ obtained from numerical simulations of various model geometries [21, 22]. However, experimental validation is only available for particle based materials, but not for fibrous media. Therefore, a method that allows measuring this quantity both as a function of compression and direction is developed in collaboration with KRAMER and FLÜCKIGER in this section.

The effective diffusivity $D_{\text{eff}}$ in porous media is correlated to the free stream diffusivity $D$ by normalized functions of porosity $\varepsilon$ and liquid saturation $s$

$$D_{\text{eff}} = D \cdot f(\varepsilon)g(s), \quad \varepsilon = V_p/V, \quad s = V_l/V_p$$ \hspace{1cm} (3.12)

The function $g(s)$ accounts for pore blocking due to liquid phase and has been reported as $g(s) = (1 - s)^m$ with $m \leq 4$ [21, 22].

In this work we focus on the dry medium effective diffusivity, which is determined by $f(\varepsilon)$. Most generally the correction may be expressed by scaling the free stream diffusivity with the porosity and a tortuosity $\tau \geq 1$ that accounts for a prolonged diffusion path length through the porous medium

$$D_{\text{eff}} = D \cdot \frac{\varepsilon}{\tau}$$ \hspace{1cm} (3.13)

Herein, $\tau$ incorporates all structural aspects such as shape and arrangement of the solid. Generally it increases with decreasing porosity and may also incorporate $g(s)$. In the literature on transport in porous media various functions $f(\varepsilon)$ are used to capture the diffusion hindrance due to the solid fraction of the porous medium. Effective medium theory leads to

$$D_{\text{eff}} = D \cdot \varepsilon^m$$ \hspace{1cm} (3.14)

with $m = 1.5$ for packed spherical particles, which is also known as Bruggeman-correction and most commonly used in fuel cell models\(^2\). Other than that

$$D_{\text{eff}} = D \cdot [1 - (1 - \varepsilon)^m]$$ \hspace{1cm} (3.15)

\(^1\)The method shown here is to be published in:
\(^2\)Relations Eq. 3.13 and Eq. 3.14 may be transformed into each other by $m = 1 - \log \tau / \log \varepsilon$ or $\tau = \varepsilon^{1-m}$
was proposed by KAVIANY [19] with $m = 0.5$ and $m$ later on re-fitted to 2D model solutions of multi-length scale particle based structures (MEZEDUR et al. [21]). For random fibrous porous media a percolation-type correlation is suggested by TOMATAKIS et al. [20] with

$$D_{\text{eff}} = D \cdot \varepsilon \left(\frac{\varepsilon - \varepsilon_p}{1 - \varepsilon_p}\right)^m$$  \hspace{1cm} (3.16)

with an empirical constant $m$ and the percolation threshold porosity $\varepsilon_p$. For for randomly oriented fibers in multiple layers they are reported as $\varepsilon_p = 0.11$ and $m = 0.521$ and $m = 0.785$, for in-plane and through-plane direction, respectively.

### 3.2.1 Measuring the effective relative diffusivity of GDLs

For the measurement of diffusivities in porous media various methods that employ concentration sensors are reported. E.g. the diffusion limited flux of oxygen through the medium towards an O$_2$ sensor similar to a lambda probe was used [22]. Although having the advantage of directness, the difficulty of elaborate measurement equipment is encountered. As an alternative to diffusion experiments the physical analogy of Fick’s law of diffusion and the migration term in the Nernst-Planck equation may be used:

$$n = -D \cdot \text{grad}(c) \quad \text{and} \quad n = -\sigma \cdot \text{grad}(\phi)$$  \hspace{1cm} (3.17)

That is, the effective ionic conductivity of a porous sample soaked with electrolyte may be used to determine the effective conductivity relative to free electrolyte conductivity, which is identical to $D_{\text{eff}}/D$. The apparatus used for measuring the conductivity of an electrolyte volume with the GDL sample inserted is shown in Fig. 3.9a for the in-plane direction. The electrolyte soaked sample is compressed in a controlled way between two flat plates and divides two electrolyte reservoirs. Current is applied by two Pt electrodes placed in those reservoirs and the voltage drop measured using Pt wires in a 4-point setup. Two molar H$_2$SO$_4$ is used as the electrolyte. For measuring effective conductivity in the through-plane direction the sample is compressed between stiff sintered porous glass plates. The two electrolyte reservoirs are divided through this sandwich. Voltage drop is sensed between the outer sides of the glass plates. An electrochemical impedance device (IM6c, Zahner, Germany) was used for current perturbation and frequency response analysis.

The Nernst-Planck equation describes the transport of a charged species in an electrolyte generally to be composed of a migration, diffusion, and convection term with gradients in electric potential, concentration and pressure as driving forces. In order to justify exclusive consideration of the migration term, concentration gradients and convection must be avoided. Therefore, electrolyte conductivity is best measured by high frequency impedance with small current amplitude. However, when applying this to electrolytes in conductive porous materials current is capacitively coupled into the conductor. This phenomenon is
known from porous electrodes and may be described by a transition line equivalent circuit [23]. The applicable equivalent circuit of the setup is shown in Fig. 3.9b together with a typical impedance spectrum obtained with the above apparatus. At high frequency (to the left end) current is capacitively coupled into the by far better conducting GDL, which bridges the electrolyte resistance \( \sum R_i \). Therewith, the free space electrolyte conductivity is inherently measured with \( R_0 \). At quasi-dc frequencies both the electrolyte resistance in the free space and the GDL sums up. The effective relative diffusivity \( D_{\text{eff}} / D = \varepsilon / \tau = f \) results from the conductivities associated with \( R_0 \) and \( \sum R_i \). The measurements are performed in a frequency range from 10 kHz to 100 mHz.

**Figure 3.9:** (a) Apparatus for measuring effective relative electrolyte conductivity in in-plane direction with controlled sample compression. (b) A typical spectrum obtained with (a) and the applicable equivalent circuit.

Figure 3.10 shows results for Toray TPGH-060 with 40 wt% PTFE loading in in-plane direction as a function of relative thickness \( d_r = d/d^0 \) and porosity\(^3\). All data are compared with the aforementioned literature models. Data show roughly linear decrease of \( f \) vs. \( d/d^0 \) with an intersection at \( d_r = 1 - \varepsilon^0 \), where the void space vanishes. That is, there was no significant enclosed pore volume that causes a percolation threshold above a thickness of \( d_r = 1 - \varepsilon^0 \). This linear decrease may be expressed as

\[
f(d_r) = (d_r - 1 + \varepsilon^0) \frac{f^0}{\varepsilon^0}
\]

(3.18)

where \( f^0 \) is the value of the uncompressed sample. This linear fit is also transformed into the plots of \( f \) vs. \( \varepsilon \) and \( \tau \) vs. \( d/d^0 \) (Fig. 3.10b+c).

The measured data show significantly lower diffusivities than predicted by the literature models. Solely the model of Mezudur approaches the data of the uncompressed GDL. With further compression the tortuosity tends up to 3.4 at \( \sim 40\% \) relative thickness, which is double the highest model prediction. This divergence may be explained by films the PTFE forms at the junctions of the fibers. Although cutting the porosity very marginally, they may have strong impact on the diffusion pathlength.

\(^3\) The porosity of a compressed sample is obtained from \( \varepsilon(d_r) = (d_r - 1 + \varepsilon^0)/d_r \) with \( \varepsilon^0 \) being the porosity of the uncompressed sample.
3.2. Gas Transport Properties of Gas Diffusion Layer Materials

Figure 3.10: Measured results for Toray TPGH-060 in in-plane direction compared with literature models. (a) Effective relative diffusivity \( \frac{D^\text{eff}}{D} \) vs. porosity. (b) \( \frac{D^\text{eff}}{D} \) vs. relative thickness \( \frac{d}{d^0} \). (c) Tortuosity \( \tau \) vs. \( \frac{d}{d^0} \). See text for linear fit of measured data.

The impact of the obtained effective diffusivities obtained above on mass transfer is shown in Fig. 3.11. Superficial diffusive fluxes at a constant concentration difference between the opposed sides of the variously compressed GDL are normalized to the respective free space diffusion flux. Diffusion flux is given as

\[
n = -A \cdot D \cdot f \cdot \frac{\Delta C}{\Delta x} \tag{3.19}
\]

where \( A \) is the cross section area normal to the respective direction and \( x \) parallel to its normal vector. Hence, the normalized fluxes are given by

\[
n/n^0 = f \cdot \frac{d}{d^0} \quad \text{and} \quad n/n^0 = f \cdot \frac{d^0}{d} \tag{3.20}
\]

for the in-plane and through-plane direction, respectively. The upper limit for diffusion flux through a compressible porous medium is given with a tortuosity of 1 and therefore \( f = \varepsilon \) as shown for comparison in Fig. 3.11.

Compression of the GDL reduces the in-plane flux in either case since the cross section area decreases. A different behaviour may be observed for through-plane flux, since the layer...
thickness decreases along with porosity. This results for moderate increase of tortuosity with compression as predicted by the models in a facilitated diffusion through the GDL. Increased fluxes are predicted down to a relative thickness of 0.5 with Tomataki's model and 0.35 with the Mezudur model, whereas the measurements show increased hindrance with compression. Note that measurements in Fig. 3.11b are obtained in in-plane direction. However, tortuosities in through-plane direction are expected to be higher than in in-plane direction due to the layered structure of the GDL. Therefore, the shown measured trend in Fig. 3.11 is likely to overestimate the true flux.

3.3 Concluding Remarks

In Section 3.1 a generalized transport model (BFCM) developed by Fimrite and coworkers for charge and water transport in ion exchange membranes was implemented for use with a general purpose CFD solver. The model is promising for use in CFD-based PEFC model since it provided more consistent fit to experimental data over the entire range of water contents and relevant temperatures. An up to date percolation type model from the literature was used to obtain the properties of the reaction layer in terms of active surface and phase compositions. Therewith, the membrane model was embedded into a model for the entire MEA cross section. Results have shown that practically applicable ionomer contents in the catalyst agglomerate cause significant ohmic drop across the CL even with high water contents. The transport characteristics of the BFCM were compared with the so far most widely used Springter model. Significant differences in terms of voltage drop and water transport suggest considerable influence on simulations of entire cells depending on the used model.

A method was developed in Section 3.2 that allows measuring effective relative diffusivities of dry GDL materials both as a function of compression and direction with reasonable experimental effort. First results suggest that models available in the literature underestimate the tortuosity factors of usual GDL materials. Measurements with a variety of materials and PTFE loadings both in in-plane and through-plane direction are subject to work in progress.
Chapter 4

Current Density Distribution on the Scale of Flow Field Channels and Ribs

"There's Plenty of Room at the Bottom."
Richard P. Feynman, classic 1959 talk

The most crucial contributor to voltage losses in PEFC remains to be the cathodic CL. Already poor ORR kinetics is additionally hampered by transfer limitations of protons and reactants in the CL. Extensive experimental [26, 27, 28] and theoretical studies have been performed to optimize the composition of the CL in terms of void, carbon, and ionomer fraction and the morphology, and to rationalize the polarization behaviour [29, 14, 30]. A prerequisite, however, for the function of the CL is an optimized supply with reactants, removal of product and heat, and electrical connection to the current collector. All of this is governed by the interplay of GDL, channels, and ribs.

Up to now localized investigations of the current density on the channel and rib scale reported in the literature have been solely theoretical [31, 32, 33, 34, 35, 36, 37, 38, 39, 40]. They treat effects leading to inhomogeneous current distribution with varying comprehensiveness. The level ranges from exclusive consideration of oxygen transport [31] to multi-physics simulations also including liquid water formation, heat transfer, and electron transport. Essentially, all authors find diminished current production under the ribs in the high current density range due to oxygen starvation, which can be partially overcome by forced convection. When electron transport is accounted for an inverse distribution with the minimum under the channel is found in the low current range due to prolonged electron

\footnote{Results shown in this chapter were presented in:}

pathways there. However, uncertainties in the mathematical description of the occurring phenomena and physical properties are common shortcomings to all of these investigations. E.g. none of the mentioned authors accounts for the highly anisotropic behavior of the gas diffusion layer (GDL) in terms of electrical conductivity and permeability.

The mentioned theoretical work brought already some basic insight into possible current distributions between channels and ribs and underlying factors. In summary, they show that even small changes of properties or phenomena involved may affect the obtained distribution significantly. However, none of the simulations is verified beyond matching trends in the integral polarization curves as compared to experimental ones. This is in contrast to simulated current distributions on the full cell level, where localized measurements are used to validate the predictions and to unveil weaknesses in the model leading to more useful simulations [41, 42, 43, 44]. As the current distribution is very sensitive to a multitude of partly weakly understood phenomena these simulation results are therefore of very limited reliability.

In particular the link between electrochemical performance, the behaviour of liquid water in porous media, and the material properties is still poorly understood. Even more, there is no clear link between electrochemical performance and liquid water hold up in the GDL. Using neutron radiography ZHANG et al. [45] have compared the in-situ liquid water content of certain GDL materials with their performance. They found on the one hand very different behavior in terms of liquid water accumulation and its partitioning between areas under the channels and the ribs. On the other hand even substantial amounts of liquid phase in the GDL do not necessarily impede the integral cell performance. Without having information on the current generation under channel and rib general conclusions on the impact of liquid on the mass transfer remain difficult. This finding is also supported by the fact that the performance of cells operated on pure oxygen seemed to be essentially decoupled from the liquid content. To get more detailed insight, influence of liquid water on mass transport and the local cell performance even more sophisticated experiments are required. This was first done by SCHNEIDER and KRAMER [46] by combining liquid water detection with localized impedance spectroscopy.

Altogether, neither the mentioned simulations nor the experiments can so far provide a clear view on the dependence of the cell performance on phenomena that occur on the scale of channels and ribs. But they do clearly point out that this scale is of prime importance for the understanding of substantial losses in the high current operation. In particular a current measurement method with sufficient spatial resolution is required, which has not been available so far.

In this chapter first, possibilities to expand established methods for localized current measurement to the desired resolution are discussed, which leads to the demand for the novel measurement principle presented here. Second, experimental issues are treated in detail. Third, the algorithms to eventually obtain the current distribution are discussed compre-
hensively. Finally results from PEFC investigations are given, mainly to demonstrate the validity and power of the method. The method is applied successfully to a cell operated on pure O₂ and air up to high current densities. The results show that electrical and ionic resistances govern the current distribution at low current regimes, whereas mass transport limitations locally hamper the current production at high loads.

### 4.1 Method of Sub-Millimeter Resolved Current Measurement

#### 4.1.1 Concept

In the fuel cell literature numerous methods for localized current measurement with different levels of sophistication are reported [47, 48, 49, 50, 51, 52]. They may be divided into different groups. The first and most frequently used method is an in some sort segmented current drain where the current in the single branches is measured using shunt resistors or Hall-effect sensors. The degree of development ranges from first simple applications [47] to recently the most advanced setup that allows for simultaneous local impedance spectroscopy [51]. The resolution of this segmentation approaches is in the best case limited to the area from which a single rib collects current, i.e. the area covered by the rib and the half of the two adjacent channels as illustrated in Fig. 4.1. Furthermore, the use of partially catalyzed cells is proposed [47]. However, hardly any useful information can be drawn from such setups. A totally different way is gone by Haukr et al. [52] with magnetotomography that reconstructs the current distribution from its magnetic field in the ambiance of the cell. In contrast to all other methods this method is totally non-invasive and provides 3-dimensional current information. However, the spatial resolution is limited to centimeters and the time resolution to minutes owing to the scanning process.

![Figure 4.1: Schematic of the limitation of the segmentation approach in terms of spatial resolution. Inhomogeneities on the channel and rib scale are averaged over the minimum segment width, i.e. the repetitive unit.](image)

When attempting to obtain current density distributions with a resolution better than the size of the flow field channels and ribs all mentioned methods fail due to a lack of achievable
resolution. It would be thinkable, however, to modify two of these methods to get at least a rough idea what happens on this scale. First, a partly catalyzed electrode with catalyst alternately under channel and rib could be used. Due to the mutual interaction of channel and rib area in terms of mass and electron transfer in the fully catalyzed cell only falsified information on mass transfer can be drawn. Second, channel and rib area may be discriminated with a modified segmentation approach. Highly porous material in the channel would allow for segmented current drain both from channels and ribs. However, massive changes in the electric potential drop and in the mechanical pressure distribution have to be taken into account.

To overcome the limitations of the mentioned methods a novel measurement principle was considered that uses the voltage drop over the electronic conductors in the current drain, i.e. the GDL and the FFP. However, due to the relatively high conductivity of these components only minor voltage drops are expected. To assess the feasibility of this approach the simple experiment shown in Fig. 4.2 was realized. The current generated in the CL is simulated by a segmented conductor that allows for individual application of current at areas under channel ($i_{ch}$) and ribs ($i_{rib}$). The difference in voltage drop between channel ($U_{ch}$) and rib ($U_{rib}$) vs. FFP is plotted in Fig. 4.3b for cloth- and paper-type GDLs. Also the influence of pressure distribution under the channel is investigated by measuring the paper type GDL also with a filled channel, which reveals reduced voltage drop at the channel due to lower contact resistance there. Overall, the appearing differences in voltage drop are sufficient to be accurately measured and to discriminate channel and rib areas with the method developed in the following.

![Figure 4.2](image_url)

The limitations in resolution of the mentioned methods are overcome by the method presented in this chapter. Figure 4.3 illustrates its principle, where the electron conductors in a plane perpendicular to the membrane and the channel direction are considered as a 2-dimensional resistor. The potential drop between CL and current collector is measured with a resolution of a few measuring points per channel and rib width. Therefore, potential probes in the form of thin wires are placed along the channel direction side by side between CL and GDL. In order to justify a 2-dimensional treatment homogeneous operating conditions along the channel must be assured by excessive reactant flows. The
Figure 4.3: Schematic of the measurement principle that uses the potential drop over FFP and GDL for gaining information about the corresponding current distribution. The potential field is illustrated by means of iso-potential contours. Its value at the GDL-CL interface is probed using thin gold wires.

electronic current density field in GDL and FFP is obtained from the solution of Laplace's equation with the potentials at current collector and CL as boundary conditions. As the current density is indirectly obtained from the ohmic drop the precise knowledge of all resistances involved is of prime importance. In particular the strongly pressure dependent contact resistance between the GDL and the flow field rib causes a substantial fraction of the total ohmic drop and therefore requires careful consideration.

Figure 4.4 summarizes all steps involved in the measuring method. Besides the potential distribution measured at the CL, detailed material characterization is required to eventually gain the current density distribution. Both the bulk conductivity of the GDL and its contact resistance to the rib are pressure dependent. Therefore, the pressure distribution in the GDL bulk and the contact pressure to the rib are obtained from structural mechanics calculations using linear elasticity theory. Methods and results of respective material characterization in terms of electrical and mechanical properties are given in Section 4.1.5 (p. 43). Further physical and geometrical properties of the materials and the cell are given in Table 4.1. Details on the experimental setup for measuring the potential at the CL, the structural mechanics calculations, and the calculation of the current density field are given in the following sections.
Table 4.1: Geometrical and physical properties of the materials and the cell.

<table>
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<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>Channel width</td>
<td>$2 \times 10^{-3}$ m</td>
</tr>
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<td>Channel depth</td>
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</tr>
<tr>
<td>Channel length</td>
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<tr>
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<td>MPL in-plane conductivity, $\sigma_{xx}$</td>
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<td>MPL through-plane conductivity, $\sigma_{yy}$</td>
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</tr>
<tr>
<td>Plate conductivity, $\sigma$</td>
<td>$1.1 \times 10^5$ S/m</td>
</tr>
<tr>
<td>Young’s modulus diffusion layer$^1$, $E_x$</td>
<td>$5 \times 10^5$ MPa</td>
</tr>
<tr>
<td>Young’s modulus membrane$^2$, $E_2$</td>
<td>50 MPa</td>
</tr>
<tr>
<td>Young’s modulus plate material$^2$, $E_3$</td>
<td>30 MPa</td>
</tr>
<tr>
<td>Poisson’s ratio diffusion layer$^1$, $\nu_{xy}$</td>
<td>0.35</td>
</tr>
<tr>
<td>Poisson’s ratio plate material$^2$, $\nu_{xy}$</td>
<td>0.3</td>
</tr>
<tr>
<td>Friction coefficient plate-diffusion medium$^2$, $\mu$</td>
<td>0.2</td>
</tr>
</tbody>
</table>

$^1$Referring to the tensile strength.  
$^2$Assumed.

4.1.2 Cell design and potential measurement

Inhomogeneous operation in the along-the-channel direction of the technical fuel cells occurs due to reactant consumption, product water formation, exchange of water between anode and cathode through the MEA and heating of the coolant. Subject of the present method is the mapping of the current density in across-the-channel direction for conditions, which occur locally in the along-the-channel direction in technical cells. These local conditions are represented by the gas composition (H$_2$O$_2$ content, humidity, liquid content), cell temperature and current density. For this purpose a quasi-two-dimensional cell with virtually homogeneous conditions in the along-the-channel direction due to excessive reactant flows is used. Therefore, its advantageous to keep the channel length short, which
4.1. Method of Sub-Millimeter Resolved Current Measurement

Figure 4.5: Cross section scheme of the FFP and half MEA in the used test cell and the applied coordinate system. All measures are in millimeters. For clarity small items are not to scale.

facilitates at the same time the potential measurement.

Figure 4.5 shows the half cross section of the specialized test cell. Anodic and cathodic FFP are identical. The rather wide channel and rib width of 2 mm was chosen for demonstration purposes of the method in order to possibly get strong current density inhomogeneities. The cross section has two channels and therefore one inner rib and two outer ribs. It contains the repetitive unit of multichannel cells and enables furthermore for the discussion of different diffusion path lengths. With a channel length of 10 mm the cell has an active area of 1 cm².

The measurement of potentials with high spatial resolution in electrochemical cells may be accomplished using fine probes. In the case of liquid electrolytes usually Luggin-capillaries are used. In fuel cells with solid electrolyte fine gold wires may be used for the same purpose as shown first by Büchi and Scherer [55]. That way they investigated the transversal water profile in the membrane of a working fuel cell by sensing the ionic potential drop on discrete positions within the membrane thickness. Fine gold wires with 25 μm diameter are also used in the present work to probe the electronic potential at the interface of GDL and CL. The wires were placed with 0.5 mm spacing, this is four per channel and per rib, parallel along the channel. To assure parallel and accurate positioning the wires were fixed on a frame that surrounds the active area. In order to prevent perturbations the wires were electrically insulated outside the active area. This measurement was applied to the anodic flow field plate and GDL.

The flow fields were made from sintered carbon (Diabon NS 2, SGL Carbon). The used electrochemical components are Nafton 112 as the membrane with the CL applied to it and Toray TPGH-060 with micro porous layer (MPL) as GDL, all provided by umicore. The cell was operated on an in-house built test bench. Reactant feed was controlled by mass flow controllers (Bronkhorst) and humidified by passing it through heated water reservoirs whose temperature was assumed to equal the resulting gas dew point. The humidified gas was heated up to cell temperature and led to the cell through electrically heated tubes. The cell temperature was adjusted by electrical heating. Current was drawn with a galvanostat (Amel Instruments) and all potentials were measured with a multimeter type Hewlett-Packard 3468A.
4.1.3 Structural mechanics of the MEA

Since both the bulk conductivity of the GDL and its contact resistance to the rib are pressure dependent the respective pressure distribution is required to get the actual resistances in the assembled fuel cell from ex situ conductivity measurements. It is obtained from structural mechanics calculations. The GDL material shows both, non-linear and orthotropic mechanical properties. A comprehensive description of all phenomena involved with the compression of a complete MEA between the flow field ribs is an extremely expensive task. It would include very detailed material characterization as well as intricate computational procedures. These procedures can be facilitated by a linearization of the material properties without adding substantial error. The strong anisotropic stiffness is also still accounted for. Moreover, the numerical results remain an approximate solution when fluctuations in material properties on small scales occur.

The linear relations between the components of stress and the components of strain are expressed by Hooke’s law in the form

$$\sigma = D\varepsilon$$  \hspace{1cm} (4.1)

in absence of body forces and thermal strain [56]. In Eq. 4.1

$$\sigma = (\sigma_x, \sigma_y, \tau_{xy})^T$$  \hspace{1cm} (4.2)

denotes the stress vector with normal components $\sigma_i$ in i-direction and the shearing component $\tau_{xy}$.

$$\varepsilon = (\varepsilon_x, \varepsilon_y, \gamma_{xy})^T$$  \hspace{1cm} (4.3)

is the total strain vector with normal elongation components $\varepsilon_i$ and shearing components $\gamma_{xy}$. The components are given by derivatives of the displacement $u = (u, v)$

$$\varepsilon_x = \frac{\partial u}{\partial x}, \quad \varepsilon_y = \frac{\partial v}{\partial y}, \quad \gamma_{xy} = \frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}$$  \hspace{1cm} (4.4)

The compliance or flexibility matrix $D^{-1}$ is given by

$$D^{-1} = \begin{bmatrix}
\frac{1}{E_x} & \frac{\nu_{xy}}{E_x} & 0 \\
-\frac{\nu_{xy}}{E_y} & \frac{1}{E_y} & 0 \\
0 & 0 & \frac{1}{G_{xy}}
\end{bmatrix}$$  \hspace{1cm} (4.5)

where $E_i, \nu_{ij}, \nu_{ji}$ and $G_{ij}$ denote Young’s modulus, major and minor Poisson’s ratio and shear modulus. Symmetry of the matrix $D^{-1}$ imposes the relation

$$\frac{\nu_{ij}}{E_i} = \frac{\nu_{ji}}{E_j}$$  \hspace{1cm} (4.6)

The shear modulus $G_{xy}$ is given by

$$G_{xy} = \frac{E_x}{2(1 + \nu_{xy})}$$  \hspace{1cm} (4.7)
In the present 2-dimensional problem a cross section \((x-y\) plane\) in a prism with no change in compression along the channel direction is considered (cf. Fig. 4.5). Therefore, the model domain is in plane stress condition, i.e. all strain and shear but not necessarily stress components with \(z\)-index are per definition zero. The treatment of Eq. 4.1 to 4.5 for this case can be found in textbooks concerning structural mechanics [56, 57, 58].

The model domain (cf. Fig. 4.5), a slice perpendicular to the channel direction, is comprised of the membrane with GDLs and FFPs on either side. For symmetry reasons the repetition unit of half a channel and half a rib is covered. Boundary conditions applied are symmetry conditions at the center lines of channel and rib and displacement conditions at the outer surfaces of the plates. At the interface between GDL and rib friction is considered. The material properties and geometrical data are given in Table 4.1. The Young's modulus \(E_y\) of the GDL was linearized by taking its value from the stress-strain curve (see Fig. 4.9, Section 4.1.5, p. 43) at the respective final compression. The governing equations are solved using the commercial multiphysics software package ANSYS (version 7.1) with the finite element method (FEM) [59].

Figure 4.6 shows results for structural mechanics calculations and partial experimental verification with the geometries and materials used in the experiments. The deformed shape of the MEA for a compression of 25% of the GDL thickness is shown in the upper part of Fig. 4.6a. The GDL penetrates the channel area but is still compressed to some extent even at the channel center due to the high in-plane stiffness of the material. Therefore, the GDL is pressed onto the catalyst layer throughout the domain and assures contact between them. The related compression stress \(\sigma_y\), which is eventually transformed into conductivities is drawn in the lower part of Fig. 4.6a on the undeformed shape. Due to penetration of the GDL into the channel, fibers close to the edge of the rib are bent around it and lead to a stress maximum there. The dependence of through-plane and in-plane conductivity on the compression stress \(\sigma_y\) is shown in Fig. 4.8a and b (Section 4.1.5, p. 43).

The contact pressure at the interface between GDL and rib, which is eventually transformed into the contact resistance, is shown in Fig. 4.6b for various compressions. The obtained curves exhibit the same behaviour as discussed for the cross section of the GDL. The bending of fibers around the edge leads both to a pressure maximum at the edge and due to bending stiffness to a minimum closely aside. For very small compression the GDL even nearly detaches as seen in the curve for 10% compression, where the pressure nearly vanishes. A mainly qualitative verification for the calculated contact pressure distributions is given in Fig. 4.6c by means of a measurement with pressure sensitive film (Fuji Inc., Super Low type). The resolution of this film is limited to roughly 0.2 mm, i.e. force from a sharp edge produces a peak with a width of this extend. The curves show the relative intensity of color evolution averaged over 10 mm length together with its upper and lower bounds. The main trend of the calculation is clearly reflected and renders the
Figure 4.6: Stress and deformation in the MEA from structural mechanics calculations for the repetition unit of half a channel and half rib. (a) Initial (—) and deformed (—) shape for 25% compression of the GDL (top half) and corresponding distribution of the normal stress \( \sigma_y \) mapped onto the initial shape (lower half). (b) Contact pressure between GDL and rib for different compressions. (c) Qualitative pressure distribution from measurement with pressure sensitive film.

results to be valid for obtaining the contact resistance. The pressure dependence of the contact resistance is given in Fig. 4.8c (Section 4.1.5, p. 43).

4.1.4 Calculation of the potential and current field

Electron transport in two dimensions is governed by the charge conservation equation

\[
\frac{\partial}{\partial x} \left( \sigma_{xx} \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma_{yy} \frac{\partial \phi}{\partial y} \right) = 0
\]

(4.8)

where \( \sigma_{xx} \) and \( \sigma_{yy} \) denote the conductivity in \( x \)- and \( y \)-direction and \( \phi \) the electric potential. Referring to Fig. 4.5 \( \sigma_{xx} \) and \( \sigma_{yy} \) correspond to the in-plane and through-plane electric conductivity in the case of the GDL and MPL. The local values for \( \sigma_{xx} \) and \( \sigma_{yy} \) in the GDL are obtained from the calculated pressure distribution shown in Fig. 4.6 and their pressure dependence as given in Fig. 4.8. The conductivities of the MPL and the flow field material are given in Table 4.1.

Equation 4.8 is solved on the entire cross section of the cell perpendicular to the channel direction comprising of one GDL with MPL and the FFP including its parts outside the
active area. Insulating boundary conditions

$$\frac{\partial \phi}{\partial n} = 0$$  \hspace{1cm} (4.9)

apply to all boundaries except for the side of the flow field plate contacting the current drain \((y = 0)\) and the side of the GDL contacting the CL \((y = y_{c/d})\). As the potential of the current collector is taken as the reference potential the appropriate boundary condition is

$$\phi \mid_{y=0} = 0$$  \hspace{1cm} (4.10)

The remaining boundary condition at the CL is given by

$$\phi \mid_{x,y=y_{c/d}} = \phi_{cl}(x)$$  \hspace{1cm} (4.11)

where \(\phi_{cl}(x)\) is the potential measured at the CL against the current collector. Equations 4.8 to 4.11 apply for cells with the CL applied to the membrane and a separate GDL attached to it during cell assembly like that used in the present work. In this case the potential probes are placed between GDL and CL. When a MEA with the CL applied to the GDL is used in the measurement the potential probes have to be placed between CL and membrane. The charge conservation equation for the CL that is additionally involved in the potential drop becomes

$$\frac{\partial}{\partial x} \left( \sigma_{xx} \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma_{yy} \frac{\partial \phi}{\partial y} \right) = J$$  \hspace{1cm} (4.12)

where \(J\) denotes the current source term in the CL. Numerous theoretical works find an inhomogeneous current density distribution over the thickness of the CL. However, without knowledge about its actual profile the assumption of a homogeneous rate throughout the thickness seems justified best. As the membrane is electrically insulating the respective boundary condition becomes

$$\frac{\partial \phi}{\partial y} \bigg|_{x,y=y_{cl,m}} = 0$$  \hspace{1cm} (4.13)

instead of Eq. 4.11. The total local current source

$$\int_{y_{cl}}^{y_{cl,m}} J \cdot dy = j_{y,cl}$$  \hspace{1cm} (4.14)

throughout the thickness of the CL at every lateral location in the cell equals the local current density \(j_{y,cl}\) at the interface of CL and GDL. During the solution process it has to be adjusted to fulfill the measured condition

$$\phi \mid_{x,y=y_{cl,m}} = \phi_{cl,m}(x)$$  \hspace{1cm} (4.15)
Data Interpolation

The numerical solution of Eq. 4.8 requires a grid resolution finer than the distribution of the measuring points and therefore data interpolation. For that, the charge conservation equation Eq. 4.8 imposes the first and second derivative of the potential to be continuous on each point in the solution interval. At the borders of the GDL zero in-plane flux requires the potential there to satisfy Eq. 4.9. As the conservation equation is source free the solution shows minimal possible curvature with the respective boundary conditions. All of these requirements can be met with cubic splines.

A numerical estimation of the data interpolation error with splines is given in Fig. 4.7 for homogeneous current density on the repetition unit of half a rib and half channel. Backcalculation of the computed potential profile at the active layer into current matches the target current with a relative error of less than $10^{-6}$ and is referred to as exact. Figures 4.7a and c show the potential and therefrom calculated current distributions for different potential measurement resolutions. The respective relative error is given in Fig. 4.7b and d and was found to be less than half a percent for a resolution of 0.5 mm in the geometry used in the actual cell. This case must be considered as the lower bound of the possible error. Errors are minimal at the measurement positions and have in between a value that justifies to consider the interpolation method to be physically consistent.

**Figure 4.7**: Numerical estimation of the interpolation error using cubic splines. A homogeneous current density of 10000 A/m² is applied to the repetitive unit. (a) Exact potential distribution at the reaction layer and interpolated curves for two different potential measuring resolutions. (b) Relative error between exact and interpolated curves. (c) Calculated current distribution for the exact and the two interpolated potential distributions. (d) Relative error between exact current and current obtained with the interpolated potential distributions.
4.1 Method of Sub-Millimeter Resolved Current Measurement

Numerical Implementation

Equation 4.8 is solved using a finite volume formulation [60] with non-uniform grid spacing realized in the software package MATLAB. Based on the error estimate the grid is refined at corners and interfaces. Careful grid study has been conducted to ensure accurate numerical results. Contact resistances at the GDL-rib interface are accounted for by thin-wall boundary conditions, i.e. a thin layer with thickness divided by conductivity inversely proportional to the contact resistance $r_c = \delta_c / \sigma_c$ is formally introduced. The local contact resistance is obtained from the contact pressure distribution (Fig. 4.6) and its dependence on pressure (Fig. 4.8).

In a working fuel cell, the MEA is compressed and therefore distorted from its initial shape as shown in Fig. 4.6a. On such deformed domains, a rigorous numerical application of Eq. 4.8 with orthotropic conductivities is possible in two ways. First, the model domain is the deformed shape. Here, the surface integrals for fluxes over volume faces are calculated under consideration of distorted unity vectors, corresponding to the local displacement $u$. In this case, conductivities are referred to the compressed thickness of the sample. Second, the model domain is the undeformed shape. Here, the unity vectors remain unchanged and conductivities refer to the initial thickness of the compressible material. The coordinates for these two possibilities are transformed into each other by the coordinate transformation

$$x = x' + u$$

with $x$ and $x'$ denoting coordinates in the deformed and undeformed space, respectively. From that it can easily be shown that the conductivities are transformed by

$$\sigma'_{ii} = \sigma_{ii} \cdot (1 + \epsilon_i)/(1 + \epsilon_j)$$

For the sake of convenience the solution was done in the undeformed space.

4.1.5 Electrical and mechanical properties of the materials

Both, the in- and through-plane conductivity and the contact resistance between GDL and flow field material are pressure dependent. In-plane conductivity is measured using a four point probe technique with the sample pressed between two insulating plates to a certain pressure. The through-plane conductivity and the contact resistance may be measured in two ways. (1) Four point measurements may be conducted by passing current through the GDL pressed between two FFPs. The potential at the surfaces of the GDL is measured by very fine unloaded probes inside the current loaded area. The potential difference between the two surfaces and the two plates, respectively, relate to bulk and contact resistance. (2) The extrapolation of the total resistance to zero thickness of samples of the same material, but different thickness, allows for separation of the contact resistance [61]. For the results in Fig. 4.8 the two methods are cross checked.
4.2 Results for Air and Oxygen Operation

The main focus of this section is to demonstrate the validity of the developed measuring method and to discuss the principal underlying phenomena that govern the current distribution on the scale of channels and ribs. Therefore, the influence of \( O_2 \) content, mean current density, and membrane humidification, which are the predominant factors for the current distribution at a given flow field geometry are examined in detail.

The flow of both reactants was set to a constant value that refers to a stoichiometry of \( \lambda_{\text{air}} = 32 \), \( \lambda_{O_2} = 19 \), and \( \lambda_{\text{H}_2} = 19 \) at the highest respective current drawn in order to ensure virtually homogeneous conditions in the along-the-channel direction. The cell was operated at 65°C with minor gas humidity to prevent electrode flooding, which is assumed to make the interpretation of the measured potential profiles more difficult. The gas pressure was set to 1.5 bar\textsubscript{n} for both gases. Potential distributions were obtained for
both oxidants at a variety of average current densities on the whole width of the active area of the cell shown in Fig. 4.5. With air the cell could be operated up to 7500 A/m², with O₂ it was operated up to 14000 A/m².

A first check of the method may be done by comparing the calculated integral current with the experimentally applied one. In particular the correctness of the involved resistances is reflected in matching values. These resistances are at the same time the main uncertainties as the GDL material may vary in certain bounds on the small scales of interest. Figure 4.10 shows the correlation between applied and calculated average current density $\bar{j}$ for both oxidants. Most calculation results match the applied current with less than 10% deviation which renders the described procedure suitable for quantitative evaluation of the measured potential distributions.

Figures 4.11 and 4.12 show the obtained underlying locally resolved potentials and the resulting current distributions at the MPL-CL interface for air and O₂ operation. Since the cell shows a symmetrical cross section (cf. Fig. 4.5) the measurements gave an approximately symmetrical potential and therefore current distribution. For better clarity only one half of the cell is therefore shown. It consists of the right half of the inner rib, the right channel, and the adjacent outer rib. The measured potential differences between current collector and CL and the respective interpolation for a variety of loads is given in Fig. 4.11a and 4.12a. The corresponding calculated current density distributions are plotted in Fig. 4.11b and 4.12b. In either case it becomes obvious that the shape of the potential distribution cannot be correlated with the current distribution in a trivial way without comprehensive mathematical evaluation. Both figures illustrate that the general pattern of the current distribution is strongly load dependent. For both oxidants the profile changes from a maximum reaction rate underneath the rib at low loads to a current peak under the channel for high loads. The main difference in the behavior of air and O₂ arises at the area under the rib where the cell is able to produce considerably more current, when O₂ is fed. Both oxidants show a shift of the peak maximum from the center of the rib to near its edge resulting in a decrease of current in the rib center from a certain
load onward.

A closer inspection of Fig. 4.11b and 4.12b in comparison with Fig. 4.10 scrutinizes the degree of reliance on the strong partitioning of current between channel and rib. Figure 4.10 points out a slight tendency that the total current is underestimated when little current is produced under the channel and the opposite when a current peak is there. This identifies the high aspect ratio of GDL thickness and channel width along with the high ratio of in- and through-plane conductivity of the GDL to be the main difficulty of the method. Both factors together cause a high sensitivity of the resulting current density under the channel on inevitable measurement inaccuracies. However, the good match proves widely trustworthy results.

**Figure 4.11:** Right half of the symmetric cell for air operation at various average current densities. (a) Measured potentials against current collector (symbols) and related interpolation (lines). (b) Corresponding calculated current density distributions. (c) Schematic cross section of the related part of the FFP.

**Figure 4.12:** The same as in Fig. 4.11 but for O₂ operation.

A comparative view on the evolution of the local current density at the center of the inner
4.2. Results for Air and Oxygen Operation

rib and the channel with increasing total current for both oxidants is given in Fig. 4.13. While current production under the middle of the rib passes through a maximum for both oxidants the area under the middle of the channel produces up to a multiple of the mean current density at high loads. It reaches up to 250% with air and up to 160% with O2. Together with the distributions in Fig. 4.11 and 4.12 it becomes evident that the actual current profile at a specific load is given by the superposition of two limiting regimes: kinetic control at low loads and mass transport controlled at high loads.

At low loads the distribution is controlled by kinetics and resistances. As mentioned, the gases were fed relatively which gives rise to some increase of the membrane resistance due to drying. Since transport of product water from the CL to the channel is hindered more from areas under the ribs the membrane resistance there will be lower as compared to the channel area. Moreover, the pathway for electron transport from the channel area into the flow field is prolonged as compared to the rib area. Therefore, resistive overpotentials take a bigger portion of the total polarization at the channel area. This results in significantly lower current due to the steep slope of the activation overpotential curve at low currents. This holds true in the case of air up to an average current density of $0.2 \times 10^4 \text{ A/m}^2$ and for O2 up to $0.8 \times 10^4 \text{ A/m}^2$.

At higher loads, the regime determining the position of the current maximum is changing. With increasing integral current reactant starvation begins to take place under the rib promoting the current production under the channel. The large inhomogeneities now developing are due to reaction rate limitation by O2 transport. As clearly seen in Fig. 4.13 the current production under the middle of the rib is approaching zero when operating on air above $0.8 \times 10^4 \text{ A/m}^2$. This leads to high local current peaks under the channel of more than double the average current density. Using O2, the same effect can be observed in an alleviated way: the regime change from kinetics to diffusion control occurs at a higher integral current density of 0.8 to $1.0 \times 10^4 \text{ A/m}^2$. Also for O2 operation the current under the center of the rib is diminished, but it is not completely suppressed as in the case of air.

![Figure 4.13: The local current density in the center of the inner rib and the channel as a function of the applied average current density for air and O2 operation.](image-url)
An inspection of the transition region of this two regimes in Fig. 4.11 to 4.13 elucidates these two limiting cases even better. It is known from theoretical [62, 44] and experimental work (cf. Section 6.6) on the full cell level that increased local current prevents the membrane from drying by the dry air feed. The same becomes apparent at the channel area for both oxidants due to the steepening increase of current there (cf. Fig. 4.13). The superposition of kinetic, resistance, and mass transport control on the current profiles leads to characteristic peaks close to the edge of the inner rib, which is particularly pronounced with air between 0.3 to 0.6×10^4 A/m^2 when O2 starvation already begins to take place under the rib and the resistive overpotentials at the channel are too high for higher current there.

The behavior of the outer rib needs special consideration as the whole width of 2 mm is fed from one side only. Current production essentially vanishes at two third of the width for both oxidants, which gives rise to assume that the GDL is blocked by liquid water in the remaining area.

Figure 4.14 gives a different, but consistent view on the phenomena discussed above. Integral current density-voltage (j/U) curves are compared with the local ones from the local current data in Fig. 4.13 for the center of the rib and the channel. The results support the previous discussion regarding the two superposed limiting regimes. In particular the far lower curve at the center of the channel for low to medium currents supports the discussion on membrane drying under the channel as the voltage difference at a certain local current density is by far bigger than the difference in ohmic drop in the GDL (cf. Fig. 4.11a and 4.12a). Moreover, parts of the cell have already reached the limiting current density, whereas the integral j/U curve is still far away from its limiting current, i.e. the current where increasing polarization does not change the current. However, this "back folding" of the local curves lowers the integral curve already at currents, where the shape of the latter one does not give rise to assume strong transport losses.

![Figure 4.14](image)

**Figure 4.14**: Comparison of the integral with the local polarization curves at the center of the inner rib and the channel. (a) Air operation and (b) O2 operation.

What is referred here to as starvation and diffusive mass transport limitations under the rib is not equivalent with what is usually understood under diffusion limitations in
pertinent textbooks [2, 3]. There, the diffusion limited current arises from the diffusion of an electro active species through a finite layer to an uniformly accessible electrode, i.e. planar or (hemi-)spherical diffusion to a non-concave electrode surface. Local $j/U$ curves show a slope of lower or equal infinite at the limiting current for such systems. A fundamentally different behavior is observed for concave electrodes, i.e. electrodes with larger active area than access area to the stirred reservoir. This is given for PEFCs, where the (superficial) active area supplied by one channel area is larger than this channel area. In that case, parts of the cell show from a certain potential on a negative slope of the local $j/U$ curve (cf. Fig. 4.14), whereas the integral one shows at most an infinite slope. This means that an increase of the total polarization results locally in decreasing current density. This behavior is unique to electrodes where the surface concentration at one site is heavily influenced by the current at neighboring sites, whose concentration is in turn not influenced by the first site. Despite the fact that solely diffusion is involved in this phenomenon, it is no diffusion limitation in the classical sense but $O_2$ starvation along its transport pathway from the rib edge to the rib center due to depletion at the passed area.

An analogon to this one-way interference at the channel and rib scale is the effect of stoichiometric ratio on the current density distribution in the along-the-channel direction. There, the current density at upstream regions influences the $O_2$ concentration at downstream regions but not the other way round. By localized current measurement along a single channel PEFC BRETT et al. [63] have first shown that for constant flow operation downstream segments can show the same back folding of the local $j/U$ curves as seen in Fig. 4.14. The effect becomes more pronounced with lower the stoichiometric ratio. KULIKOVSKI et al. [64] gave the recently most comprehensive discussion on the underlying phenomena by means of a theoretical model. They have shown that this back folding of downstream $j/U$ curves due to starvation only appears with constant flow operation of the cell where the stoichiometric ratio decreases with increasing total current. This is in contrast to the phenomenon under the rib where there is always entering a $O_2$ mass flow referring to a stoichiometry of one.

4.3 Conclusions

By introducing a new principle, a method has been developed that enables measurement of the current density distribution in PEFC with sub-millimeter resolution. The current density is obtained from the ohmic drop in the electron conductors of the cell. The detailed experimental setup, the concise procedures for obtaining all involved resistances, and the quantitative data evaluation is described. The validity of the novel method is demonstrated by applying it successfully to a test cell under air and oxygen operation.

The method enables the comparison of current production from areas covered by a flow
field rib and areas under the gas channel. The general pattern of the sub-millimeter scale current distribution is strongly dependent on the load of the fuel cell and results from the superposition of control by kinetics and mass transport. At low loads the current maximum lies under or at the edge of the rib. At higher loads, the regime determining the position of the current maximum is changing. With increasing integral current, reactant starvation begins to take place under the rib, promoting the current production under the channel. The large inhomogeneities developing now are due to reaction rate limitation by O₂ transport.

Along with the steps involved in the measuring method, the possible error sources have been discussed. It was found that the involved resistances and the resolution and accuracy of the potential measurements are crucial issues. Although having room for improvement, a powerful tool for in-situ diagnostics of PEFCs has been developed. For future work a combination with other diagnostic methods, such as neutron imaging or impedance spectroscopy is considered. Valuable information about the influence of membrane resistance and GDL water management on the local current production is expected to be obtained.
Chapter 5

Modelling and Diagnostics of Processes on the Single Cell Level

5.1 1+1 Dimensional Modelling of Transport Processes in PEFC\textsuperscript{1}

3D CFD models are often employed to model complete cells with detailed description of relevant processes [65, 66, 67]. However, major computational difficulties arise from full 3D modeling of strongly coupled phenomena with a multitude of solution variables on a domain with a high aspect ratio. Despite massive parallelization yet long computation times are required [68].

Convective transport along the channel by far dominates parallel diffusive fluxes in the GDLs and the membrane. Therefore, the model can be formulated in a 1 + 1 dimensional manner, \textit{i.e.} local transport phenomena are treated 1D in through-plane direction and coupled in-plane by convective transport in the gas and coolant channels. Thus, a 2D slice running through the repetitive unit of a cell from the anode channel via membrane-electrode assembly (MEA) and cathode channel to the coolant channel and from inlet to outlet is modeled.

First attempts in the quasi-two-dimensional modeling were accomplished in the early 90’s by FULLER and NEWMAN [69] and NGUYEN and WHITE [70] followed more by recent ones [71, 72, 73, 41, 42], which contributed to the understanding of certain processes in the cell. However, they all contain simplifications which probably prevent an accurate description of a real cell. DANNENBERG \textit{et al.} [71] accounted for heat removal into a coolant but assumes constant temperature in through plane direction. The model of JANSSSEN [72] was focused

\textsuperscript{1}The model shown here was presented in:
on the water management, but assumed homogeneous current density distribution, \textit{Berg et al.} [41] have assumed a fully isothermal cell, an approach, which can experimentally be fulfilled in the in-plane direction of the MEA, but not in the through-plane direction. \textit{Kulikowski} [42] neglects liquid water transport and oversimplifies the water transport in the membrane by making transport coefficients independent on local water content and forbidding water transfer between the gas streams. The latter process, however, is crucial for a proper description of the cell water balance as shown in this paper.

The approach presented in Section 6.2 has a more comprehensive treatment of the through-plane processes than all previous 1+1D model approaches, including the thermal effects in the through plane direction.

This allows, in further addition to previous work, for the idea of combining individual 1D sub cells, for which the flow regime of the gases can be co or counter flow, to a more complex network which can be used to model complex technical cells. In combination with the feature to solve for a given total current, by adjusting the current distribution, this enables simulation of complex technical flow fields as shown in Section 6.2.

5.1.1 General considerations

A single PEFC with conventional gas distributors (plate with channels between gas in- and outlet) is considered. A two-dimensional region running from inlet to outlet and through the cell from the anode channel via cathode channel to the coolant channel, as shown in Fig. 5.1 is modeled. This unit consists of 8 layers, from top to bottom in Fig. 5.1 these are

1. Bipolar plate with liquid cooling channels.
2. Solid part of cathode side bipolar plate.
3. Channel part of cathode side bipolar plate.
4. Cathode gas diffusion layer (GDL) including cathode catalyst layer.
5. Membrane.
6. Anode GDL with catalyst layer.
7. Anode side channel part of bipolar plate.
8. Anode side solid part of bipolar plate.

The anode and cathode active layers are treated as interfaces. In transversal cell direction, locations of the main interfaces are the coolant channel (cw), the gas channels on anode and cathode side (a, c), and the GDL-membrane interfaces on anode and cathode (am, cm). Interface locations are indicated, together with the definition of the coordinate system in Fig. 5.1.
5.1. 1+1 Dimensional Modelling of Transport Processes in PEFC

Figure 5.1: Schematic representation of the modelling domain, the coordinate system and the modelled interfaces with their labeling. Air is flowing in positive y-direction, hydrogen either in parallel or anti parallel direction. In the sandwich model fluxes from anode to cathode flow in positive z-direction. The predominant species and heat transport pathways which are accounted for in the model are depicted by the arrows in the right part.

For the model the following transport phenomena in the different layers are taken into account:

1. Migration of protons through the membrane electrolyte.
2. Transport of water through the membrane by diffusion and electro-osmotic drag.
3. Multi-component diffusion of gaseous species through the porous anode and cathode GDLs.
4. Flow of liquid water through the GDLs.
5. Transport of reactants and water in the channels.
6. Heat generation and transport in the cross section of the cell and along the channels.

In the case of the dedicated use of the model for cells of technical size with active areas of several 100 cm$^2$ the model domain shows an aspect ratio of about 1000, tens of centimeters along the channels and several 100 µm in perpendicular direction. This fact allows for the assumption that transport phenomena in along-the-channel (y) direction are dominated by convection inside the flow channels. An inspection of the general steady transport equation

$$\text{div}(\rho \mathbf{u} \Phi) - \text{div}(\Gamma \text{grad} \Phi) = S$$  \hspace{1cm} (5.1)$$

for the property $\Phi$ for the orders of magnitudes in strength of convection $\rho \mathbf{u}$ and diffusion conductance $\Gamma/\partial x$ leads to the dimensionless Péclet-number $Pe = \mathbf{u} L/\Gamma$. Herein $\rho, \mathbf{u} = (u, v, w), \Gamma$ and $S$ are the density, convection velocity, transport coefficient and the source term, respectively, $L$ represents the characteristic length. Formal application of Eq. 5.1 on the in-plane transport of reactants or water in the complete cell sandwich including both flow fields leads to a Péclet-number in the order of $10^{10}$. This indicates that convective transport inside the flow channel by far dominates parallel diffusive fluxes in the gas diffusion media or the membrane. Especially in technical cells the channels are long and the flow velocity high, so that this approximation applies. This estimation generally holds for the flow direction, but not in perpendicular direction. In-plane transport normal to
the channel (x) direction may occur in meander like flow fields at the border of distinct bundles of channels. This will, however, only affect the very next channels to the border and may be neglected in good approximation for multi-channel meanders. Thus, it is reasonable to neglect in-plane transports perpendicular to the flow.

Consequently, local transport through the MEA shall be one-dimensional in z-direction only. Boundary conditions governing these local transports vary along the flow direction with the species composition in the channel. The local reactant consumption and water balance in turn serve as source terms for the flow in the gas distributor. Thus, the resulting 1+1D model is represented by slices through the cell coupled by the flow in the channels only.

The resulting model is able to describe both, domains with parallel (co flow) and anti parallel (counter flow) flowing fuel and oxidant streams. Only simple cells consist of a single domain. The analysis of the flow geometry of more complex cells shows that they can be described by a combination of domains of these flow regimes. Consequently, such a combination of domains allows for describing complex cells by the low-dimensional model with adequate accuracy and low computational effort. The analysis of a cell, requiring a coupling of domains is shown in the results section of this paper.

### 5.1.2 The model and its implementation

**Assumptions**

For the mathematical formulation of the model the following assumptions were made:

1. The stationary state operation of the FC is considered.
2. The media flows in channels are assumed to be one-dimensional in y-direction with no axial dispersion, i.e. ideal plug flow is assumed.
3. Gas mixtures obey the ideal gas law.
4. Uniform temperature throughout the flow field is assumed. In liquid cooled cells quasi-isothermal conditions may be achieved when they are operated with quasi-infinite coolant stream. However, temperature gradients in through-plane direction, which have a severe impact on phase equilibria and mass transfer, are considered.
5. A uniform gas pressure is assumed, neglecting the pressure drop along the gas flow in the channels and in the GDLs.
6. The catalyst layers are treated as interfaces. Compared to the other layers in the MEA they are comparatively thin and their influence on the transport of heat and
water is of a minor degree. However, additional voltage losses due to drying of the catalyst layers may occur.

7. The layers of the MEA are homogeneous in their transport properties (permeability, tortuosity, porosity) except for the membrane, which properties are highly dependent on the local water content.

8. The membrane transports only water and hydronium ions and is impermeable for reactant gases.

Species and heat transport through the MEA

Membrane.— Water flux through the membrane is coupled with the proton transport and is expressed in the form

$$N_m = n_j \frac{j}{F} - \frac{D_m}{V_m} \frac{d\lambda}{dz}$$

with the molar volume $V_m$ as

$$V_m = V_{\text{polymer}} + \lambda V_w$$

A similar equation to Eq. 5.2 is found in the literature where it is deducted from an Onsager–approach [74, 4, 17, 75, 31, 72].

Gas diffusion layers.— For the transport in the electrodes both gas and liquid transport are considered. The multi-component gas transport is described by the Stefan–Maxwell equation, which takes the form [72]

$$\frac{dp_w}{dz} = \frac{RT}{pD_{\text{hw}}^\text{eff}} \left( p_w \frac{j}{2F} - p_h N_{w,v} \right)$$

$$\frac{dp_w}{dz} = \frac{RT}{pD_{\text{nw}}^\text{eff}} \left( -p_w \frac{j}{4F} - (p - p_w) N_{w,v} \right)$$

for water in anode and cathode, respectively. The cathode is approximated as a binary system consisting of N$_2$ and water because of the very similar behavior of N$_2$ and O$_2$.

Liquid water transport is expressed according to JANSSON [72] similarly to the other transports in terms of gradients of the chemical potential in the liquid phase

$$N_1 = \kappa \frac{d\mu_{w,l}}{dz}$$

The Stefan–Maxwell formulation for N$_2$ diffusion in a ternary mixture with O$_2$ and water is given by

$$\frac{dx_n}{dz} = \frac{RT}{pD_{\text{no}}^\text{eff}} x_n \frac{j}{4F} + \frac{RT}{pD_{\text{nw}}^\text{eff}} x_n N_{w,v}$$
The gas and liquid mass balance equations in addition to the Eqs. 5.2 and 5.4a - 5.6 take the form

$$\frac{dN_i}{dz} = 0 \quad (5.7)$$

for all involved species since phase change and reactions are only accounted for at interfaces.

**Heat transfer.**— The governing equations for heat transfer in the cross section of the cell are obtained from energy balance [60]. Assuming temperature independent heat capacities and taking into account convective and conductive transport the energy conservation equation takes the following forms for the different domains,

$$k_c \frac{d^2 T}{dz^2} = \frac{j^2}{\sigma_c} \quad (5.8)$$

$$\frac{k_c}{2} \frac{d^2 T}{dz^2} = \frac{j^2}{\sigma_c} + \alpha A(T - T_g) \quad (5.9)$$

$$\left(\sum_{j=1}^{3} \rho_{js}v_{js}C_{p,js} + \rho_{i}v_{i}C_{p,i}\right) \frac{dT}{dz} - [(1 - \varepsilon)k_c] \frac{d^2 T}{dz^2} = \frac{j^2}{(1 - \varepsilon)\sigma_c} + q_{gl} \quad (5.10)$$

$$\rho_{i}v_{i}C_{p,i} \frac{dT}{dz} - [\varepsilon k_l + (1 - \varepsilon)k_m] \frac{d^2 T}{dz^2} = \frac{j^2}{\sigma_m} \quad (5.11)$$

where Eq. 5.8 refers to solid carbon, Eq. 5.9 to the channel layer, Eq. 5.10 to the GDLs and Eq. 5.11 to the membrane, respectively. The source terms are composed of ohmic heating $j^2/\sigma$ and heat transfer between the gas phase in the channels and the channel walls $\alpha A(T - T_g)$. Equation 5.9 implicates, that the ribs cover half of the electrode surface. The last term in Eq. 5.10 corresponds to the heat of evaporation. For the sake of simplicity phase change is only allowed at the membrane–GDL interface and at the GDL–channel interface. At the first interface phase change refers to the water transported in the gas phase. Therefore, this term becomes an interface source and is transformed to

$$Q_{gl} = N_{w,gl} \Delta H_{gl} \quad (5.12)$$

At the GDL–channel interface the liquid flux $N_{w,gl}$ evaporates when the channel is under saturated and gives an analogous expression to Eq. 5.12 for the interface heat source. In Eq. 5.11 the volume fraction $\varepsilon$ of water in the membrane is obtained from

$$\varepsilon = \frac{\lambda V_w}{V_{\text{polymer}} + \lambda V_w} \quad (5.13)$$
Transport in the channel and coupling to the transports through the MEA

Plug-flow in the channel without axial dispersion is governed by convection only according to \( \text{div}(\rho u n M) = S \) where \( n \) is the molar flux and \( M \) the molar weight of either a single species or the entire flow and \( S \) the source term. Obeying the continuity equation, this equation may be rewritten in the form

\[
\frac{dn_i}{dA} = N_i \tag{5.14}
\]

where \( N_i \) is the local mass source of species \( i \). Thus, this formulation becomes independent on the channel cross-section as well as on the channel-rib ratio and the width-to-length ratio of the cell area. Therefore, no distinction between cell area under the channels and the ribs is made. Equation 5.14 is formulated for hydrogen and oxygen by using Faraday’s law for the source term. The source term for the water flow in the channels is represented by local water balance.

Energy conservation in the coolant flow is governed by \( \text{div}(\rho u h) = S \) for convection only. Similarly to the mass conservation this may be cast into

\[
\frac{dT}{dA} = \frac{Q M_w}{m_{cw} C_{p,w}} \tag{5.15}
\]

where \( Q \) is the local heat source and \( m_{cw} \) the coolant mass flow.

The local conditions in the channels then serve as boundary conditions for the 1-D transport model in \( z \)-direction perpendicular to the membrane.

Boundary and Interface conditions

**Gas inlets.**— The conditions needed to describe the partial flows in the feed gases are given by

\[
n|_{\text{inlet}} = \frac{\lambda j A}{zF}, \quad n_a = \frac{\lambda j A}{4F 21}, \quad n|_{\text{inlet}} = \frac{\lambda j A}{zF} \frac{p_w}{p - p_w} \tag{5.16}
\]

for the reactants, \( N_2 \) and water inlet flows, respectively. \( z \) denotes the number of electrons involved and becomes two for the anode and four for the cathode.

**Interfaces relevant to mass transfer.**— Referring to Fig. 5.1, boundary conditions are required at the anode-channel and cathode-channel interface (i.e. \( z = z_a \) and \( z = z_c \), respectively), as well as at the anode-membrane (\( z = z_{am} \)) and the cathode-membrane interface (\( z = z_{cm} \)). For the solution of the equations describing the water transport in the GDLs (Eq. 5.4a–5.5) these are at \( z = z_a \) and \( z = z_c \) (anode-fuel channel and cathode-oxidant channel interface):

\[
\mu_g = \mu_{g\text{ref}} + RT \ln \frac{p_w}{p_{g\text{ref}}}, \quad \mu_l = \mu_{l\text{ref}} + RT \ln \frac{p_{l\text{out}}}{p_{l\text{ref}}} \tag{5.17}
\]
where \( p_w \leq p^{\text{sat}} \). If liquid phase exists in the channel its chemical potential is obtained from bulk water (Eq. 5.17).

At \( z = z_{\text{am}} \) and \( z = z_{\text{cm}} \) (anode-membrane and cathode-membrane interface):

\[
\mu_g = \mu_g^{\text{ref}} + RT \ln \frac{p_w}{p^{\text{ref}}}, \quad \mu_l = \mu_l^{\text{ref}} + RT \ln \frac{p_w}{p^{\text{ref}}}, \quad p_w > p^{\text{sat}}
\]  

(5.18)

At the membrane-electrode interfaces local equilibrium is assumed, i.e. the liquid phase in the membrane is in equilibrium with the water phases in the porous electrode. Following the approach in Ref. [72] water is transported in the GDL only in vapor phase as long as the vapor pressure at the GDL–membrane interface is lower than the saturation value. When the vapor pressure at this interface reaches the saturation value part of the water transport will take place in liquid form according to Eq. 5.5. Vapor transport is therefore allowed in both directions, whereas liquid transport only occurs from membrane to channel.

The \( N_2 \) mole fraction in the gas channel is given by

\[
x_{n,c} = \frac{n_{c,v}}{(n_{c,v} + n_a + n_o)} \quad \text{with} \quad n_{c,v} = \frac{(n_a + n_o) \cdot p_{w,c}/p}{1 - p_{w,c}/p}
\]  

(5.19)

In the present model, the diffusive water transport in the membrane is driven by the gradient in the number of water molecules per sulfonic acid group (\( \lambda \)) as the driving force. The values at the interfaces with the GDLs are taken from water uptake isotherms reported by Springer [17] for 303 K and Hinatsu et al. [76] for 353 K which both may be approximated by a third-order polynomial with an Arrhenius-type temperature dependence (see Table 5.1).

The fluxes through the distinct domains are coupled at the interfaces fulfilling mass balance in the form

\[
N \mid_{\text{interface}^-} = S \mid_{\text{interface}^+} + N_{\text{interface}}
\]  

(5.20)

where local flow equilibrium at the interface obeys possible sources \( N_i \) at the interface. This condition leads for the anodic and cathodic interface of the membrane (am, cm) to

\[
N_{a,v} + N_{a,1} = N_a = N_m \quad \text{and} \quad N_{c,v} + N_{c,1} = N_c = N_p + N_m
\]  

(5.21)

Equation 5.21 accounts for the product water source at the cathode-membrane interface.

**Interfaces relevant to heat transfer.** — For the heat transport additional interfaces have to be considered. When neglecting thermal contact resistances, therefore assuming continuity in value and flow of energy and considering the reaction layers as interfaces, the solution at interfaces in general has to fulfill

\[
T \mid_{\text{interface}^+} = T \mid_{\text{interface}^-} \quad \text{and} \quad Q \mid_{\text{interface}^+} = Q \mid_{\text{interface}^-} + Q_{\text{interface}}
\]  

(5.22)
where $Q_{\text{interface}}$ is the source at the interface. At the reaction layers the heat source term becomes

$$Q = j \left( \frac{-T \Delta S}{zF} - \eta_{\text{ct}} \right)$$  \hspace{1cm} (5.23)

**Reaction kinetics.**— Under the assumption of isopotential flow field plates (FFPs), the external cell potential is constant throughout the cell. Since local over potentials will vary along the channel the local current density is adjusted to fulfill the condition$^2$

$$U = E^0 - \eta_{\text{ct}} - \eta_{\text{conc}} - \eta_R$$  \hspace{1cm} (5.24)

In order to capture oxygen transport limitations inside the catalyst layers without solving oxygen transport inside finite reaction layers, a limiting current density $j_l$ is introduced [2]. The limiting current density is determined in the fitting procedure to experimental data.

$$\eta_{\text{ct}} = \frac{RT}{\alpha z F} \ln \frac{j_i^0}{j_l} + \frac{RT}{\alpha F} \ln \frac{j_i - j}{j_l}$$  \hspace{1cm} (5.25)

The concentration overpotential

$$\eta_{\text{conc}} = -\frac{RT}{\alpha z F} \ln \left( \frac{j_{\text{ref}}}{P_{0,\text{cm}}} \right)$$  \hspace{1cm} (5.26)

accounts for oxygen transport limitations through the cathode GDL. The ohmic over potential is determined by the electronic and ionic transport losses according to Ohm’s law

$$\eta_R = \frac{j}{\sigma_{\text{m}}}$$  \hspace{1cm} (5.27)

For the membrane conductivity $\sigma_m$ a fifth-order polynomial fit to conductivity data of Nafion membranes by Huslage et al. [77] is used (see Table 5.1).

**Numerical implementation**

The solution of the model was realized in the software package MATLAB. The code embeds the solution of the boundary value problems that describe the processes in through-plane direction into the solution of the simple flow equations for along-the-channel species and energy conservation. For specified total cell current and operating conditions, the inlet flow compositions are calculated from Eq. 5.16 and a respective water vapor pressure is initialized for the cathodic (c, cm) and anodic (a, am) interfaces. As an initial guess a constant current density and temperature is assumed. The steps of the iterative solution are different for co and counter flows due to the explicit stepping technique used for $^2$In Section 2.3 (p. 13) $\eta_{\text{conc}}$ was treated as a part of $\eta_{\text{ct}}$. Charge transfer polarization is decomposed here into the contribution referring to reference concentration and an additional contribution by O$_2$ starvation ($\eta_{\text{conc}}$).
the along-the-channel problem and are treated separately, as described below. With a resolution of 300 steps along the channel and 10 steps per layer in through-plane direction a computation for a single domain lasts 10 - 60s on a 2.4 GHz Intel Pentium 4 CPU.

**Co flow.** Equation 5.14 is solved for all components using the explicit Euler method starting at the gas inlets. Before each step the local sources $N_i$ are obtained from the water balance that is governed by the boundary value problem given by Eqs. 5.2, 5.4a, 5.4b, and 5.5, which is solved using low order finite difference methods, and from the reactant consumption according to the assumed local current. The local oxygen partial pressure is obtained from the solution of Eq. 5.6, which takes the form

$$x_{n,cm} = x_{n,c} \cdot \exp \left[ d_n RT \left( \frac{j}{4FpD_\text{ref}} - \frac{N_{w,n}}{pD_\text{ref}} \right) \right],$$

(5.28)

together with Dalton’s law

$$p_{o,cm} = p \cdot [1 - x_{n,cm} - p_{w,cm}/p]$$

(5.29)

By solving Eq. 5.24 together with Eq. 5.25 - 5.27 a local voltage according to the assumed current profile is obtained. Subsequently, the local current density is adjusted using Eq. 5.24 with the uniform average voltage. This current profile is leveled to meet the specified total current. Finally the local temperature is updated by solving energy conservation in the coolant channels (Eq. 5.15) with the local heat source obtained from the solution of Eq. 5.8 - 5.11 using a finite volume formulation [60]. These calculations are iterated until the integrated local current closely meets the specified total current.

**Counter flow.** In the counter-flow case only one of the two boundary conditions for the local water balance is given initially at the respective gas inlet. The second one is defined by the exit composition of the other gas. Therefore, Eq. 5.14 is integrated separately in the appropriate flow direction using the water balance obtained from the boundary conditions given by the initial guess. These integrations are iterated with updated water balances until the water balances remain unchanged compared to the previous iteration. Current adjustment and the further steps correspond to the co flow case.

**Fitting of model parameters to experimental results**

The model contains three fitted parameters, the cathodic exchange and limiting current densities $j_\text{ref}$ and $j_l$ and the symmetry factor $\alpha$. With an initial guess of these parameters current-voltage curves are calculated and the parameters adjusted to fulfill

$$\eta_\text{fac} = E^0 - U_\text{exp} - \eta_\text{conc, model} - \eta_R_\text{model}$$

(5.30)
using Eq. 5.25. Herein $U_{\text{exp}}$ are experimental cell voltages and $\eta_{\text{conc, model}}$ and $\eta_{\text{R, model}}$ are weighted means of the calculated over potentials at corresponding average current densities. The procedure is repeated until the experimental and theoretical cell voltages match within less than 10 mV.

The general parameters of the model are summarized in Table 5.1 and base case operating conditions are given in Table 6.1. Some of them, the limiting and exchange current density and the symmetry factor were subject to the fitting procedure and were held constant afterwards in the simulations. For the symmetry factor and the limiting current density constant values were obtained whereas the superficial exchange current density could be found to obey

$$j^0 = 0.0246 \cdot \exp \left( \frac{8895}{T_{\text{ref}}} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \quad (5.31)$$

For the fitting of the kinetic parameters a set of current-voltage curves, covering both wet and dry feeds at a variety of cell temperatures and gas stoichiometries was used. The correlation between experimental and simulated cell voltages is shown in Fig. 5.2 and gives an agreement within 5% for the majority of the points.

**Figure 5.2:** Correlation of experimental and simulated cell voltages used for the fit procedure.
**Table 5.1:** Values for simulation parameters and physical properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion layer thickness</td>
<td>$3.0 \times 10^{-4}$ m</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>$6.0 \times 10^{-5}$ m</td>
</tr>
<tr>
<td>Sorption isotherm [17, 77]</td>
<td>$\sum_{i=0}^{3} k_i \cdot a_i \cdot i = a_i \cdot \exp \left[ b_i \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right]$</td>
</tr>
<tr>
<td>Drag coefficient</td>
<td>$\eta_{d}$</td>
</tr>
<tr>
<td>Water diffusion coefficient [36]</td>
<td>$1.14 \times 10^{11} \exp \left[ 2416 \left( \frac{1}{303} - \frac{1}{273 + T} \right) \right] \left( \frac{\lambda}{25} \right)^{0.15} \left[ 1 + \tanh \left( \frac{\lambda - 2.5}{1.4} \right) \right]$ m$^2$/s</td>
</tr>
<tr>
<td>H$_2$/water diffusion coefficient [74]</td>
<td>$2.45 \left( \frac{T}{146.07} \right)^{2.334}$ m$^2$/s</td>
</tr>
<tr>
<td>N$_2$/O$_2$ diffusion coefficient [74]</td>
<td>$0.521 \left( \frac{T}{139.68} \right)^{1.833}$ m$^2$/s</td>
</tr>
<tr>
<td>Effective diffusivity</td>
<td>$D_e^{eff}$</td>
</tr>
<tr>
<td>Porosity</td>
<td>$\varepsilon$</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>$\tau$</td>
</tr>
<tr>
<td>Liquid permeability</td>
<td>$3.7 \times 10^{-7}$ m$^2$/s</td>
</tr>
<tr>
<td>Carbon electric conductivity</td>
<td>$3.0 \times 10^4$ S/m</td>
</tr>
<tr>
<td>Membrane ionic conductivity</td>
<td>$\sum_{i=0}^{6} K_i \cdot A_i \cdot \exp \left[ B_i \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right]$ S/m</td>
</tr>
<tr>
<td>Carbon thermal conductivity</td>
<td>$k_c$</td>
</tr>
<tr>
<td>Cathodic transfer coefficient</td>
<td>$0.35$ W/mK</td>
</tr>
<tr>
<td>Equilibrium potential</td>
<td>$E_0 = 1.229 - 0.85 \times 10^{-3} \cdot (T - 298.15) + 4.309 \times 10^{-5} \cdot T \cdot \ln(p_{a}) + \frac{1}{2} \ln(p_{o})$ V</td>
</tr>
<tr>
<td>Reference exchange current density</td>
<td>$</td>
</tr><tr>
<td>ho_{o, ref}$</td>
<td></td>
</tr>
<tr>
<td>Limiting current density</td>
<td>$j_l = 7.2 \times 10^4$ A/m$^2$</td>
</tr>
<tr>
<td>Reference pressure</td>
<td>$p_{o, ref} = 1.0 \times 10^5$ Pa</td>
</tr>
<tr>
<td>Reference temperature</td>
<td>$T_{ref} = 303$ K</td>
</tr>
</tbody>
</table>
5.2 Advanced in-situ Diagnostics in a Model Cell of Technical Size

5.2.1 Cell design and test facilities

As stated earlier co and counter flow regimes form the building blocks for more complicated flow fields as sometimes used in technical cells like that developed by Ruge [78] for an electrical power train [79] and investigated in detail by Santis [80]. Such complex flow fields have shown to be an obstacle for the application of diagnostic methods as well as for the interpretation of the results [80, 81, 82, 83] and therefore not well suited to get insight into basic phenomena originated by the flow arrangement. Hence, a linear cell setup was chosen. This provides several advantages: (i) well defined co or counter flow operation, (ii) clear segmentation along the flow path and easy access to the single segments, (iii) linear arrangement avoids serpentines and therefore convection under the ribs through the GDL.

A schematic drawing of the cell is given in Fig. 5.3. It consists of an MEA sandwiched between two semi-segmented FFP and segmented current collectors and is clamped together by two aluminium end plates. The MEA is made from a Naion membrane inserted between two cloth type GDLs that hold the CL on them. The design of the remaining cell components was guided by a list of requirements for intended experiments and applicable diagnostic methods:

- Both measurements in the single cells and in a 2-cell stack must be enabled. In the case of stack operation the cells need to be fed individually with reactants. The possibility for stacking makes in particular demands on the manifolding of the FFPs. Stackability is required for the experiments shown in Chapter 7.

- Inhomogeneous temperature that arises from limited liquid cooling in technical cells shall be adjustable. Therefore liquid shall be employed for (localized) temperature regulation.

- Localized current, voltage and ultimately EIS measurement shall be applicable both to the single cell and the stack.

- Neutron radiography for liquid detection.

- Localized gas sampling.

The FFPs for which a detailed drawing is provided in Fig. 5.4 consist of 2mm thick polyvinylidene difluoride (PVDF) bonded carbon plates (Sigracet BMA5, SGL carbon group). The plates hold flow fields with 28 parallel linear 400 mm long channels that cover
Figure 5.3: Schematic of the linear diagnostic cell setup with 10-fold segmented current and voltage measurement in either a single cell or a stack.

an active area of 200 cm$^2$ and a width of 50 mm. Channels and ribs have a width of 0.7 and 1 mm, respectively, and a depth of 0.55 mm. Sealing both against ambiance and between the gas manifolds is accomplished by PTFE gaskets with a thickness of 220 μm on either side of the membrane and additionally by a fluoropolymer elastomer (Viton, DuPont) string, 0.8 mm thick, in a 0.7 mm deep groove situated in the perimeter of the cathode plate (cf. Fig. 5.4 left). The PTFE sealings serve at a time also as spacers to ensure uniform compression of the GDLs and hence even contact resistance. Contact resistance is further minimized by polishing the graphite plates.

Figure 5.4: Scheme of the BPP of the linear cell. Left: View on the gas side of the air plate with groove for the sealing and design of the gas manifolding. Right: View on the back side of the H$_2$-plate integrated coolant flow field, the ribs for sealing with flexible graphite foil and the holes for gas sampling.

Stackability requires the distinct gas manifolds to form a continuous channel along the stack. To separate this channels from the gas room supplying the active area with the at a time other reactant ducts underneath the sealing are used$^3$. In bipolar plates these

$^3$Excellent reading on this constructive issue is provided in the Ph.D. theses of RUGE [78] and SCHMID [84].
ducts are integrated between its two parts. In terminal FFPs the ducts are machined into the current collector. Channels for liquid cooling are integrated into the back side of the anodic FFP (cf. Fig. 5.4 right for the last items). In the case of a BPP they are enclosed by the adjacent cathodic FFP; in the case of the anodic end a flat carbon plates between FFP and current collector provides the same. In either case the cooling flow field is sealed using expanded graphite sheets (Sigráflex, SGL carbon group) whose effect is enhanced by a pair of circumferential ribs on the back side of the anodic FFP that press into the sheets. This technique is described in Refs. [84, 85].

The segmented current collectors consist of copper plates with gold coating to reduce contact resistance and inhibit corrosion. The terminal plates at the in-/outlet region hold gas ducts and serve as spacers between end plate and FFP and do not carry current. Partial segmentation of the FFP for the reduction of leak current (cf. following Section 5.2.3) is realized by 1 mm deep grooves spanning the width of the active area on the back side of the plate. The electrically insulated aluminium end plates clamp together the entire sandwich using 26 screws tightened by a torque wrench. All parts are aligned by guiding rods. Besides internal cooling temperature control is additionally provided by heated water tubes attached to the endplates. The temperature is monitored by thermocouples inserted through the endplates into the FFP.

Figure 5.5 provides a schematic of the in-house built testbench with the air loop at the left side and the H₂ loop right-hand. Reactant feed is controlled by mass flow controllers (5866, Brooks, Netherlands) and humidified by passing it through heated water reservoirs. The humidified gas is fed to the cell through electrically heated tubes and gas humidification measured by humidity sensors (HMP 243, Vaisala, Finland) prior to entering the cell. For the sake of measuring water balances water in the exhaust air may be condensed in a cooled tube and collected in a strainer. For the individual supply of cells in a 2-cell stack both reactant supply systems are available twice. The cell is electrically controlled by an electronic load (ZS3606, Höcherl & Hackl) with integrated power supply for low voltage sources. Flow controllers and electronic load are controlled with the software LabView, the latter one interfaced via IEEE488.

5.2.2 Localized current and voltage measurement

Current density measurement has become a standard diagnostic tool in the recent years. Starting from first approaches by Stumper et al. [47] numerous methods for localized current measurement with different levels of sophistication are reported in the fuel cell literature [48, 49, 50, 51, 52]. All reported methods achieve in the best case a minimum resolution of the area from which one rib collects current, i.e. the rib and the two adjacent halves of the channels as sometimes exploited [86, 87]. This limitation was first overcome by our high resolution method presented in the preceding Chapter 4.
The most frequently used conventional low resolution method is an in some sort segmented current drain where the current in the single branches is measured using shunt resistors or Hall effect sensors. The degree of development ranges from first simple applications [47] to recently the most advanced setup by SCHNEIDER that allows for simultaneous local impedance spectroscopy [51]. Hall sensors bear the advantage over shunt resistors of the lowest possible series resistance, which is required to minimize leak current and the influence of the measuring equipment on the current distribution itself. Theoretical considerations on this aspect are given in the following section. The use of Hall sensors was introduced by WIESER et al. [49] by directly applying them into the FFP and has found further use in modified form in various further works [50, 55, 80, 51]. Another possibility is the use of a multi-channel potentiostat that controls the segment current in such a way that all segments show identical voltage. This eludes the need for the lowest possible branch resistances but requires an elaborate and expensive setup and restricts to potentiostatic operation. In spite of that this approach introduced by BRET et al. [63] is used by other groups, e.g. [88].

A totally different approach is taken by HAUER et al. [52] with magnetotomography that reconstructs the current distribution from its magnetic field in the ambiance of the cell. In contrast to all other methods this method is totally non-invasive and provides 3-dimensional current information. However, the spatial resolution is limited to centimeters and the time resolution to minutes due to the scanning process. Overall, the use of segmented current drains with the single branches measured by Hall sensors appears to be the currently most favourable setup for low resolution measurements.

Hall sensors rely upon the Hall effect that refers to the potential difference (Hall voltage) on opposite sides of a thin sheet of semiconducting material through which current is flowing, created by a magnetic field applied perpendicular to the Hall element. The magnetic field is induced by the current to be measured by passing it through a ferrite toroid that at a
time shields against stray magnetic fields.

There are two techniques in use in technical applications [89]. (i) In open-loop technology that the magnetic flux created by the primary current is concentrated in the toroid and measured in the air gap using a Hall device. The output voltage from the Hall device is then signal conditioned to provide an exact proportional representation of the primary current at the output. This voltage is amplified and provides the current proportional signal. (ii) With closed-loop technology the magnetic flux created by the primary current is balanced by a complementary flux produced by driving a current through secondary windings around the toroid. A Hall device and associated electronic circuit are used to generate the secondary (compensating) current that is an exact proportional representation of the primary current. That way the magnetic field is canceled and the Hall voltage vanishes. The output is provided by measuring the secondary current via the voltage drop in a precision shunt resistor. By canceling the field errors by offset drift, sensitivity drift, and saturation of the magnetic core as associated with the open-loop technology are overcome. In either case the output signal may be multiplied by wrapping the primary current lead around the toroid with a proportional gain per loop.

In the current setup closed loop Hall effect sensors (LAH 25-NP, LEM Switzerland) are used. The primary current conductor along with three possible windings around the toroid for appropriate gain is integrated into the device. Therefore, the sensor is connected in series in the current drain which introduces a small series resistance of 0.18 mΩ and 12 nH for the chosen gain of 1000:1, i.e. the ratio of primary to secondary current.

For dc measurements both the current proportional signals from the Hall sensors and the local cell voltages were recorded using a multiplexed data acquisition device (NI6033E, National Instruments). The setup for ac measurements is described in Section 5.2.4 below.

5.2.3 Theoretical considerations on current density measurements in segmented cells

A segmented cell is a parallel circuit of individual sub cells. Varying current and non-zero resistances causes different voltage drops in the single branches. Hence, when some part of the electronic conductors is not completely segmented down to the CL leak currents may appear between the branches. The measurement error due to leakage current for totally unsegmented FFPs was estimated with an analytical model by Andreaus [90]. He found even for large ratios of segment width and thickness considerable errors. However, to obtain an analytical solution drastic simplifications were necessary. A numerical solution is required to account for anisotropic GDL conductivity, partial or total segmentation, channel geometry, and additional shunt resistors to the knot.

Clearly, a fully segmented FFP reveals the lowest possible error as long as the GDLs are
not segmented as well. However, full segmentation of large and thin plates is very costly to manufacture. The possibility for only partly segmentation in the cell described in section 5.2.1 is therefore analyzed with a 2D numerical model that involves all above issues. Figure 5.6 shows the model domain consisting of GDL, FFP with variable segmentation depth and possible additional resistors. When the GDL remains intact the leak current is governed by the segment width and the resistance to the knot and grows with increasing current difference between adjoining segments. In Fig. 5.7 the relative error for a cell with linear current profile and measurement in two segments is shown as a function of the segment width. The FFP is 2 mm thick and either fully segmented or unsegmented and a constant additional resistor of 1 mQ may be added.

When no additional resistor is added the relative error tends to zero as the segment width is increased. Segmentation becomes in turn less important. As the voltage drop over a constant additional resistor increases with growing segment area and therefore the leak current grows from a certain minimum on. The position of the minimum is given by the resistor and shifts to bigger width with lower resistance.

Errors for the actual geometry of the test cell are calculated for different resistances in the drain in Fig. 5.8. The active area of the cell is 40 x 5 cm large and divided in 10 segments along the channel. In order to keep rigidity the 2 mm thick plate is segmented only 1 mm deep. The measured distribution in the single branches is compared to a given profile with a strong gradient in Fig. 5.8a. The corresponding potential distributions at active layer and current collector/FFP interface are shown in Fig. 5.8b. Besides inducing large errors in the measurement the strong potential gradients associated with large resistances also will change the current distribution itself. In the setup as described in Section 5.2.1 a
5.2. Advanced in-situ Diagnostics in a Model Cell of Technical Size

b) \[\begin{align*}
0.1 & \ 0.2 & \ 0.3 & \ 0.4 \\
\text{channel length [m]} & \text{active layer} & \text{current collector} & \text{FFP interface}
\end{align*}\]

Figure 5.8: Numerically estimated errors of the current measurement in the linear test cell. (a) Prescribed current profile and measured values in the single branches for different resistors. (b) The corresponding potential distributions at active layer and current collector/FFP interface vs current knot.

total resistance of 0.3 to 0.4 mΩ per branch is achieved. Regarding to Fig. 5.8, this ensures both negligible influence of the measurement on the current distribution and errors in the measurement.

5.2.4 Localized electrochemical impedance spectroscopy

Although localized current density measurement provides the distribution of local performance it does not provide insight into the underlying loss mechanisms associate with the transport of charge and matter. Electrochemical impedance spectroscopy (EIS) takes advantage of the differing time constants of ohmic, kinetic and mass transfer processes in order to separate them. Thereby, the system at steady state is perturbed with a small sinusoidal signal and the way it follows the perturbation is observed. Commonly the cell current is the perturbed and the voltage the observed dependent quantity while keeping all other parameters constant. However, any other variable of state may be perturbed while keeping either current or voltage constant.4

Cell impedance \(Z\) is calculated by

\[
Z = \frac{U_{\text{mod}}}{i_{\text{mod}}} 
\]  \hspace{1cm} (5.32)

with \(U_{\text{mod}}\) and \(i_{\text{mod}}\) being complex valued ac voltage and current. Extending on the pioneering work on EIS in PEFC by Springer et al. [91] numerous researchers have addressed issues regarding interfacial charge transfer, catalyst layer properties, and reaction mechanisms [91, 92, 93], humidification aspects [94], and mass transfer and flooding [91, 95, 51, 46, 96]. Consequently, there has been effort to expand EIS having these capabilities to a locally resolved method. Using a multi-channel potentiostat Brett et al. [97] reported the first work on a small scale PEFC. Recently Schneider [51] realized

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4We take advantage of this in Section 6.5, where we use a galvanostatic PEFC to detect sinusoidal feed gas concentration oscillations.
the method in a highly flexible device, which is, contrary to previous work, capable of handling even large scale cells and cells in a stack. All locally resolved EIS (LEIS) measurements reported in this work are measured jointly with Schneider using his setup as described in detail in [51] but modified to handle the large cell and segment currents.

The configuration relies on a cell with simultaneous local current and voltage measurement in low impedance single branches alike the segmented cell setup as described in Section 5.2.2 above. Its suitability for ac measurements was developed with Schneider. Differing from the configuration in [51] for dc measurements, where the cell is electrically controlled by a single electronic load (ZS3606, Höcherl & Hackl), an additional N3300A series load (N3304A, Agilent Technologies) is connected in parallel to carry a small part of the dc current and the ac current [96]. Sinusoidal perturbation is achieved by partly controlling the latter load with a sine wave generator. Segment currents are simultaneously measured by the Hall sensors. Both the current proportional signal and the segment voltage are measured by in-house built differential electrometers and analyzed by a 10-channel frequency response analyzer. Segment impedance $Z$ is obtained after discrete Fourier transformation of current and voltage [51]. The reason for separately measured segment voltage is improved accuracy. The uniformity of the ac modulation voltage throughout the cell is assured as far as possible by a very low inductive current drain to connect the single branches with the common load drain. Nevertheless possible remaining slight voltage differences are accounted for by this. Further on, local voltage measurement is required for LEIS in individual cells of a stack as measured in Chapter 7.

5.2.5 Neutron radiography

The conduction mechanism of the currently predominantly used per-fluoro sulfonated ionomer in PEFC requires sufficiently humidified feed gases to ensure good ionic conductivity. However, technically feasible air flow rates in fuel cell systems are not capable to completely remove all product water as vapour. Formed liquid water in turn is prone to impede gaseous mass transport in the fuel cell and to limit performance therefore. Consequently, the issue of liquid water formation in PEFC has been subject to various theoretical (e.g. [98, 33, 65]) and experimental studies (e.g. [99]). Experimental studies often employed optically transparent flow field plates, which, however, may impose considerable changes in terms of heat management and wettability as compared to technically us materials. Other than that, shock freezing after quick shut down of the working cells and weighting of the segmented MEA is used to determine local liquid content [100].

A method that avoids this requirement is neutron radiography. It was first introduced to PEFC at PSI by Geiger and Tsukada [101] in 2002 and later on turned into a practically useful, quantifiable method by Kramer et al. [102, 45]. Neutrons interact with light atomic nuclei such as $^1$H much stronger than with heavier nuclei of usual materials used
in FC housings and flow fields. Therefore, neutrons are suited for non-invasive detection of liquid water inside PEFCs.

All neutron-radiography measurements reported in this work are performed by Kramer at PSI's spallation neutron source SINQ using the radiography beamline ICON (Imaging with COld Neutrons) [103]. ICON employs cold neutrons that have longer wavelength (2...8 Å) than thermal neutrons (NEUTRA beamline at SINQ) and therefore have higher interaction cross section with protons. Hence, the spatial resolution and the signal-to-noise ratio is improved considerably. The cell is placed in the collimated neutron beam, which is attenuated by nuclei with high neutron interaction in the optical path. The attenuated local beam intensity is detected using a scintillator plate and a CCD-camera. High light intensity refers to low attenuation, whereas dark areas indicate high attenuation by mostly water [101]. Quantitative image evaluation requires referencing of the image intensity against images taken with the dry cell. Details on data treatment and quantification of neutron images as well as on the neutron source and the detector system are given in [102]. In this work neutron radiography is used in concert with other in-situ techniques in Section 6.6.
Chapter 6

Results from Modelling and Experiment on the Single Cell Level

6.1 Simulation of the Cell Internal Humidifier in PowerPac

In course of the joint PowerPac project between ETH Zürich and PSI a cell with 136 cm² active area and 22 cm² large internal humidification device for the process air was developed by Schmid et al. [78, 84] and characterized by Santis et al. [104, 105]. Here we make theoretical considerations on the dimensioning of this humidification device.

External devices require additional controls and energy for heating and enlarge the system through disintegration. Cell internal humidification in contrast scales with stack size and makes the system simpler, cheaper and more compact. In this project this is achieved by transferring water from the moist exhaust air through a membrane to the fresh air. Since the internal humidifier is a passive element, there is no possibility to regulate it according to the actual operation. Hence, its size has to be dimensioned for the best possible compromise covering a wide range of operating conditions especially in temperature and air stoichiometry. The section should be as small as possible to have a minimum impact on the weight and volume of the stack, but should be big enough to ensure sufficient humidification of the process air under a range of working conditions.

For simulating the device a simplified version of the model presented in Section 5.1.2 was used. Flow in the channels is considered by Eq. 5.14 with the exchange flux $N_w$ between the two sides of the membrane solely given by water diffusion through the membrane (last term in Eq. 5.2). Both co and counter flow operation are considered. Fig. 6.1 shows

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1Results shown here were presented in:

the local exchange flux and water partial pressures in the two streams for a counter flow device. As the local difference in partial pressure in the two streams is nearly constant for the counter flow case and the water diffusion coefficient in the membrane is strongly humidity dependent the exchange flux becomes maximal at the entrance of the humid cell exhaust.

As compared with conventional cells having external humidification the cell shows different reaction on stoichiometry and temperature [104]. (i) The voltage drops with growing stoichiometry. This is explained by Fig. 6.2a, where the resulting dew point is given as a function of humidifier area and stoichiometry. According to that, the humidifier area may be well below 20% of the active cell area without loosing effect. The insert in Fig. 6.2a shows $T_d$ vs. $\lambda$ for the realized fraction of 16%. (ii) An increase of temperature up to 70°C raises the cell voltage and decreases it strongly above. Fig. 6.2 gives the corresponding explanation for co flow (as realized) and counter flow. It is found that $T_d$ decreases from a certain temperature on. This is, because the amount of water for saturation increases exponentially with temperature, which may not be exchanged any more by the membrane for the possible humidity gradient between the two streams.

In conclusion, the model calculations appeared to be a useful tool for dimensioning of a passive cell internal process gas humidifier. Furthermore, the influence of operating conditions such as cell temperature and air stoichiometry, and the flow arrangement on the effect of the device could be rationalized. There appears to be an optimum air stoichiometry in terms of humidification efficiency and $O_2$ supply for the cell. Counter flow in the humidifier area appears to be superior as compared to co flow.
6.2 Isothermal Operation of Co and Counter Flow Regimes

The numerical model developed in the preceding Chapter 5 constitutes an efficient tool for the simulation of phenomena that appear along the flow path in PEFC. In this section the model is employed to investigate the basic flow arrangements of co counter flowing reactants. The influence of operating conditions such as feed gas humidities and stoichiometric ratios on the along-the-channel current density distribution is elucidated and the distinct underlying voltage loss mechanisms are identified. Furthermore, a complicated technical flow field is modeled by a combination of co- and counter-flow sub domains and compared with experimental current densities.

The base case operating conditions for the simulations shown in this section are given in Table 6.1.

### Table 6.1: Base case operating conditions for simulations of in-plane isothermal cells (this section 6.2).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>coolant temperature, $T$</td>
<td>343 K</td>
<td>dry gas relative humidity</td>
<td>0.2</td>
</tr>
<tr>
<td>H$_2$ stoichiometry, $\lambda_h$</td>
<td>1.5</td>
<td>moist gas relative humidity</td>
<td>0.8</td>
</tr>
<tr>
<td>air stoichiometry, $\lambda_{air}$</td>
<td>2.0</td>
<td>average current density, $j$</td>
<td>5000 A/m$^2$</td>
</tr>
<tr>
<td>total gas pressure, $p$</td>
<td>$2\times10^5$ Pa</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The salient difference between co and counter flow regimes arises from the possibility that water may exchange between the two gas streams through the MEA. Model predictions for the water transfer in terms of the effective drag, i.e. water molecules carried per proton

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2Results shown in this section were in part presented in:

are shown in Fig. 6.3. Since the relative humidities at adjacent points in the anode (\(\varphi_a\)) and cathode (\(\varphi_c\)) channel serve as boundary conditions for the sandwich model, the water transfer is shown as a function of those. A positive value means transfer of water from the anode to the cathode.

\[\text{Figure 6.3: Assessment of the sandwich model for the entire range of possible boundary conditions (relative humidities in anode channel } \varphi_a \text{ and cathode channel } \varphi_c \text{) at base case temperature and pressure. (a) Zero effective drag contour lines for different current densities (indicated in thousands of } \text{A/m}^2\text{) in a plane of anode and cathode channel relative humidities. (b) Effective drag contours for a current density of } 5000 \text{A/m}^2.\]

The upper graph depicts the current density dependence of conditions leading to zero flux. The diffusion term is dominant at small currents giving a contour line close to the main diagonal, whereas the drag term becomes dominant for high currents, which makes the flux virtually independent on the cathode condition. Water production at the cathode and its transport resistance towards the channel give rise to a fully saturated membrane at the cathodic interface already for an under saturated cathode stream. Consequently high conductivity of the membrane and insensitivity of the exchange flux to higher cathode saturation is observed. Therefore the regions in Fig. 6.3 where vertical contours occur indicate conditions where the membrane resistance depends mainly on the anode channel humidity. Hence, the range of sufficient air humidification extends with higher current.

### 6.2.1 Comparison of isolated co and counter flow regimes

An important feature of the presented model is the inclusion of heat transfer in the cell cross section where the reaction sites heat up with respect to the FFPs. This is important, because temperature has a prominent influence on all fuel cell processes. Fig. 6.4 compares the resulting current densities and the through-plane temperature distribution obtained for a totally isothermal cell and for a cell with consideration of the temperature profile. Results for a counter flow cell at 10 000 A/m² and base case conditions with dry hydrogen and moist air otherwise are shown. The higher current has been chosen in order to emphasize the
effect which is less pronounced for lower current. The observed change in the current density distribution with variation of the transversal temperature profile is caused by the preferential rise of the temperature at the membrane and reaction layers. Consequently, in areas of full saturation all processes are enhanced, whereas in under saturated areas the relative humidity and therefore the membrane hydration are even diminished. In all other simulations the temperature profile was considered. For the special case of fully humidified gases DJH.LAI and LU [106] observed a severe impact of thermal conductivities on gas and water transport which is in-line with our results.

Figure 6.4: Influence of through-plane temperature gradients on the local current density for a counter flow cell operated at 10000 A/m² and base case conditions with dry hydrogen and humid air otherwise. Curves for (a) a totally isothermal cell and (b) with inclusion of the through-plane heat transfer model are shown. The insert shows the temperature profile of (b) in the cross section, where the current density meets the average.

The difference between co and counter flow in terms of water management and subsequent local current production is shown in Figs. 6.5-6.7. Since moist conditions were specified as a relative humidity of 0.8 (corresponding to a dew point of 338 K at a cell temperature of 343 K) even humid gases enter the cell under saturated. In Figs. 6.5 and 6.6 along-the-channel water fluxes, local vapor pressure, current density and overpotentials for the case of moist air and dry hydrogen feed are drawn for both co and counter flow cells to compare the different behaviour of these two regimes with the same base case operating conditions.

The exchange of water from the moist cathode to the dry anode leads to a characteristic humidity minimum in the cathode channel after the inlet in the case of co flowing gases. For the conditions in Figs. 6.5 and 6.6 this does not lead to a depression in current density due to the shielding of the membrane by the GDL against drying out. However, for lower inlet humidities or lower average current densities the drying is also reflected in a local current minimum after the inlet as seen in Fig. 7a. In particular the porosity of the cathodic GDL plays an important role for these phenomena. On the other hand drying out due to dry hydrogen feed appears on the entire current density range as can be seen in Fig. 6.4 exemplarily for 10000 A/m². In contrast to the cathode side, electro-osmosis removes more water from the anode the higher the current climbs, and therefore a shielding of the anode side against a dry anode channel does not occur.

Generally, for the co flow it takes a longer fraction of the flow path to achieve fully
humidified gases as compared to the counter flow. Hence a bigger portion of the cell area produces less current, imposing more load to the remaining area. Additionally, in the co flow case the maximum membrane resistance is higher. In the case of counter flow there is enough humidity in the opposite gas to humidify the dry gas quickly and to restrict the drying to a smaller fraction of the cell area.

The water transfer remains negative (transport from cathode to anode) throughout the cell for base case conditions with dry hydrogen shown in Fig. 6.6a. Therefore the dry hydrogen is humidified by the moist air to a certain level. As Fig. 6.3 points out, a positive effective drag (from anode to cathode) will occur with rising current density for an increasingly under saturated anode stream. Therefore, a dry hydrogen feed becomes less humidified by a moist cathode side the higher the current density rises. This reflects the well known problem of anode drying at high current density operation [94, 55], which is usually overcome with increasingly thin membranes. Anode drying at high current densities can be avoided only partly by a saturated hydrogen feed since the hydrogen stream will be dehydrated due to water dragged to the cathode side by electro-osmosis.

The effect of oxygen depletion on the concentration polarization and consequently on the current density is illustrated in Fig. 6.6. After a peak current density is reached when optimal humidification is achieved the reaction rate drops with slightly increasing slope towards the air outlet.

The case of reverse humidification with dry air and humid hydrogen is examined in Fig. 6.7 where the local current is drawn for different total currents. For the co flow case (Fig. 7a), water transfer from the anode into the dry air results in a current minimum after the inlet up to an average current density of 10000 A/m², an effect, which is not observed in the counter flow case. The minimum disappears when the water production at the inlet is high enough in order that the water flux through the membrane becomes zero or negative, i.e. the humid hydrogen does not dry due to water transfer into the dry air. Similarly, the decline in current density in the counter flow case at the dry air inlet vanishes as soon as the water production rate there is high enough to yield a humidity gradient between cathode channel and reaction layer that is high enough to fully humidify the membrane at the latter site. Therefore, with increasing current the current density distribution becomes less governed by dry air but rather by oxygen depletion effects and membrane drying due to hydrogen dehydration.

6.2.2 The model in comparison with experimental results

The fit parameters of the model, the cathodic exchange and limiting current densities \( j_{\text{ref}} \) and \( j_i \) and the symmetry factor \( \alpha \) (cf. Section 5.1.2) as used in the results given above have been obtained from measurements with a cell containing an MEA with cloth type GDLs and MPLs an both electrodes. To examine the versatility of the model, further cell
6.2. Isothermal Operation of Co and Counter Flow Regimes

Figure 6.5: Along-the-channel distributions for co and counter flow cells operated at base case conditions with moist air and dry hydrogen. (a) Water fluxes inside the flow channels. Air is flowing in positive direction. Thin lines refer to co flow and bold lines to counter flow. Water vapor pressure at the indicated interfaces for (b) co flow and (c) counter flow.

Figure 6.6: Results for the same operating conditions as in Fig. 5 for co and counter flow cells. Thin lines refer to co flow and bold lines to counter flow. (a) Normalized current density and effective drag. (b) Local ohmic losses $\eta_R$ and mass transfer losses $\eta_{conc}$.

Figure 6.7: Influence of the average current density (indicated in thousands of A/m²) on the current distribution of (a) co and (b) counter flow cells operated at base case conditions with dry air and moist hydrogen. Air flows from left to right, hydrogen in the appropriate direction.

setups and extreme operating conditions are modeled without changing the fit parameters. Figure 6.8 compares such measured and simulated $j/U$ curves with MEAs made from (a) cloth and (b) paper in cells in co flow mode. The impact of the cathodic MPL on the performance with cloth is captured both under saturated and dry conditions in Fig. 6.8a. Slightly better performance is observed with cathodic MPL as water dragged by electro-osmosis towards the cathode is encounters higher resistance against removal to the air
channel and is retained better in the membrane. The validity of simulations for high temperature operation is shown in Fig. 6.8b for paper type MEAs equipped with MPLs on both sides. Membrane drying at 110 °C and dry feeds is slightly overestimated, whereas operation at 95 °C is matched remarkably well.

![Figure 6.8](image)

**Figure 6.8:** The effect of GDL material and MPLs with hot and dry cell operation. Comparison of experimental with simulated j/V-curves for a) cloth and b) paper backings.

Further validation is accomplished by comparing measured with simulated current distributions. Experimental current density data from Schnick et al. [107] obtained with pure hydrogen and oxygen and thicker membrane (Nafion 115) than used in the fit procedure, are compared with simulated curves in Fig. 6.9. The cell, a 30 cm² flow field with three parallel channels in nine meanders, is operated in co and counter flow mode with gases humidified to a relative humidity of 50%. Locally resolved impedance spectroscopy was employed for spatially resolved diagnostics, that enables for distinction of the different voltage losses [51].

The drying of the electrolyte, due to under saturated gases, is apparently the reason for the decrease of the current density towards the dry gas inlets. Although the extent of the drying is not fully captured by the model the deviation can be justified following the argumentation in Ref. [107]. Besides dehumidification of the membrane in the low performing region, an additional resistance was related to a drying of the catalyst layers and hence reduced catalyst utilization. This effect is not captured in the model, since the catalyst layers are not resolved.

### 6.2.3 Description of a technical flow field by a combination of co and counter flow regimes

Cells of technical relevance often consist of a combination of co and counter flow parts due to constraints in the positioning of the media manifolds. As an example the cell used in a fuel cell powered car [81, 108] with a roughly square active area of 200 cm² is taken
and simulated with the described numerical model. The flow arrangement is schematically shown in Fig. 6.10a. Each stream drawn there depicts a bundle of 13 parallel gas channels both on the anode and the cathode side. The total inlet streams from the manifolds at the upper corners split up into two half-streams. These half-streams enter either a counter flow section followed by a co flow section or vice versa before they meet at the outlet manifolds in the lower corners. Except for small cross flow sections in the corners, this arrangement can be described by a combination of interlinked counter flow (A+D) and co flow (B+C) regimes as shown in Fig. 6.10b. An attempt to model this precise flow field by the use of CFD was done by Greenway and coworkers [109] and had shown the difficulties that arise from the full 3D modeling of strongly coupled phenomena on a domain with a high aspect ratio. Furthermore, the CPU time for the CFD solution in the order of $> 300$ h imposes a tremendously higher effort for parameter studies as is possible with the model presented here, that is solved in roughly 5 min for this actual cell.

The calculation is accomplished as follows. Half of the inlet streams is taken as inlet into domain A, whose outlets serve at a time as one of the inlet streams into the domains B and C, respectively. The air (hydrogen) exit of domain B (C) in turn yields the inlets of domain D. Since iso-potential endplates are assumed, the calculation of the local current density is the same as for the simple domains.

Experimental data of the described cell were obtained with a current mapping technique based on a semi-segmented cathode endplate and unsegmented MEA as described earlier [81, 50]. The electrochemical components used were Elat-A7-Type E-Tek gas diffusion electrodes with a Pt loading of 0.6 mg/cm² and Nafion 112 as the membrane. The test cell was operated on a test bench with stoichiometric flow regulation in the constant current mode, with feed gas humidification control by humidity sensors. The cell temperature was controlled by integrated, water fed cooling jackets placed adjacent to both, the anode and cathode side. Measurement segments of 10 cm² size were placed in the corners at the gas in- and outlets as shown by the gray areas in Fig. 6.11a.

Comparisons between predicted and measured current densities in the four segments, shown in Fig. 6.10a, are provided in Fig. 6.11 as a function of air stoichiometry for fully
humidified gases. The four segments lie with respect to the relative area overflown by the air path from its inlet, from top to bottom, at the air inlet, at one third, at two third, and at the air outlet. Clearly, the starvation of oxygen content along the air path is evident with decreasing air stoichiometry. The model predictions of the second and third segment match the measured values within 2% on the whole range. While the segment at the air inlet deviates 5% at low stoichiometry, the segment at its outlet does so for stoichiometries of 1.4 onwards. Similar inaccuracies must be accounted for the measurement.

6.2.4 Conclusions

The numerical model developed in Chapter 5 has been validated and employed to assess the influence of operating conditions on the along-the-channel current density distribution and to identify the distinct underlying voltage loss mechanisms. The validation was done both with integral current-voltage curves and localized current distribution data, for the limiting cases of low humidification and low air stoichiometry. Arbitrary arrangements of relative hydrogen, air and coolant direction can be described. In this section the in-plane isothermal case was examined by applying quasi-infinite coolant flow on cells with co and counter flowing air and hydrogen. Due to its prominent influence on all fuel cell processes the incorporation of a heat transfer model in the through-plane direction is essential. As the salient differences in the along-the-channel current density distribution between co and counter flow cells arise from the possibility of water exchange between air and hydrogen through the MEA, special attention was paid to the modeling of the water transport in
membrane and GDLs. The comparison with validation data has shown, that the treatment of the catalyst layers as interfaces imposes limitations for cases with dry feed gases and high current density.

In addition to results for cells consisting of single co or counter flow regimes the possibility of combining sub cells to a more complex network is shown. This enabled to describe a complex technical cell with reasonable agreement to experimental local current data. The very fast computation time facilitates parameter studies of large scale PEFC tremendously as compared to CFD models.

6.3 The Influence of Cooling Strategy on Cell Performance

The last section was dedicated to the elucidation of inhomogeneities in large scale cells provoked by technically relevant operating conditions. Hence, the influence of feed gas humidities, stoichiometric ratios, load, and reactant flow direction has been investigated in detail. However, to keep the discussion concise, we have restricted ourselves to the idealistic case of a homogeneous temperature in the cell plane. This section addresses the implications of in-plane temperature gradients that additionally occur in realistic operation due to limited coolant flow.

In addition to the restrictions of reactant mass flow and humidification, limitation of the fuel cell system parasitic power also limits the coolant flow. This results in in-plane temperature gradients that significantly influence all processes in the cell. In particular the relative humidity of the reactants is strongly temperature dependent. This alters both the water uptake of the membrane and hence its conductivity and the water vapor carried in the saturated reactant streams, leading to strong in-plane gradients. Regarding the issue of thermal management in PEFC first basic work was done in early mathematical models of Nguyen and White [70] and Fuller and Newman [69] which account for energy conservation in the gas streams but assume the solid parts isothermally. Consecutive approaches of CFD-based fuel cell models increasingly included thermal aspects ranging from detailed studies of through-plane heat transfer by Djilali and Lu [106] to more dimensional models [65, 66, 33, 39]. In all of them in-plane temperature gradients are only apparent within the scope of isothermal outer surfaces of the cell.

Issues of liquid cooling on in-plane heat management are addressed experimentally in the patent literature by Ballard Power Systems [110] and theoretically with focus on heat exchange between coolant and plates by Senn et al. [111].

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3Results shown in this section were in part presented in:
In Section 6.3 we analyze the influence of in-plane (along-the-channel) temperature gradients on the local and overall FC performance. These temperature gradients are governed by the interaction of the coolant flow direction and rate relative to the reactant flow and local current production. Therefore a range of flow rates, feed humidifications, cell currents and flow arrangements is examined using the aforementioned 1+1D model. The model is able to describe both domains with parallel (co flow) and anti parallel (counter flow) flowing fuel and oxidant streams. Therefore, arbitrary flow arrangements of fuel, oxidant and coolant stream directions can be described. In terms of possible cooling strategies in fuel cell systems, regulation to constant flow or temperature difference and to constant inlet or outlet temperature, respectively, are examined. Besides the influence on the overall cell performance the underlying local impacts are studied.

6.3.1 Linear temperature profiles and model validation for non-isothermal cases

Along the channel temperature profiles that arise from the heat up of coolant on its way through the cell are governed by the local heat source, i.e. the current distribution, which is in turn seriously influenced by the temperature. Before we turn to temperature profiles that arise in such a way from liquid cooling, we look into the effect of linear temperature gradients. For that, the capability of the diagnostic cell described in Section 5.2.1 for impressing temperature profiles is employed. MEAs were manufactured using ETEK ELAT V2.1 gas diffusion electrodes (0.6 mg Pt/cm², 20 wt% Pt/C) for both anode and cathode and Nation 115 membrane. PTFE gaskets 250 μm thick were used to seal the cell.

Figure 6.12 shows measurements with H₂/air in counter flow mode at 1 bara pressure and stoichiometries of λ_H₂/air = 1.5/2. H₂ enters dry from the right side and air with variable humidity from the left side. In the upper row the temperature rises linearly from 65 to 75°C, in the lower row the profile is in the opposite direction. Corresponding j/U-curves are given in Fig. 6.13, where data for isothermal operation and the two aforementioned temperature profiles are compared for each humidification.

As the gases stream in counter flow mode the influence of local temperature on the drying at the respective inlets may be studied. Dry fed H₂ humidifies in either case within a short portion of the flow path. This shows clearly that although having a rather thick Nafion 115 membrane water can relatively easily be exchanged between cathode and anode. However, extrapolation suggests nearly vanishing current right at the H₂ inlet, in particular in the case of elevated temperature there. For all cases except d) shown in Fig. 6.12 H₂ reaches most likely high saturation for at least part of the area. Out of the cases with rising

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4As it was shown in the previous Section 6.2 H₂ hardly ever reaches full saturation due to electro-osmosis. This becomes more pronounced with growing current.
6.3. The Influence of Cooling Strategy on Cell Performance

Figure 6.12: Current density distribution for counter flow operation with dry hydrogen and variously humidified air at different total current. Air enters from the left side. Upper row: temperature rises along the air path from 65 to 75°C (a)-(d)). Lower row: inverse profile with decline from 75 to 65°C (c)-(h)). Air humidification $\varphi_{\text{air}}$ decreases along the rows. Air feed humidity regarding inlet temperature is given in each graph.

temperature profile along the air path a) and b) reveal no current drops at the air inlet since widely saturated conditions appear. In case c) air saturates after a short fraction of the flow path, which becomes apparent by the slight decreasing slope in the middle of the cell that indicates O$_2$ depletion at saturated conditions. This does not appear in case d).
The $j/U$-curves in Fig. 6.13 show only slightly worse performance of cells with elevated temperature at the dry H$_2$ inlet as compared to isothermal ones.

The opposite situation with high temperature at the air inlet and its drop downstream underscores the predominant influence of air humidity as compared to H$_2$ humidity (Fig. 6.12c

Figure 6.13: Comparison of the cell performance for the cases shown in Fig. 6.12 compared with the respective isothermal operation. $\varphi_{\text{air}} = a) 100\%$, b) 75\%, c) 50\%, d) 25\% @ 70°C.
to h). Water production along with dropping temperature causes a steepening increase of current along the flow path. Since high saturation in the outlet region enhances membrane conductivity current production becomes more and more confined there with decreasing air humidity. In turn the extend of the low current region grows as well as the peak current value does. Along with high resistance at large fractions of the cell and high peak currents the cell performs more and more worse with increasing current as compared with isothermal operation or opposite temperature profile. Furthermore, none the examined non-isothermal cases with constant mean temperatures shows significantly better performance than the isothermal case.

In contrast to the idealized linear profiles studied so far liquid cooled cells show a more complicated profile as mentioned above. When attempting to emulate this temperature profiles in single cell experiments utmost attention has to be paid to thermally insulate the endplates, where in a cell in the stack environment other cells would attach. Much easier than in the experiment this thermal symmetry boundary condition may be applied to a numerical model. Therefore, we use the model described in Section 5.1 to further examine cooling strategies. It has already been validated in the preceding Section 6.2 with local current density data obtained under in-plane isothermal conditions both in a cell in co and counter flow operation and in a cell consisting of a combination of those regimes. In addition to that further validation against data obtained in a cell with strong in-plane temperature differences is provided in Fig. 6.14. For that both data for counter flow as already shown in Fig. 6.12a and c and co flow are used. These conditions are chosen to cover a wide range of phenomena involved and already discussed above, i.e. membrane dehydration both from under saturated air and hydrogen and areas with fully saturated conditions at a time as well as co and counter flow operation. Generally, the model predictions agree well with the experimental data and clearly reflect the main trends.

Figure 6.14: Comparison of measured (symbols) and calculated (lines) current densities for (a) co and (b+c) counter flow cells operated with dry hydrogen and air humidified to \( T_d = 70\,^\circ\text{C} \) at 3000 and 5000 A/m². The temperature drops along the air path from 348 to 338 K in (a) and (b) and rises in opposite direction in (c), respectively. Data in (b) and (c) are taken from Fig. 6.12a and c.
Regulation modes in FC systems.— In FC systems various regulation modes of the cooling system are thinkable. The most simple arrangement keeps the coolant flow constant which results in increasing temperature differences between its in- and outlet with growing current density. Another possibility is the regulation of the flow in the way that the temperature difference is kept constant. In both cases the temperature may be constant at the coolant inlet or outlet, which results in a raise of the temperature at the outlet or its decline at the inlet for rising temperature differences. Furthermore, these strategies may be combined in a way that both local cooling and heating counteract the predominant limiting processes there. I.e. cooling at dry inlets and heating at wet outlets may be coupled while keeping the mean temperature constant.

Regarding the relative flow direction of the reactants, these may flow either in parallel (co flow) or anti parallel (counter flow) manner. The same holds true for the coolant flow direction, which may flow in or against the direction of the air. Since in the given coordinate system air flow is always in positive y-direction (see Fig. 5.1) the coolant flow direction is referenced to the air stream and denoted as positive or negative, respectively. In the following, the above described cases of flow regulation and reference temperature are analyzed for their influence on overall and underlying local cell performance. As base case operating conditions air is fed at a dew point of 50 °C and hydrogen fully humidified (relating to a relative humidity of 0.4 / 1.0 in relation to the coolant regulation temperature of 343 K / 70 °C).

The base case operating conditions for the simulations shown in this section are given in Table 6.2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coolant regulation temperature, $T$</td>
<td>343 K</td>
<td>Hydrogen dew point, $T_{lh}$</td>
<td>70 °C</td>
</tr>
<tr>
<td>$H_2$ stoichiometry, $\lambda_h$</td>
<td>1.5</td>
<td>Air dew point, $T_{d,air}$</td>
<td>50 °C</td>
</tr>
<tr>
<td>Air stoichiometry, $\lambda_{air}$</td>
<td>2.0</td>
<td>Average current density, $j$</td>
<td>5000 A/m²</td>
</tr>
<tr>
<td>Total gas pressure, $p$</td>
<td>$2\times10^5$ Pa</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.3.2 Constant coolant flow

For the case of constant coolant flow with constant temperature at its inlet, the temperature rises increasingly towards the coolant outlet with growing current density. The resulting polarization curves for co flowing reactants and a constant coolant flow of 0.1 or 1.0 kg/m²s and positive or negative coolant direction are drawn in Fig. 6.15 together with a closer look on the underlying local current density and coolant temperature. In order to elucidate the combined effects of rising temperature and membrane dehydration the curve for a cell operated with saturated gases and quasi-infinite coolant flow is shown as well.
Coolant flowing in parallel with the dry air raises the temperature at the moist air outlet and facilitates the reaction there. Hence, the load at the dry inlet is further diminished, the more the temperature rises with current. Therefore, at sufficiently high current, the performance comes close to that of a cell operated isothermally but moist, as apparent in the curves with positive coolant flow (Fig. 6.15a). However, if the temperature mounts as high as necessary to keep all product water gaseous the membrane becomes under saturated in the entire cell, which results in growing ohmic losses. This becomes true for the example of 0.1 kg/m²s coolant flowing in positive direction from 11000 A/m² onward.

For coolant flowing in negative direction the temperature reaches a maximum at the dry air inlet and consequently shifts the load to regions downstream in the air path (see dashed lines in Figs. 6.15a to c). Hence, the cell voltage drops the more, the higher the maximum temperature rises with decreasing coolant flow and growing current.

In Fig. 6.16 the effect of the coolant mass flow rate on the cell voltage for co and counter flow cells each with positive and negative coolant flow direction is shown. As discussed earlier the cases with positive direction perform better than those with negative flow. Counter flow cases show better performance in either case. This is because there the air is humidified faster than in the co flow case due to transport of water from the moist air outlet towards the inlet with the hydrogen stream, as discussed in Section 6.2. Therefore, the fraction of the active area, where the membrane is saturated, is greater. Besides a generally better performance level, a counter flow cell also behaves differently with decreased coolant stream; for positive direction the elevated temperature is able to keep the voltage and for the negative direction the sharp decline at little flows is attenuated.

![Figure 6.15: Comparison of calculated polarization curves for the co flow configuration with parallel and anti-parallel flowing coolant at base case conditions.](image)

(a) The distinct polarization curves for 1 and 0.1 kg/m²s of cooling water compared with an isothermal cell and wet reactants. (b) The current density distributions at 5000 A/m². (c) Local coolant temperature for the four cases.
6.3. The Influence of Cooling Strategy on Cell Performance

Figure 6.16: Dependence of the cell potential on the coolant flow for co and counter flow cells with coolant flowing in positive and negative direction at base case conditions.

6.3.3 Constant temperature difference

Regulation of the coolant mass flow for a constant temperature difference of 10 K is examined in Fig. 6.17 for its influence on the polarization curve. The results are in-line with the findings discussed above. The fostered case of a counter flow cell with coolant flowing in parallel with the air shows the best performance over a wide current range. Compared with the operation at constant coolant flow an increase in performance is observed in the range below 1 A/cm² for the case with all media in parallel due to higher temperature in moist regions of the cell.

Figure 6.17: Current-voltage characteristics of co and counter flow cells operated at base case conditions with a constant heat up of the coolant of 10 K.

In Fig. 6.18 the sensitivity of different arrangements on the applied temperature difference is shown. For base case conditions (Fig. 6.18a) heat up of the cell at the air outlet slightly raises the performance for the counter flow case and keeps it nearly constant for the co
flow. Besides the generally higher performance level of the first one, the main difference between co and counter flow again becomes apparent when the cell temperature is raised at the inlet of the dry gas (negative flow direction).

If the gases are fed drier, a growing temperature difference causes in either case a performance decline (Fig. 6.18b). Figure 6.18 illustrates that restrictions in gas humidification and coolant flow, which stem from system efficiency concerns call for careful considerations of the flow arrangement. Especially when operated on dry gases, the performance is substantially governed by the way of cooling; e.g. for the cases shown in Fig. 6.18b unfavorable conditions result in a relative voltage drop of almost 30% compared to the best case.

### 6.3.4 Nominal temperature at coolant inlet versus outlet

Up to now, the special case of constant temperature at the inlet of the coolant was examined. Hence, the average temperature grew under all conditions. However, in a fuel cell system under practical operation this may not be the chosen mode of operation. Therefore, another limiting case is studied where the outlet of the coolant is held constant and hence the inlet temperature adjusted appropriately. The difference in the reaction of the cell on those two possibilities on temperature difference is elucidated by means of a co flow cell at base case conditions with coolant in positive direction in Figs. 6.19 and 6.20.

Constant inlet temperature leads to a temperature growth towards the moist air outlet. As already discussed in the section that treats constant coolant flow, the temperature towards the air outlet can reach a value where the entire product water is kept in the gas phase and the membrane nowhere reaches full saturation (see e.g. thin full line in Fig. 6.15a). Therewith the membrane resistance increases due to dehydration. For the cases shown in Fig. 6.19 this is reached with a temperature difference of 15 K and higher. The respective relative humidities in the air channel are drawn in Fig. 6.19c. With increasing heat up, the fraction of the cell area with saturated air becomes smaller, the humidity more equal on a lower level and the load therefore distributed more homogeneously but resulting in decreasing cell voltage (see Fig. 6.18a).

If the coolant outlet is held constant its temperature drops at its inlet when the flow is diminished. For the case of positive coolant direction this means that air which is fed undersaturated in relation to the constant coolant outlet temperature approaches saturation with dropping temperature at the coolant inlet when entering there. The respective relative humidity in the air channel is plotted in Fig. 6.20c. Because of water production at the cathode catalyst layer, the cathode-membrane interface reaches higher humidity than the air in the adjacent channel. Therefore, slightly undersaturated air in the channel does not dry the membrane, and does hence not affect the local current density as apparent for temperature differences of 10 K and upward in Fig. 6.20a. The dependence of the cell
voltage on the temperature decrease at the dry air inlet, which is shown in the insert in Fig. 6.20c, gives a better view on this phenomena. As soon as the air reaches a relative humidity at its inlet that does not affect the membrane any more, the cell voltage depends only on the temperature and drops with declining temperature.

Clearly the cell performance may be boosted when the dry gas inlets are cooled towards their saturation temperature and heating up of the coolant is allowed in downstream parts of the cell which are already saturated by the product water. For the case of co flow operation, this arrangement is obviously effective when both gases are fed dry. In counter flow cells the same effect can be achieved by an appropriate slightly more complicated arrangement with distributed coolant inlets at the gas inlets.


6.3.5 Conclusions

Both the numerical model and the cell described in Chapter 5 has been employed to examine the influence of gas flow and coolant flow arrangements. In-plane temperature gradients are found to be able to either enhance the cell performance or show detrimental effects, mainly when under saturated gases are fed. Generally the performance of a cell operated on under saturated gases with respect to the local cell temperature at the respective inlet leads to voltage losses due to locally increased membrane resistance. Hence, the performance can be increased by adjusting the local cell temperature in a way that the local gas humidity becomes as high as possible at dry inlets and higher temperatures occur downstream in the reactant flow where the gases are saturated by the product water. Also the temperature should not climb as high in the downstream region to avoid drying due to excessive heat up.

6.4 Homogenization of the Current Density by In-Plane Cathode Catalyst Gradients\(^5\)

In the preceding section possibilities to beneficially counteract local drying at gas inlets and flooding in downstream regions by means of temperature inhomogeneities caused by cooling strategy have been explored both experimentally and theoretically. It was shown, that enhancement of power can be achieved by removing spots of increased overpotentials. By that, current peaks in remaining regions with both high membrane conductivity and oxygen fraction are diminished and the load distributed more homogeneously. Since electrochemical resistances grow strictly monotonously with current also reduction of current in the latter regions increases power. Besides avoiding membrane drying steering the temperature also may abate the danger of GDL and electrode blocking by liquid water. The issue of liquid water in turn arises from the need for low stoichiometric ratios. This in turn causes itself inhomogeneous current distribution when operating the FC with air. Therefore, even when operation is optimized in terms of membrane humidity and the liquid water issue, there remain major power losses due to slow O\(_2\) reduction kinetics and additionally depleted oxidant in downstream regions. Along with performance concerns the question of life time degradation due to elevated current at the inlet comes into play. Santis addressed the issue of inhomogeneous current due to O\(_2\) depletion in his Ph.D. thesis [80] and in a related publication [83] by means of inhomogeneous cathode catalyst loading. As homogenization of the current distribution is expected to increase power and lifetime, catalyst is redistributed to counteract the current drop along the air flow path. Therefore, a stepped profile has been applied with a decreased loading at the air inlet and an

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\(^5\)Results shown in this section were part of:

increased one at the outlet while keeping the overall Pt amount unchanged at a value of 0.6 mg Pt/cm$^2$ in average. Within the scope of the present work the experimental findings have been modeled in order to identify the role of the distribution of overpotentials on the observed effects. This section will discuss the obtained theoretical results in accordance with Ref. [83] after summarizing the experimental findings there.

6.4.1 Summary of experimental results

Conversely with the expectation that homogenization by an increasing catalyst loading enhances power, previous work in the literature [112, 113] reports the opposite effect. Increased cell performance was reported by using cathodes with decreasing catalyst loading along the air flow path, i.e. higher loading at O$_2$ rich regions. Such catalyst profiles lead to a strongly non-uniform current distribution. To examine this option also such a loading has been investigated. Effects of membrane resistance are excluded by fully humidified feed gases in all experiments.

It is vital for meaningful results that the average electrochemical active area scales with catalyst loading. This is not necessarily ensured because growing catalyst loading on the same amount of carbon is prone to foster agglomeration effects of the metal particles, which would decrease the active area per mass of catalyst. To ensure that the active area of the used CLs scales with loading hydrogen under potential deposition measurement [114] was used to determine the active surface and found to be in very good agreement with the expectations. Four loading profiles have been used: standard (STD, 0.6 mg Pt/cm$^2$), weak (WP, 0.5..0.7 mg), medium (MP, 0.4..0.8 mg), and negative medium profile (MP$^{-}_m$, 0.8...0.4 mg).

Catalyst redistribution has shown strong impact on the current distribution, with the expected effect of homogenization with growing loading along the channel and increased slopes with the inverse profile MP$^{-}_m$. Inhomogeneities, expressed in terms of standard deviation of current distribution, grow with decreasing $\lambda_{\text{air}}$ for STD and MP$^{-}_m$ profile, whereas all profiles with growing loading reveal a clear minimum in the region $1.2 < \lambda_{\text{air}} < 2$. The position of the minimum shifts the higher in $\lambda_{\text{air}}$ the higher the current and the weaker the catalyst gradient. Nonetheless, in terms of power the STD profile was superior among all profiles on the entire stoichiometry and current range. Surprisingly, the cell power diminished the more the stronger the catalyst gradient was. Furthermore, the direction of the gradient did not have an influence on power as MP$^{-}_m$ and MP performed practically equally.

The obtained results show that, surprisingly, current density homogenization by means of catalyst redistribution does not seem to have a beneficial effect on power output of the cell, although having strong impact on the current distribution. To bring light in the underlying reasons for these results, modelling calculations are carried out.
6.4.2 Theoretical results

For the present case the model described in Section 5.1 with quasi-infinite cooling flow, is employed. The exchange current density $j^0$ has been a fit parameter to experimental $j/U$ curves obtained with a homogeneous loading of 0.6 mg Pt/cm$^2$. Varying catalyst loadings are accounted for by a proportional change of the active catalyst surface and therefore the local exchange current density. In contrast to the experiments, where stepped catalyst gradients were employed, in the model continuous linear gradients are simulated. Also the total active catalyst area can easily be held constant. For continuously changing catalyst loading, the catalyst distribution is described by the dimensionless parameter $\beta$ that tunes the local exchange current density $j^0,\ref$ by

$$j^0,\ref = (1 + \beta - 2\beta \frac{x}{L}) \cdot j^0,\ref \quad \text{with} \quad \beta = 1 - \frac{j^0,\ref}{j^0,\ref} \quad (6.1)$$

where $j^0,\ref$ is the value for 0.6 mg Pt/cm$^2$ and $\beta = \frac{1}{2}$. Therefore, a homogeneous electrode has $\beta = 0$, and an electrode with a linearly increasing catalyst loading has a $\beta = 0.5$, when the start loading is half the average and the loading at the end is 1.5 times the average. For the WP cathode $\beta = 0.17$ and for the MP and MP$\_\text{neg}$ cathodes $\beta = 0.33$ and -0.33, respectively. Therefore, $\beta < 0$ denotes decreasing loading. Calculations were performed for fully saturated gases for 2 bara gas pressures, 70°C cell temperature, an average current density of $3.9 \times 10^3$ A/m$^2$ and $\text{H}_2$ and air in counter flow arrangement. For the ETEK electrodes a thickness of 300 µm, a porosity of 0.68, and a tortuosity of 3 were used for the calculations.

Figures 6.21a and b provide current distributions for $\lambda_{\text{air}}$ between 4 and 1.2 both for STD and MP cathodes. Like in the described experiments the current distribution is turned around a center point by doing so with the catalyst loading. Quantitative comparison with measured current distributions given in Fig. 6.21c for points close to in- and outlet prove very reasonable correlation between measurement and simulation. The STD cathode is closely reproduced, while for graded cathodes the model overestimates the current gradient to some extent. This could partly be because of the difference between the stepped profile in the measurement and the smooth one in the model. Nonetheless, the correlation renders the model semi-quantitatively valid for interpreting the cell performances as function of parameter $\beta$.

As for experimental current distributions [83] the homogeneity of the profiles can be expressed in terms of standard deviation of current distribution. It is plotted against $\lambda_{\text{air}}$ for the three basic cases (STD, MP, MP$\_\text{neg}$) in Fig. 6.22a. Homogeneous catalyst distribution and decreasing catalyst gradient do not show a minimum, confirming the experimental results. For stoichiometries lower than 3 the MP cathode leads to more homogeneous current than the STD cathode.

Like aforementioned, both the MP and MP$\_\text{neg}$ profiles show experimentally similar per-
6.4. Homogenization of the Current Density by In-Plane Cathode Catalyst Gradients

Figure 6.21: Simulated current density distributions for (a) STD ($\beta = 0$) and (b) MP ($\beta = 0.33$) cathode. (c) Correlation between simulated and measured current densities at $x/L = 0.03$ (in) and $x/L = 0.97$ (out) with STD, WP and MP at $\lambda_{\text{air}}$ as partly given in (a) and (b).

performance although leading to highly different current distributions. Therefore, the effect of magnitude and direction of the gradient on performance is examined in Fig. 6.22b for stoichiometries well below and above the intersection point between STD and MP in Fig. 6.22a. The data is plotted as the voltage difference to the homogeneous STD cathode as $\Delta U(\beta) = U(\beta) - U(\beta = 0)$. As suggested by the experiment the maximum performance is close to $\beta = 0$.

The voltage differences are for all gradients only in the mV-range, even though the current distributions were found to be heavily changed on that gradient-range. The simulated voltage differences are considerably smaller than those found in the experiments at the same current density. It seems probable that the stepped catalyst profiles in the experiment, as compared to the smooth profiles in the calculation are responsible for this difference.

Figure 6.22: (a) Standard deviation of the current density distribution for STD ($\beta = 0$), MP ($\beta = 0.33$) and reversed MP ($\beta = -0.33$) cathodes. (b) Change of cell voltage with catalyst gradient $\beta$ for $\lambda_{\text{air}} = 4$ and $\lambda_{\text{air}} = 1.5$.

An inspection of the underlying overvoltages at $\lambda_{\text{air}} = 1.5$, as provided in Fig. 6.23, clarifies this finding. In Fig. 6.23, data for the distributions of the current density (taken from Fig. 6.21a+b) and the respective overvoltages are given for the STD ($\beta = 0$) and MP ($\beta = 0.33$) cathodes. The current density distribution for the MP cathode is significantly more homogeneous. To examine the contribution of the single overvoltages on the power change as shown in Fig. 6.22b first changes in power loss vs. the STD profiles are calculated via $\int_{0}^{L} (j \cdot \eta)^{\text{STD}} \text{d}L - \int_{0}^{L} (j \cdot \eta)^{\text{MP}} \text{d}L$. This unveils that the intended effect of reducing the concentration polarization $\eta_{\text{conc}}$ is achieved both on the most part of the cell as well as overall. Smoothing out current peaks also reduces the overall ohmic losses $\eta_{R}$ due to
reduced anode drying therewith. However, gains in those two losses are lost by increased charge transfer overpotential. The net change is $-2.22 \text{ W/m}^2$ for the shown results.

Figure 6.23: Comparison of the distribution of current and underlying voltage losses for STD and MP cathodes at $\lambda_{\text{air}} = 1.5$. (a) Current distribution, (b) ohmic and concentration polarization, and (c) charge transfer overpotential.

The underlying local changes in power losses between STD and MP profile are provided in Fig. 6.24. The majority of changes appear in the inlet region, where losses by concentration and ohmic polarization are reduced but overcompensated by the charge transfer losses due to reduced catalyst loading.

Figure 6.24: Change of local charge transfer, concentration, ohmic, and overall polarization between the STD and the MP catalyst loading profile.

6.4.3 Conclusions

In summary it has been shown that a homogenization of the current density in PEFCs working at air stoichiometries below 2 can be achieved through a non-uniform distribution of the catalyst along the air channel. The gradient needed to homogenize the current distribution best is dependent on stoichiometry. However, no increase in cell performance was observed by homogenization of the current density. The modelling results confirmed the experimental findings and explain the lower performances obtained with the cells with the tailored cathodes. The integral losses increase with the magnitude of the catalyst loading gradient independent on its direction. For this reason no performance increment
can be achieved by catalyst redistribution under the studied working conditions. Previously reported performance improvements due to catalyst redistribution could not be confirmed. It seems probable that the reported improvements were due to other factors such as differences in the properties of the catalyst layer. Nevertheless, it might be possible to increase the lifetime through a homogenization of the current density distribution by equally utilizing the active area of the cell, since areas of accelerated degradation due to operation at significantly higher currents than average can be avoided.

6.5 Low Frequency Behaviour of H₂/Air Cells with Electrochemical Impedance Spectroscopy

Most of the preceding part of the thesis was concerned with lateral inhomogeneities in the cell which become generally apparent in terms of current density distribution as it is closely linked to all other transport phenomena. Using the model insight could be gained into the underlying loss mechanisms. However, to get experimental insight into the loss mechanism electrochemical impedance spectroscopy (EIS) may be applied in addition to localized current measurements. EIS uses the differing time constants of ohmic, kinetic and mass transfer processes in order to separate them. Mass transfer as the slowest of these processes is reflected in the low frequency features of the spectra. Detailed understanding of all features in the spectra, however, are prerequisite for gaining the information from EIS measurements.

The low frequency capacitive arc that appears with air-fed cells is commonly assumed in the literature to stem from diffusive mass transport through the MEA. Hereby, finite (Nernstian) diffusion confined to the thickness of the GDL is accounted for in models published in the scientific literature [91, 95, 115]. These models were able to fit measured spectra by using – unrealistically – low diffusivities or high thicknesses of the GDL. Pioneering work in localized EIS by Brett et al. [97] has even shown negative resistive loops at downstream positions under low air stoichiometry which, however, could not possibly be explained with the mentioned models.

In order to develop a comprehensive physical picture of the phenomena that cause low frequency capacitive arcs in the EIS spectra of air-fed PEFC SCHNEIDER designed a meaningful experiment [96]. This experiment proves local current perturbations to cause O₂ concentration oscillations in the channels, which further on affect both subsequent local spectra downstream and the integral spectrum. Therewith, finite diffusion could be disproved and the formation of both positive and negative resistive low frequency arcs com-

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prehensively explained based on the uncovered physical processes. Schneider developed the concept, experimental design and interpretation. The experiments were performed jointly with the cell presented in Section 5.2.1 owing to its suitability for localized EIS. All results and discussions are adopted from [96].

6.5.1 The experimental setup

Local impedance measurements [46, 107] were performed in the linear PEFC described in Section 5.2.1 by using the measurement setup of Schneider for locally resolved EIS described earlier [51]. Differing from the setup described there, the load setup was changed to cope with the high cell currents. In addition to the N3300A series load (N3304A, Agilent Technologies) as used in Ref. [51] for ac and dc current, another electronic load (ZS3606, Höcherl & Hackl) was connected in parallel to carry the main part of the dc current. To assure a uniform ac modulation voltage throughout the cell a very low inductive current drain was developed to connect the single branches with the common load drain.

Membrane electrode assemblies were manufactured using ETEK ELAT V2.1 gas diffusion electrodes (0.6 mg Pt/cm², 20 wt% Pt/C) for both anode and cathode and a Nafion N112 membrane. PTFE gaskets 250 μm thick were used to seal the cell. The cell was operated with air at $T_{cell} = 70 \degree C$ in co-flow mode using air stoichiometries of $\lambda_{air} = 1.2, 1.67$, and $2.5$ and a hydrogen stoichiometry of $\lambda_{H_2} = 1.5$. Both gases were humidified to a dewpoint of $T_{dp} = 80 \degree C$ and fed to the cell by using pipes heated to $80 \degree C$ and causing the gases to be at the same temperature at the inlet.

All impedance measurements shown here were performed in a frequency range of $f_{mod} = 100 \text{mHz} - 10 \text{kHz}$ (10 pts./dec.) in galvanostatic operation mode ($i = 100 \text{A}$) with $i_{mod} = 2 \text{A}$ modulation amplitude if not mentioned otherwise. Integral spectra were calculated from the respective locally resolved impedance spectra.

Additionally taken local $j/U$ curves were taken in galvanostatic mode with constant gas flow. During the measurement the gas flow rates were kept at a constant level corresponding to stoichiometries of $\lambda_{air} = 1.2, 1.7$, and $2.5$ and $\lambda_{H_2} = 1.5$, all at $100 \text{A}$.

A second $30 \text{cm}^2$ square cell with parallel flow field was assembled using a MEA manufactured from ETEK ELAT LT W140E-W gas diffusion electrodes (0.5 mg Pt/cm², 30 wt% Pt/C) for both anode and cathode and a Nafion N1135 membrane. Channels and ribs of the flow field had a width of 1 mm, respectively, and a depth of 0.5 mm. The flow field plates were made from 1 cm thick Diabon NS2 (SGL carbon group). This cell was sealed by 250 μm PTFE gaskets.

The purpose of this small cell is to provide a galvanostatic sensor for oxygen concentration in the outlet of the large cell during EIS measurement. Oscillations of the oxygen concentration in the cathode exhaust gas induce a voltage perturbation in the galvanostatic
sensor cell. Therefore, the cathode inlet of this cell (in the following called sensor cell) was connected to the cathode outlet of the main cell by using a heated pipe. The setup is schematically shown in Fig. 6.26a. Hydrogen from the test bench ($T_d = T_H = 80 \°C$) was fed to the anode gas inlet in counter flow mode. The temperature of the sensor cell was like the large cell kept at 70 °C. The sensor cell was operated at constant current $i_{sensor}$ by a second load. At any given air stoichiometry $i_{sensor}$ was adjusted to equalize $U_{sensor}$ with the dc cell voltage $U_{cell}$ of the large cell.

The voltage of the sensor cell was measured using SCHNEIDER's setup for locally resolved EIS [51]. Therewith, phase and amplitude of $U_{sensor}$ vs. ac modulation voltage $U_{mod}$ of the main cell during EIS could be measured.

### 6.5.2 Proving and explaining the impact of channel oscillations on spectra

Previous literature concerning ac impedance in PEFC reported that the size of low frequency arcs increases with decreasing air stoichiometry $\lambda_{air}$ [95]. In fact, integral cell spectra taken at $\lambda_{air} = 2.5, 1.7,$ and 1.2 provided in Fig. 6.25 exhibit the same behaviour. A low frequency capacitive arc starts to evolve at a modulation frequency of $f_{mod} = 7.9 \ Hz$ for all air stoichiometries and increasing diameter with decreasing stoichiometry. However, to get a more precise understanding of its origin beyond the interpretation that it would be solely caused by mass transport limitations in the GDL, the underlying phenomena are unveiled in the following.

![Figure 6.25: Integral impedance spectra of the H₂/air PEFC taken at $\lambda = 1.2, \lambda = 1.7, \lambda = 2.5,$ and $\lambda_{H₂} = 1.5$. Adopted from [96].](image)

**Proving O₂ concentration oscillations in the flow channels**

The O₂ concentration oscillations in the CL induced by the sinusoidal perturbation during EIS measurement spread out towards the channel with decaying amplitude because of
diffusive transport resistance [3]. If this decay is steep enough to confine the oscillations in the GDL no concentration perturbation is encountered in the channels. However, a sinusoidal ac voltage could be detected in the galvanostatic sensor cell during EIS in the main cell at modulation frequencies below \( f_{\text{mod}}=10 \text{ Hz} \). The frequency of \( U_{\text{sensor}} \) matched the frequency of \( i_{\text{mod}} \) in this frequency range. The detector signal is exemplarily shown for \( \lambda_{\text{air}} = 1.67 \) and a frequency of \( f_{\text{mod}} = 3.97 \text{ Hz} \) in Fig. 6.26. It must be attributed to \( \text{O}_2 \) concentration oscillations in the exhaust of the perturbed main cell.

Lessons learned.— From the findings shown in Fig. 6.26 three conclusions about the processes occurring in the \( \text{H}_2/\text{air} \) PEFC during an EIS measurement can be drawn.

1. Oxygen concentration oscillations are not confined to the GDL. The decay of the concentration perturbations at the electrode towards the reactant reservoir is frequency dependent and reaches further with decreasing frequency [3]. Therefore, the magnitude of perturbations in the channels is frequency dependent as examined later on in Fig. 6.27.

2. Forced convection in the flow channels carries concentration oscillations caused by local current perturbation downstream. The progression of this oscillation depends on local phase and amplitude of the modulation current.

3. Ac voltage \( U_{\text{sensor}} \) induced in the sensor cell by concentration oscillations must be considered also to be induced at any other position within the perturbed cell. This concentration induced voltage \( U_c \) contributes locally to the modulation voltage \( U_{\text{mod}} \).
By recalling the definition for the local cell impedance

$$Z = \frac{U_{\text{mod}}}{i_{\text{mod}}}$$

(6.2)

with $U_{\text{mod}}$ and $i_{\text{mod}}$ being complex valued ac voltage and local current, we can furthermore rationalize the influence of a concentration oscillation - inducing $U_c$ - on the impedance for general cases. In a properly designed cell, the ac modulation voltage $U_{\text{mod}}$ is equal in phase and amplitude along the flow field, no matter if the total cell is perturbed in potentiostatic or galvanostatic mode [51]. Local ac current $i_{\text{mod}}$ is therefore governed by local $Z^7$ and $U_{\text{mod}}$ and not subject to control by the EIS setup. From conclusion 3) SCHNEIDER deduced and further proved in [116] that $U_{\text{mod}}$ is partly composed of a concentration oscillations related part $U_c$. Only the remaining part $U_i$ is contributed by $i_{\text{mod}} = Z/U_i$. During EIS measurement only $i_{\text{mod}}$ and $U_{\text{mod}} = U_{\text{meas}} = U_c + U_i$ are accessible, but not the single contributions. Therefore, the measured impedance

$$Z_{\text{meas}} = \frac{(U_c + U_i)}{i_{\text{mod}}}$$

(6.3)

deviates from $Z$ as it would be obtained without concentration oscillations by $U_c/i_{\text{mod}}$ [116].

Factors governing the concentration oscillations.— Before turning to the consequences of $U_c$ for the local spectra its build up is explored. Like aforementioned the decay rate of concentration perturbations through the GDL is frequency dependent. In turn the magnitude of oscillations in the channel as well as the downstream induced $U_c$ is frequency dependent. $U_c$ is measured in terms of $U_{\text{sensor}}$ in the galvanostatic sensor cell. Figure 6.27 shows the ratio $U_{\text{sensor}}/U_{\text{mod}}$ in dependence on modulation frequency $f_{\text{mod}}$ and air stoichiometry in the main cell and the phase shift between $U_{\text{sensor}}$ and $U_{\text{mod}}$.

![Figure 6.27: Frequency response of the detector cell](image)

The amplitude ratio $U_c/U_{\text{mod}}$ increases with decreasing modulation frequency, whereas the phase shift between $U_c$ and $U_{\text{mod}}$ disappears at low frequencies ($f_{\text{mod}} < 100\, \text{mHz}$). In

$^7$Note that $Z$ is here the value as it would be measured if no concentration oscillations would be present in the channel.
addition, the ratio $U_c/U_{mod}$ is larger at lower $\lambda_{air}$, i.e. lower dc oxygen concentrations. Therefrom, one may conclude that $U_c/U_{mod}$ increases monotonously along the air path as $O_2$ is successively depleted. Oxygen depletion in turn is governed by air stoichiometry as it becomes also apparent in the appropriate current density distributions given in Fig. 6.28.

Influence of $O_2$ oscillations in the channel on local spectra – a mechanistic model

Figure 6.29a to c provides the local spectra according to the integral ones in Fig. 6.25, the frequency response in Fig. 6.27, and the current distributions in Fig. 6.28.

The local spectra increasingly gain in diameter downstream for $\lambda_{air} = 2.5$. Like in the integral spectra the a low frequency arc builds up below 7.9 Hz. For lower stoichiometrics a negative resistive low frequency loop appears. This was earlier shown by Brett et al. [97] also for segments near the air outlet at low air stoichiometry. Its intercept with the real axis near dc was correlated with the slope in the equilibrium point of the local $j/U$-curves obtained at constant gas flow [97, 64]. This correlation is also given in our measurements for all segments at any given air stoichiometry (Fig. 6.29a-c vs. Fig. 6.29d-f). However, the underlying physical processes were not further identified in the pioneering work of Brett et al. [97].

Model considerations along the channel.—— The above results and discussion give strong evidence that the ac voltage $U_c$ induced locally by the oxygen concentration oscillation evokes the formation of the low frequency arc in impedance spectra of $H_2/air$ PEFCs.

The above proven build up of concentration oscillation induced voltage $U_c$ along the air flow path can explain the evolution of the low frequency part of the local impedance spectra shown in Figs. 6.29a–c, even without a mathematical treatment. For the sake of simplicity, the discussion is performed for low modulation frequencies, i.e. the local ac
6.5. Low Frequency Behaviour of H2/Air Cells with Electrochemical Impedance Spectroscopy

\[ b) \lambda = 1.7 \]

\[ d) \lambda = 2.5 \]

\[ e) \lambda = 1.7 \]

\[ f) \lambda = 1.2 \]

Figure 6.29: (a – c) Locally resolved impedance spectra taken at (a) \( \lambda_{\text{air}} = 2.5 \), (b) \( \lambda_{\text{air}} = 1.7 \), and (c) \( \lambda_{\text{air}} = 1.2 \) at \( i_{\text{cell}} = 100 \) A in a frequency range of \( f_{\text{mod}} = 100 \) mHz – 10 kHz (10 pts./dec.), \( i_{\text{mod}} = 2 \) A

(d – f) Local \( j/U \) curves recorded at constant flow. The gas flow rates correspond to \( \lambda_{\text{H2}} = 1.5 @ 100 \) A for all curves and (d) \( \lambda_{\text{air}} = 2.5 @ 100 \) A, (e) \( \lambda_{\text{air}} = 1.7 @ 100 \) A, and (f) \( \lambda_{\text{air}} = 1.2 @ 100 \) A. (g) Scheme used for the discussion of the low frequency characteristics of the local impedance spectra along the flow field of a H2/air PEFC for five discrete probing locations S1 to S5. The insert on the right shows the corresponding local spectra. Adopted from [96].

current \( i_{\text{mod}} \) is assumed to be either in phase (\( \phi \approx 0^\circ \)) or out of phase (\( \phi \approx 180^\circ \)) to the modulation voltage \( U_{\text{mod}} \). Moreover, \( U_c \) and \( U_{\text{mod}} \) were shown in Fig. 6.27b to be in face near dc.
We recall the earlier findings on the formation of $U_c$ along the channel and on the therewith measurable local impedance $Z_{\text{meas}} = (U_c + U_i)/i_{\text{mod}}$ as given in Eq. 6.3. This we apply to several discrete positions S1 to S5 along the channel under the assumption of an air stoichiometry low enough to cause an outlet segment to show a negative resistive loop (cf. Fig. 6.29c). Figure 6.29g provides a schematic for the visualization of the discussed correlations and quantities. Since the probing positions are discrete ac current there does not contribute to the local concentration perturbation in the channel but only to downstream positions.

According to the scheme in Fig. 6.29g, the oxygen concentration is constant at the air inlet (S1). In this case, solely the ac voltage $U_i$ induced by the local ac current $i_{\text{mod}}$ contributes to $U_{\text{mod}}$. However, the local contribution of $U_c$ induced by the local oxygen concentration oscillation increases downstream along the cathode flow field channels from S1 to S3. As $O_2$ is cumulatively depleted the dc $O_2$ concentration $c$ decreases towards the air outlet. In addition, the local amplitude of the oxygen concentration oscillation $\Delta c$ in the gas channels grows as locally generated concentration oscillations accumulate downstream (S1 – S3). Because of $Z_{\text{meas}} = (U_c + U_i)/i_{\text{mod}}$ (Eq. 6.3) the measured impedance in S2 and S3 is already influenced by $U_c$. As long as $i_{\text{mod}}$ and $U_c$ are out of phase $\Delta c$ is in phase with $U_c$ and we find $U_c < U_{\text{mod}}$ and therefore increased impedance. At the same time this causes $\Delta c$ to grow on the same part of the cell. This amplification effect by $U_c$ blows up the local impedance values for S2 and S3 at low frequencies and becomes larger towards the air outlet. Since $i_{\text{mod}}$ and $U_c$ are out of phase the low frequency part of the spectrum is on the positive real axis. For the quasi–dc case this coincides with the finding that the intersection with the real axis is determined by the slope of the local $j/U$ curve (cf. segment 1–5 in Fig. 6.29f).

The concentration oscillation $\Delta c$ grows as long as the induced voltage $U_c$ equals $U_{\text{mod}}$ (S4). Along with that, both $i_{\text{mod}}$ and $U_i$ virtually vanish and impedance $Z_{\text{meas}}$ tends to infinity at low frequencies as well as the radius of the arc does. Hence, a virtually vertical line is observed in the local spectrum (cf. S4 in the insert in Fig. 6.29g).

The ratio of $\Delta c/c$ determines the ratio $U_c/U_{\text{mod}}$. By moving further down the channel from S4 dc current lowers $c$ even without $i_{\text{mod}}$ there. This causes $U_c$ to exceed $U_{\text{mod}}$ in the downstream probing position S5. Hence, ac voltage $U_i$ that drives the ac current $i_{\text{mod}}$ gets out of phase with $U_{\text{mod}}$. Consequently, $i_{\text{mod}}$ and $U_{\text{mod}}$ are in phase, which yields a negative low frequency real part of the local spectrum in S5 (cf. insert in Fig. 6.29g). Again the intersection with the real axis is determined by the now positive slope of the local $j/U$ curve (cf. segment 6–10 in Fig. 6.29f).

The discussion so far points out that there are no differences in the underlying physical processes leading to the formation of a low frequency negative or positive resistance loop. In either case there is an ac voltage $U_c$ caused by upstream perturbations and reducing the ac voltage $U_i$ to be lower than the modulation voltage and therewith amplifying
the impedance. It merely indicates the ratio $U_c/U_{\text{mod}}$ to be either smaller one (positive resistance loop) or larger than one (negative resistance loop).

**Application of the model on the measured spectra.**— The scheme in Fig. 6.29g can be used to explain the low frequency characteristics of the local spectra observed experimentally at different air stoichiometries in Fig. 6.29a-c. Whereas the probing positions S1 to S5 in the above discussion were discrete, measuring segments in the segmented cell have finite extension. However, each of the 10 segments can be treated analogously to the discrete positions, when $U_c$ in the segment is predominantly determined by the upstream entering gas stream. Hence, $i_{\text{mod}}$ at the beginning of the segment has negligible influence on $U_c$ in the segments' remainder.

At high air stoichiometry of $\lambda_{\text{air}} = 2.5$ (Fig. 6.29a) the oxygen depletion along the cathode flow field is rather small. The ac voltage $U_c$ locally induced by the oxygen concentration oscillation does not exceed the modulation voltage $U_{\text{mod}}$ along the air path ($U_c/U_{\text{mod}} < 1$). Hence, the modulation voltage $U_{\text{mod}}$ and the local ac current $i_{\text{mod}}$ are out of phase along the flow field and the real part of all local impedance spectra is positive (Fig. 6.29a+g).

At a lower air stoichiometry of $\lambda_{\text{air}} = 1.7$ (Fig. 6.29b) and higher $O_2$ depletion along air path, the locally induced voltage $U_c$ reaches values close to the modulation voltage $U_{\text{mod}}$ within the outlet segment 10. In this case ($U_c \approx U_{\text{mod}}$) a nearly vertical line is observed in the spectrum of segment 10 (Fig. 6.29b+g).

At an even lower air stoichiometry of $\lambda_{\text{air}} = 1.2$ (Fig. 6.29c), $O_2$ depletion along the air path suffices to amplify $\Delta c/c$ as much that $U_c$ exceeds $U_{\text{mod}}$ for segments 6 to 10. Hence, the low frequency arcs of these segments turn to the negative real axis (cf. Fig. 6.29c+g).

**The role of modulation amplitude.**— We conclude the discussion by raising the question if a smaller modulation amplitude will diminish the amplitude of the concentration oscillation and by this minimize the coupling along the cathode flow field via the gas phase.

To clarify this, we applied total modulation currents of $i_{\text{mod}} = 1 \text{ A}, 2 \text{ A}, 5 \text{ A}$ in a frequency range of $f_{\text{mod}} = 100 \text{ mHz} - 10 \text{ Hz}$ (10pts./dec.) to the segmented 200cm$^2$ cell at any given air stoichiometry ($i_{\text{cell}} = 100 \text{ A}$). The sensor cell was operated during the impedance measurements. In addition to the local cell impedance, the respective ratio $U_c/U_{\text{mod}}$ and phase shift between these signals $\varphi$ was determined for any given modulation amplitude $i_{\text{mod}}$ and air stoichiometry $\lambda_{\text{air}}$.

A variation of the modulation current amplitude $i_{\text{mod}}$ will indeed affect the amplitude of the oxygen concentration oscillation and by this the amplitude of the induced ac voltage $U_c$. However, the modulation voltage $U_{\text{mod}}$ is affected in the same way. The ratio $U_c/U_{\text{mod}}$ and the phase shift $\varphi$ do not vary with the modulation current amplitude $i_{\text{mod}}$ over the whole
frequency range \( (f_{\text{mod}}=100 \text{mHz}-10 \text{Hz}) \) as is exemplarily shown for an air stoichiometry of \( \lambda=1.7 \) in Fig. 6.30. Correspondingly, no difference could be observed in the low frequency range of the respective local or integral impedance spectra, when the modulation amplitude was changed.

![Figure 6.30: Frequency response of the sensor cell (setup shown in Fig. 6.26a) at \( i_{\text{cell}} = 100 \text{A} \) \( (U_{\text{cell}} = 652 \text{mV}, U_{\text{sensor}} = 652 \text{mV} \@ 4.8 \text{A}), \lambda = 1.7, f_{\text{mod}} = 1 \text{A}, 2 \text{A}, 5 \text{A}. \) (a) log gain = \( 20 \cdot \log(U_c/U_{\text{mod}}) \), (b) \( \varphi = \varphi(U_c) - \varphi(U_{\text{mod}}) \). Adapted from [96].](image)

**Continuative work.**— So far the magnitude of the \( U_c \) in relation to \( U_{\text{mod}} \) has been specified by a back consideration from its effect on \( U_i \) and therewith the impedance. In principle, \( U_c \) could be measured for the exit segment using the mentioned galvanostatic \( O_2 \) sensor cell. Consequently, \( U_c = U_{\text{sensor}} \) should be roughly equal to \( U_{\text{mod}} \) for the measurement at \( \lambda_{\text{air}} = 1.7 \), where the outlet segment shows a nearly vertical line at low frequencies. However, the measured ratio \( U_c/U_{\text{mod}} \) as given in Fig. 6.27 is too small. This can mainly be attributed to the different materials used in the sensor cell.

The response of the sensor cell during the impedance measurements (Fig. 6.29a-c) is shown in Fig. 6.27a for the frequency range below \( f_{\text{mod}}=10 \text{Hz} \). It is clearly seen in Fig. 6.27a that the amplitude ratio \( U_c/U_{\text{mod}} \) increases at lower air stoichiometries \( \lambda \), which is in agreement with the discussion. However, the absolute values of the logarithmic gain are too small.

To overcome this problem the experimental setup shown in Fig. 6.26a has been modified jointly with SCHNEIDER by integrating the electrically insulated galvanostatic \( O_2 \) sensor into the last segment of a segmented linear FC. The results therefrom given in SCHNEIDER et al. [116] have shown full agreement with the scheme presented in Fig. 6.29g as discussed above by matching materials and geometries. In conjunction with that KRAMER et al. [117] developed for the first time a mathematical PEFC impedance model that incorporates also local coupling along the channel and allows therefore to qualitatively match local and integral spectra as measured in air-fed PEFC.

### 6.5.3 Conclusions

Oxygen concentration perturbations by current perturbations during EIS measurements have been proven not to be confined to the GDL. At least below modulation frequencies of 10 Hz \( O_2 \) concentration oscillations occur in the channel, which further on affect both
subsequent local spectra downstream and the integral spectrum. Therewith, the formation of both positive and negative resistive low frequency arcs could be comprehensively explained based on the uncovered physical processes.

6.6 The Impact of Average Current on Charge/Mass Transfer and Water Balance – A Combined LEIS, Neutron Radiography, and Modeling Study

In Section 6.2.1 the influence of operating conditions such as feed humidities, stoichiometric ratios, flow arrangement, and total current on the along-the-channel current distribution was analyzed theoretically. This revealed a major impact of total current on the water balance between anode and cathode owing to electro-osmotic drag. Being the production site of water, the cathodic CL acts as the water shed in the cell (cf. also [30]). The wetting state and water transport properties of the adjacent media – the membrane and the cathodic GDL – govern the opposed fluxes toward anode and cathode channel. Increasing current raises the wetting state in the vicinity of the cathodic CL due to growing resistance against efflux through the membrane and therefore steeper water gradients toward the cathode channel to enable for water drainage. Hence, growing current density has severe impact on membrane humidity. First, the membrane becomes increasingly shielded against dry air channels owing to the steeper water gradient as shown in Fig. 6.7 (p. 79). Second, electro-osmosis fosters ionomer drying in the anodic region (cf. also [94, 55]).

Comprehensive experimental investigations of these phenomena call for detection of liquid water in the media along with measuring current density, membrane resistance, and the impact of liquid on gaseous transport on a local scale. This combination was introduced by SCHNEIDER and KRAMER using a H₂/O₂ cell [46]. The results revealed that poor ionic conductivity in the CL layer may be as detrimental as the effect of bulk membrane drying. Furthermore, the presence of a certain amount of liquid water was found to be necessary for optimum function of the cell, i.e. maximum local current was found downstream from the onset of liquid phase. For H₂/O₂ cells the hindrance of O₂ diffusion by liquid water has shown to have a low impact on performance as compared to the impact of membrane drying.

This section addresses these issues of drying and liquid water formation in an air-fed PEFC in co flow mode at different current densities. Therefore, current density measurement is simultaneously applied with LEIS and neutron radiography in cooperation with SCHNEI-

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8Results shown here were partly presented in:
and will be presented in more detail in
DER and Kramer. To get deeper insight into water management a simplified version of the model described in Section 5.1 is applied to calculate underlying water fluxes in the cell based on the measured current distribution.

6.6.1 Experimental

The cell and local electrochemical impedance spectroscopy (LEIS) setup for this investigation was identical to that used in the previous section as described in Section 6.5.1 (p. 98) except for the absence of the sensor cell. The cell was operated at stoichiometries of $\lambda_{\text{H}_2} = \lambda_{\text{air}} = 2$ at a cell temperature of $T = 70^\circ\text{C}$ with a humidification of $T_d = 59^\circ\text{C}$ ($\varphi = 61\%$) for both gases.

Other than in the earlier simultaneous LEIS and neutron radiography experiments by Schneider and Kramer [46], PSI’s neutron radiography beamline ICON at the spallation neutron source SINQ was used instead of the NEUTRA beamline. LEIS measurements were performed in-situ and contemporaneously to the radiography measurements at this facility. The cell was placed in the collimated neutron beam. It was moved to multiple measurement positions using a precision linear bearing stage to cover the whole active area, which is larger than the measurement window of ICON. Details on the neutron source, detector system, and the quantitative image evaluation are given in [102].

6.6.2 Water balance calculations

Water balance calculations are performed using the transport model described in Section 5.1. The current distribution is taken from the measurements instead of calculating it from the local conditions using Eq. 5.24 (cf. Numerical implementation in Section 5.1.2, p. 59). Therefore, emphasis was on the progression of water fluxes both in the channels and their exchange through the MEA. Additional inaccuracies due to possibly deviating calculated current distributions are avoided therewith.

6.6.3 Results & Discussion

Figure 6.31 provides the measured current distribution, high frequency (ohmic) resistance, and liquid content along the flow path for average current densities of 100, 250, 500, and 750 mA/cm$^2$. Additionally, the referenced neutron radiogram of the entire active area and parts of the outlet region obtained with 500 mA/cm$^2$ is shown. Bright and dark regions refer to dry and flooded regions, respectively [102].

Inhomogeneous current density in along-the-channel direction occurs due to membrane drying at the inlets, reactant depletion towards the outlets, and product water formation.
6.6. The Impact of Average Current on Charge/Mass Transfer and Water Balance

Drying of the ionomer is reflected in decreased current density (Fig. 6.31a) and elevated resistance (Fig. 6.31b) at the inlet. Along with the formation of product water, which eventually condensates, the membrane resistance decreases and causes the current density to grow to a maximum somewhat downstream the onset of liquid phase. The appearance of the liquid phase in the free pore volume of the GDLs is indicated by a liquid volume of more than $\sim 13 \text{mL/m}^2$, which refers to the water content of saturated Nafton 112 membrane. As soon as minimum membrane resistance is reached the local performance is governed by $\text{O}_2$ depletion and therefore declining current density towards the outlet.

There is a clear dependence of the position of the onset of liquid phase and associated minimum in membrane resistance and maximum in current density on the average current density. This is because of the above mentioned superposition of electro-osmotic drag and screening of the membrane against drying by the cathodic GDL. This superposition causes in turn the membrane resistance to drop with increasing current before it raises with even higher current due to anode dehydration by electro-osmosis. Figure 6.32 reflects this both for the local and integral resistance.

**Figure 6.31:** (a) Current density, (b) high frequency resistance (5 kHz), (c) and liquid content along the channel for co flow operation at different average current densities. $\lambda_{\text{air}} = \lambda_{\text{H}_2} = 2$, $T = 70^\circ\text{C}$, $T_{\text{in}} = 59^\circ\text{C}$ ($\varphi = 61\%$). (d) Reference neutron radiogram obtained with $500\text{mA/cm}^2$.

**Figure 6.32:** Dependence of local and integral high frequency resistance (5 kHz) on the average current density. Segment number from air inlet is indicated by the numbers.
Anode dehydration with increasing current is furthermore suggested in the maximum liquid amount reached (Fig. 6.31c). GDL materials have been shown to be able to hold a maximum amount of liquid (KRAMER et al. [102], ZHANG et al. [45]). Furthermore, liquid at anode and cathode cannot be discriminated in the used radiography setup. Liquid does not seem to reach a stable value with 100 mA/cm². However, the decreasing maxima in liquid content for current densities of 250 mA/cm² upward strongly suggest that liquid water at the anode side that seems to be present at 250 mA/cm² is gradually removed with growing current.

To further rationalize the shift of liquid onset model calculations are used to predict the water fluxes in the cell. Figure 6.33 shows both membrane resistances for comparison with the measured ones and local effective drag coefficients in the membrane, which indicates direction and relative strength of water exchange between anode and cathode. The onset of liquid water predicted by the model and measured by neutron radiography as well as the position of the peak current is given in Fig. 6.34. The model slightly overestimates membrane drying by dry feed gases, but clearly captures increased minimum membrane resistance with growing current and the onset of saturated conditions with good correlation⁹.

The higher water production rate with growing current causes the earlier onset of saturated conditions in two ways: (i) efflux to the cathode channel is increasingly hindered, which

⁹Minimum calculated membrane resistances are slightly lower than the measured ones due to additional ohmic resistances in the CL and electron conductors.
causes liquid to build up before the channel is saturated. (ii) The therewith boosted water gradient over the membrane provokes higher flux from anode to cathode relative to product water formation (i.e. the effective drag, cf. Fig. 6.33b) which accelerates humidification of the anode side. That way the local membrane resistance at the inlet sinks with growing current but increases again when electro-osmosis becomes dominant above 750 mA/cm² (Fig. 6.32)

The offset between the first occurrence of liquid phase and the peak current may be explained similarly: A certain amount of liquid is necessary to force enough water towards the anode to reduce membrane resistance to a minimum. This is not fulfilled with the first appearance of liquid. The same behaviour was observed with a H₂/O₂ cell (SCHNEIDER et al. [46]).

Figure 6.35 provides the local spectra at frequencies between 5 kHz and 100 mHz (10 pts/dec.) for the different current densities. Corresponding integral spectra and local spectra of segment 1 (inlet) and 10 (outlet) are compared for the current densities in Fig. 6.36.

Figure 6.35: Evolution of the local spectra along the channel for co flow operation at different average current densities. Segment number from inlet is denoted by the numbers.

The progression of the high frequency arc, which indicates charge transfer resistance,
unveils again the superposition of product water formation and O₂ depletion along the channel. Ionomer drying in the CL along with bulk membrane drying impairs the protonic connection to a fraction of the present active catalyst sites. This increase of overall voltage loss throughout the CL has been shown experimentally (Andreaus et al. [94]) and theoretically (Eikerling [30]). However, comprehensive experimental prove was given by Schneider et al. [51, 107] using LEIS in a H₂/O₂ cell. Reduced voltage drop in the membrane at dry regions as compared to fully saturated regions was shown to be compensated by strongly increased charge transfer resistance, i.e. expanded diameter of the high frequency arc. In turn this diameter became smallest at saturated regions. Its decrease from the inlet to the onset of saturation is also observed in Fig. 6.35. It becomes particularly clear for small current but is present for all currents.

Decrease voltage drop at dry regions as compared to better humidified regions is similarly to [51] and [107] (both H₂/O₂) also given for here as shown in Fig. 6.37. However, for the present air-fed cell this becomes only apparent for the first two to three segments. Further downstream O₂ depletion appears to govern charge transfer polarization partly already before full membrane saturation is reached. This suggests that superimposed hindered proton conduction and mass transfer contribute both to a high extend to overall charge transfer losses in the region between maximum ohmic drop and the onset of minimum membrane resistance (cf. Fig. 6.31b and Fig. 6.37).

Since the EIS measurements were performed between anode and cathode their respective contribution cannot be assigned. However, measurements of the half cell impedances by using a pseudo reference electrode have shown that both the HOR and ORR interfacial kinetics may significantly contribute to overall charge transfer resistances (Kuhn et al. [93]). Therefore, also the anode humidification level becomes crucial for charge transfer losses. The role of anodic processes on the high frequency features in spectra taken between anode and cathode was thoroughly discussed on a local level in [107]. After passing a minimum near the maximum current density the diameter of the high frequency arc grows with oxygen depletion due to diffusion losses in the CL [120, 29]. However, as discussed above O₂ depletion must already before a decisive contributor to this diameter. Decreasing charge transfer resistance with increasing current as particularly seen in Fig. 6.36a and b reflects Butler-Volmer characteristics.

The experiments discussed in the previous Section 6.5 have unveiled the implications of O₂ concentration oscillations on the low frequency features of the spectra. Local spectra conceal therefore both contributions of upstream perturbations and of local mass transport resistance. Hence, increasing diameter of the low frequency arc along the flow path may not be accounted to increasingly hindered mass transfer in simple way. However, as the stoichiometries are kept constant the O₂ depletion along the channel is equal for all currents. Its increasing diameter with current, as pointed out in Fig. 6.36c for the outlet segment 10, may yet be attributed to augmented O₂ concentration through the GDL. In
6.6. The Impact of Average Current on Charge/Mass Transfer and Water Balance

Figure 6.36: Integral and local spectra for different current density as indicated. (a) Integral spectra, (b) spectra of segment 1 at the inlet, (c) spectra of segment 10 at the outlet.

Figure 6.37: Local ohmic drop calculated from measured current density and high frequency resistance (5 kHz).

In fact, the slope with which the ohmic drop sinks along the channel and therefore charge transfer losses grow increases with growing current as shown in Fig. 6.37. This assumption is further supported by the appearance of a small second capacitive low frequency arc at the higher currents (Fig. 6.36b). How far blockage by liquid water, however, contributes to that cannot be concluded from the presented data set.

6.6.4 Conclusions

Motivated by results in Section 6.2 issues of drying and liquid water formation in an air-fed PEFC in co flow mode at different current densities were addressed. Current density measurement was simultaneously applied with localized electrochemical impedance spectroscopy and neutron radiography. To get deeper insight into water management the numerical model developed in Section 5.1 was applied to calculate water fluxes in the cell. The measurements revealed a strong impact of cell current on the superposition of membrane drying at the inlet and O₂ depletion towards the outlet on the current density distribution. Proof for that comes from the evolution of features in local spectra both along the flow path and with growing cell current. In concert with the model results, increased wetting in the vicinity of the cathodic CL due to shielding vs. the dry gas channel and higher electro-osmotic drag effect could be corroborated as the reason for falling resistance close to the gas inlet with growing current. Growing current in turn was shown to provoke
successive dehydration of the anode region both by abating liquid content and growing resistance. The analysis of the local spectra in concert with the local ohmic polarization verified earlier model and experimental results in the literature, which assign both to mass and charge transfer within the CL a crucial role for cell performance.

6.7 Conclusions

In this Chapter inhomogeneous local reaction rates as a result of constraints in technically reasonably achievable operating conditions were investigated. Altogether, we face system efficiency concerns that limit the coolant flow rate, restrict the energetically costly gas humidification to an extent well below cell operation temperature, and allow only for stoichiometric ratios that are not capable of completely removing product water as vapor. Consequently, membrane drying, hampered gas transport by liquid water and O₂ depletion cause performance losses. As a basis for improvement the loss mechanisms have to be understood most comprehensively. Both theory and experiment was used to gain understanding. In terms of experiments localized current density measurement and in cooperation with SCHNEIDER and KRAMER localized electrochemical impedance spectroscopy and liquid water detection by neutron radiography were employed. Mechanisms underlying the low frequency features in impedance spectra, that hold information about mass transfer phenomena were elucidated in cooperation with SCHNEIDER.

Possibilities to beneficially counteract the mentioned phenomena behind losses in a technically feasible way were explored both experimentally and theoretically. The relative flow direction of all media in the cell turned out to be crucial for cell performance. Internal humidification both in a passive cell internal device and within the active area by counter flow arrangement of the gases was assessed as well as the effect of in-plane temperature gradients. It was shown, that enhancement of power can be achieved by removing spots of increased overpotentials. Further on, inhomogeneous catalyst loading was investigated theoretically and was found to be able to homogenize the current density distribution but not to increase power. Finally, a comprehensive picture of the role of electro-osmotic drag, water diffusion through the membrane and liquid water transport through the GDLs for the cell’s water balance could be developed from the application of complementary sophisticated experimental and theoretical tools on a cell at different loads.
Chapter 7

Cell Interaction Phenomena in PEFC Stacks

Fuel cells stacks in the commonly used bipolar arrangement comprise of multiple stacked single cells. Bipolar plates (BPP) that serve as electrical connectors between the alternate poles of two adjacent cells separate the individual cells. This bipolar stacking of fuel cells connects them in series electrically and in parallel for the reactant and coolant flows. Therefore, all cells in a stack have to carry the same total current while receiving reactant and coolant flows that are not perfectly equal due to varying percolation resistances. This is, because single cells are not identical due to tolerances in manufacturing and the electrochemical components. The local current production in a single cell will vary significantly with reactant flow rates and temperature governed by the coolant flow and where applicable effects of the endplate. When different distributions of the local current density over the surface of adjacent cells arise the BPP plate has to redistribute the current. Hence, potential gradients along the BPP will occur that in turn influence the cells current distribution. By this, disturbances in single cells spread out to several neighboring cells.

Work on the issue of cell interactions due to anomalous operation of single cells in a stack has first been published by the group of Wetton: Promislow et al. [122] investigated thermal interactions theoretically, followed by Kim et al. [123], who elucidated experiments on a multi-cell stack using an efficient 1+1D model. The latter one focuses on the propagation of disturbances due to resistive current collectors and partially inactive cells to neighboring cells. They derive analytical expressions for the number of cells influenced by an anomalous cell. In terms of diagnostics they applied local cell voltage measurement. Further worth to mention are two papers on computational aspects of stack modeling with reduced dimensional models [124, 125]. First work that also focuses on local current density coupling was done in theoretical means by Freunberger et al. [126] and experimentally

1Results shown are to be presented in:
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by Santis et al. [82] on a short stack of technical size. Kulikovsky [127] modeled the findings in Ref. [126] using an analytical along-the-channel model. However, the model is limited to constant polarization throughout the cell, which is contradictory to the mechanism of coupling, and main power changes were therefore attributed to joule heating in the BPP, which is disproved here by looking detailed on local polarization gradients.

Electrochemical impedance spectroscopy (EIS) has been used to identify humidification aspects [94] and issues regarding interfacial charge transfer, catalyst layer properties, and reaction mechanisms [91, 92, 93]. Furthermore, aspects of mass transfer and flooding have been addressed [91, 95, 97, 51, 46, 96]. Consequently, there has been effort to expand EIS having these capabilities to a locally resolved method [97, 51, 46] and a method for H2/air-PEFC stack diagnostics [128, 129, 130, 131]. In their recently published papers Le Canut et al. [130] and Fouquet et al. [131] used multi cell stacks of technical size with 500 and 150 cm² to record integral stack spectra. Andreaus [132] and Hakenjos et al. [133] measured simultaneously the integral single cell spectra in a 2-cell and 4-cell stack. They draw conclusions on mass transfer limitations due to electrode flooding from low frequency features of the spectra, which are commonly attributed to these phenomena in the literature. However, first pioneering work in localized EIS by Brett et al. [97] and the recent comprehensive explanation of the physical processes involved by the joint experiments with Schneider (Section 6.5 and [96]) brought evidence that integral spectra are heavily misleading for that purpose. Even more, cells in a stack work never perfectly equal, which calls for a detailed investigation of the implications of coupling on EIS in fuel cell stacks.

In this chapter the mechanisms of coupling phenomena are investigated by means of a 2-cell stack experimentally and theoretically using a computational fluid dynamics (CFD) based FC model that was developed jointly with Sui (University of Victoria). The structure is as follows. First, the setup of the specialized 2-cell stack with advanced localized diagnostics is described. Second, the model is presented along with its numerical implementation. Third, the principal mechanism of electric coupling, the calculation of the in-plane current from experimental results, and experimental investigations of coupling induced by flow and temperature differences are discussed. These findings are extended using the model for more general cases of plate conductivity and cell size. Finally, EIS in fuel cell stacks is scrutinized using simultaneous localized EIS in both cells of this stack in an joint effort with Schneider.

### 7.1 Experimental Setup

The experiments described here were performed in a specialized 2-cell stack of cells with linear flow field as shown in Fig. 7.1. The cell was described in detail in Section 5.2.1
7.1. Experimental Setup

**(Figure 7.1):** Simplified scheme of the 2-cell stack with individual media supply and individual localized current and voltage measurement in 10 segments.

The methods of localized current and EIS measurement are described in Section 5.2.2 (p. 65) and Section 5.2.4 (p. 69), respectively. Membrane electrode assemblies were manufactured using ETEK ELAT V2.1 gas diffusion electrodes (0.6 mg Pt/cm², 20 wt% Pt/C) for both anode and cathode and a Nafion N112 membrane. PTFE gaskets 250 μm thick were used to seal the cell.

The test cell was operated at a temperature of 70 °C in co-flow mode. The humidified gas was heated up to 80 °C and fed to the cell through electrically heated tubes. Other operating conditions were a gas dew point of 75 °C, a fuel stoichiometry of 1.5, atmospheric pressure and 100 A cell current unless stated differently.

The electron conductors between two cells comprise of the GDLs, the flow field plates and the sealing of the BPP that is made from 0.35 mm thick Sigraflex expanded graphite (SGL Carbon Group) [134]. Taking into account the respective in-plane conductivities and cross section areas the whole assembly has a conductivity of 26 400 S/m.

All impedance measurements shown here were performed in a frequency range of 10 kHz to 100 mHz (10 pts./dec.) in galvanostatic operation mode with 100 A cell current and a modulation current of 2 A. Integral spectra (Fig. 7.15) were calculated from the respective locally resolved impedance spectra. The local \(j/U\) curves shown in Fig. 7.16 were taken in galvanostatic mode. During the measurement, the gas flow rates were kept constant corresponding to an air stoichiometry in cell 1/cell 2 of \(\lambda = 2.5/1.2\) and a hydrogen stoichiometry \(\lambda_{H_2} = 1.5\) at 100 A (500 mA/cm²).
Chapter 7. Cell Interaction Phenomena in PEFC Stacks

7.2 CFD-Based Stack Model

7.2.1 Coupled transport equations

The 2D CFD model used for investigating the cell interaction phenomena is based on the model of Mazumder and Cole [66]. The model domain is a 2D along-the-channel slice through two cells in a stack with liquid cooling in the BPP where for each cell the entire repetitive unit is taken. The layers are (i) the anode plate with the coolant channel, (ii) the anode GDL, (iii) the anode catalyst layer (CL), (iv) the membrane, (v) the cathode CL, (vi) the cathode GDL, and (vii) the cathode plate. The model solves the coupled conservation equations for mass, momentum, species, total enthalpy and charge (electrons, protons). Table 7.1 lists these conservation equations and their respective source terms in the sub domains of the fuel cell.

The following assumptions are made in the model: (i) ideal gas mixtures, (ii) isotropic and homogeneous electrodes, CL, and membrane, (iii) single-phase water transport in the GDL, CL and the channels.

The transfer current is governed by the Butler–Volmer Equation

\[
j = S_a j_0 \rho \gamma \left( \frac{C}{e^{\varepsilon_0}} \right) \left[ e^{\frac{aFf}{RT}} - e^{\frac{(1-a)Ff}{RT}} \right]
\]

with \( S_a \) being the catalyst specific area per unit volume, and

\[
\eta = \phi_s - \phi_m
\]

the driving force. Effective diffusivity in porous media is obtained from free stream diffusivity with the Bruggeman-correction \( D_{\text{eff}} = D \cdot \varepsilon^\sigma \).

<table>
<thead>
<tr>
<th>Conservation equations</th>
<th>Source terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass ( \nabla(\varepsilon \rho u) = 0 ) (7.1)</td>
<td>( S_a ) in GDL and CL ( S_a = \varepsilon^2 \mu u/k )</td>
</tr>
<tr>
<td>Momentum ( \nabla(\varepsilon \rho u) = -\varepsilon \nabla p + \nabla(\varepsilon \tau) + \varepsilon B + S_a ) (7.2)</td>
<td>( S_a, S_e ) in CL ( S_a = -j/F )</td>
</tr>
<tr>
<td>Species ( \nabla(\varepsilon \rho Y_i) - \nabla(\rho D_{ij} \nabla Y_i) = \nabla(\rho D_{ij} \nabla Y_j) + S_i ) (7.3)</td>
<td>( H_2, O_2 ) in CL ( S_i = -\nabla \frac{n_i}{\varepsilon^\sigma} )</td>
</tr>
<tr>
<td>( H_2O ) in mem. ( S_i = -\nabla \frac{n_i}{\varepsilon^\sigma} ) in CL ( S_i = -\nabla \frac{n_i}{\varepsilon^\sigma} + \frac{j}{\varepsilon^\sigma} )</td>
<td></td>
</tr>
<tr>
<td>Energy ( \nabla(\varepsilon \rho h) \cdot \nabla(k_{\text{eff}} \nabla T) = \nabla(\sum_j (\varepsilon \tau \nabla T + j^2/\sigma + S_h) ) (7.4)</td>
<td>( \varepsilon_T ) in CL ( S_h = j (\frac{\varepsilon^2}{4}) - \eta )</td>
</tr>
<tr>
<td>Protons ( \nabla(\sigma_m \nabla \phi_m) = S_m ) (7.5)</td>
<td>( \varepsilon_T ) in CL ( S_m = -j )</td>
</tr>
<tr>
<td>Electrons ( \nabla(\sigma_e \nabla \phi_e) = S_e ) (7.6)</td>
<td>( \varepsilon_T ) in CL ( S_e = j )</td>
</tr>
</tbody>
</table>
7.2.2 Boundary conditions

Equations 7.1 to 7.6 in Table 7.1 form a closed set of conservation equations for \( u, p, Y_i, h_i, \phi_m, \) and \( \phi_s \) with \( i = H_2, H_2O, O_2, N_2 \). All conservation equations are solved on the entire domain. Thus, boundary conditions are required at the external surfaces of the domain. Dirichlet conditions apply to Eq. 7.6. The potential at the anodic current collector is set to zero. The total polarization is applied to the cathodic current collector. All other boundaries of Eq. 7.6 and all boundaries of Eq. 7.5 are no-flux boundaries. Inlet velocities and species mass fractions are calculated from inlet composition, humidification, stoichiometric ratio and total current. No-flux conditions apply to Eq. 7.1 to 7.3 at all surfaces except for gas and coolant in- and outlets. Since the stack is run with prescribed polarization, the total current is initially unknown. Therefore, the total current of similar conditions is used as reference current for calculating the inlet flux and the actual stoichiometry is calculated after the solution with the actual current. To simulate internal cells in a stack cyclic boundary conditions are applied to the anodic and cathodic surfaces of the stack.

The solution of the above set of governing equations was done with the commercial CFD solver CFD-ACE\(^1\) (CFD Research Corporation, Huntsville, AL). Based on the user-coding capability non-standard relations are specified using user defined subroutines. The used physical parameters of the cell and the materials are listed in Table 7.2.

7.3 Results from Experiment and Modelling

Mechanism of electrical coupling.— The basic mechanism of cell-to-cell coupling is depicted in Fig. 7.2 in terms of partitioning of the cumulative overpotential \( \eta \) (polarization). Shares are attributed to ohmic drops in electron and ion conductors and to the electrochemical reactions. When two cells are operated at a certain total polarization, i.e. the total driving forces are the same throughout the stack, a current distribution \( j \) will appear appropriate to the local resistances. Their major contributors, the electrochemical resistances \( (R_\eta = \eta/j) \) due to charge transfer in the catalyst layers and the proton transport in the membrane are highly dependent on the local humidity and reactant concentration and therewith on the operating conditions. When \( R_\eta \) is raised equally at a certain location in both cell the current will drop there and therewith the voltage drop over the thickness of the BPP (Fig. 7.2a). This leads to an opposed in-plane current in the halves of the BPP without giving net current. Net current is induced when the local resistances at adjacent points of two cells are not equal and the potential in the BPP is distorted in a way as shown in Fig. 7.2b. At the same time this distorted potential in the BPP results in opposed changes in the measurable cell voltage and additionally depends on the measurement location. In turn a change of driving force in a cell without change in
Table 7.2: Simulation parameters for the base case and physical properties of the cell.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel depth</td>
<td>$0.55 \times 10^{-3}$ m</td>
</tr>
<tr>
<td>Channel length, $L$</td>
<td>0.4 m</td>
</tr>
<tr>
<td>GDL thickness</td>
<td>$250 \times 10^{-6}$ m</td>
</tr>
<tr>
<td>CL thickness</td>
<td>$10 \times 10^{-6}$ m</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>$56 \times 10^{-6}$ m</td>
</tr>
<tr>
<td>Plate thickness</td>
<td>$2 \times 10^{-3}$ m</td>
</tr>
<tr>
<td>Plate conductivity, $\sigma_p$</td>
<td>$2 \times 10^3$ S/m</td>
</tr>
<tr>
<td>GDL conductivity, $\sigma_s$</td>
<td>$2.5 \times 10^3$ S/m</td>
</tr>
<tr>
<td>CL conductivity, $\sigma_s$</td>
<td>50 S/m</td>
</tr>
<tr>
<td>CL ionic conductivity, $\sigma_m$</td>
<td>2 S/m</td>
</tr>
<tr>
<td>Membrane conductivity, $\sigma_m$</td>
<td>Ref. [17]</td>
</tr>
<tr>
<td>Drag coefficient, $n_d$</td>
<td>Ref. [17]</td>
</tr>
<tr>
<td>Membrane water diffusivity</td>
<td>Ref. [17]</td>
</tr>
<tr>
<td>Membrane sorption isotherm</td>
<td>Ref. [17]</td>
</tr>
<tr>
<td>Gas diffusivities, $pD$</td>
<td>Ref. [74]</td>
</tr>
<tr>
<td>Effective thermal conductivity, $k_{\text{eff}}$</td>
<td>Ref. [135]</td>
</tr>
<tr>
<td>Membrane permeability, $\kappa$</td>
<td>$1.8 \times 10^{-18}$ m$^2$</td>
</tr>
<tr>
<td>GDL permeability, $\kappa$</td>
<td>$1.76 \times 10^{-11}$ m$^2$</td>
</tr>
<tr>
<td>Membrane porosity, $\varepsilon$</td>
<td>0.28</td>
</tr>
<tr>
<td>GDL porosity, $\varepsilon$</td>
<td>0.6</td>
</tr>
<tr>
<td>CL porosity, $\varepsilon$</td>
<td>0.4</td>
</tr>
<tr>
<td>Anode/cathode outlet pressure</td>
<td>$1 \times 10^5$ Pa</td>
</tr>
<tr>
<td>Inlet relative humidity</td>
<td>100 %</td>
</tr>
<tr>
<td>Anodic transfer coefficients, $\alpha$</td>
<td>0.5</td>
</tr>
<tr>
<td>Cathodic transfer coefficients, $\alpha$</td>
<td>1.5</td>
</tr>
<tr>
<td>Anodic concentration exponent, $\gamma$</td>
<td>0.5</td>
</tr>
<tr>
<td>Cathodic concentration exponent, $\gamma$</td>
<td>1</td>
</tr>
<tr>
<td>Anodic exchange current density, $j_0^{\text{ref}}$</td>
<td>$9.23 \times 10^8$ A/m$^3$</td>
</tr>
<tr>
<td>Cathodic exchange current density, $j_0^{\text{ref}}$</td>
<td>$1.05 \times 10^6$ A/m$^3$</td>
</tr>
<tr>
<td>Catalyst specific area, $S_a$</td>
<td>7000 m$^2$/m$^3$</td>
</tr>
</tbody>
</table>

operating conditions will change its current distribution (cf. cell 1 in Fig. 7.2b). Therefore, adjacent cells couple by changing the partitioning of the total polarization between each other.

In-Plane Current, Plate Potential and Power Losses.— Differences in the current density distribution between the cells next to a BPP are redistributed in this BPP. That is, the local difference in current density $j_1 - j_2 = \Delta j$ has to be redistributed along the in-plane direction $x$ as the total stack current is the same in each cell. There are two possibilities to calculate the local in-plane current $i_x$ from cell experiments. For both the simplification applies that the length $L$ of the BPP is much larger than its thickness $d$, $L \gg d$, and therefore the differences in potential drop between the two sides of the BPP
7.3. Results from Experiment and Modelling

Figure 7.2: Principle of electrical coupling through the BPP of adjacent cells illustrated by means of a 2-cell stack at constant total polarization. Current densities (top) and overpotentials cumulating from the anode end of the stack (bottom) are shown for equal operation of the cells (a) and reduced air stoichiometry in cell 2 (b), respectively. Electron $\phi_e$ and membrane phase potentials $\phi_m$ are shown through the cross section of the stack at in- and outlet (cf. Fig. 2.3b, p. 14). The cross section is schematically shown at the bottom.

plate are negligible against its value along the channel. Furthermore, a straight channel cell is considered, where current differences occur only in the channel direction.

First, the potential $\phi$ of the plate may be measured with sufficiently high resolution along the channel and the current calculated from

$$i_x = -A \cdot \sigma \frac{\partial \phi}{\partial x}$$  \hspace{1cm} (7.9)

where $\sigma$ denotes the in-plane conductivity of all electron conductors (BPP and GDLs) and $A$ their cross section area. As the end faces of the plates are insulating $\partial \phi / \partial x = 0$ applies there for the interpolation polynomial (cf. Figs. 7.5c and d).

Second, the in-plane current and the plate potential, respectively, may be calculated from the differences in the measured current density distributions. Charge conservation over a volume element of length $\delta x$ of the BPP with unit extension across the channel direction imposes $i_c - i_w = \delta i = \Delta j \cdot \delta x$ and therewith $\partial i / \partial x = \Delta j$. Using Ohm’s law (Eq. 7.9)

$$\frac{\partial}{\partial x} \left( A \cdot \sigma \frac{\partial \phi}{\partial x} \right) = \Delta j$$  \hspace{1cm} (7.10)

yields for the potential along the BPP. Boundary conditions for Eq. 7.10 are

$$\frac{\partial \phi}{\partial x} \bigg|_{x=0,t} = 0, \quad \phi \bigg|_{x=0} = \phi_{\text{meas}}$$  \hspace{1cm} (7.11)
The first one implies that current vanishes at the insulating boundaries of the domain, which is automatically fulfilled for the other boundary when it is applied to one boundary as the cell current is conserved and therefore the integral source \( \int_0^L (\Delta j) dx = 0 \) equals zero. The second one sets the measured voltage at the end of the cell as reference point. An analogous expression to Eq. 7.10 has been derived by Kulikovsky [127].

The power dissipated in the BPP per unit active area by Joule heating is

\[
P = \frac{A}{wL} \int_0^L \frac{j_x^2}{\sigma} dx
\]

(7.12)

where \( w \) is the width of the cell associated with the BPP cross section area \( A \).

Strength of coupling and associated power change.— The degree of cell interaction, i.e. the extent of current density deflection of a cell by an anomalous neighboring cell depends on the potential gradient in the BPP required to redistribute current differences between adjacent points in the cells. The local current density in a cell may be expressed by its effective electrochemical resistance \( R_\eta \) and the polarization \( \eta \)

\[
\dot{j}_i = \frac{\eta}{R_\eta}
\]

(7.13)

Having iso-potential end plates Eq. 7.9 may also be written in terms of polarization instead of potential as

\[
r_\eta x = \frac{\partial R_\eta_1 j_1}{\partial x} = -\frac{\partial R_\eta_2 j_2}{\partial x}
\]

(7.14)

where \( r = 1/A\sigma \) is the BPP resistivity. Therewith, the in-plane current is

\[
i_x = -\frac{R_\eta_1}{r} \frac{\partial j_1}{\partial x} - \frac{R_\eta_2}{r} \frac{\partial j_2}{\partial x}
\]

(7.15)

Thus, the ability of the system to redistribute differing electrochemical performance of the cells \( (R_\eta,j) \) by in-plane current is determined by the ratio \( R_\eta/r \). For the case of high BPP resistivity \( r \) even big differences between \( R_\eta_1 \) and \( R_\eta_2 \) result in close coupling of the current density profiles due to forcing of current through parts of the cell where it would not flow in iso-potential operation. This is, increased overpotential is applied to regions with high \( R_\eta \). The associated change of average cell power density

\[
P = \frac{1}{L} \int_0^L \left( E_0 \frac{\eta}{R_\eta} - \frac{\eta^2}{R_\eta} \right) dx
\]

(7.16)

with a non-uniform change of polarization along the active area depends on the superposition of all local characteristics \( R_\eta(\eta) \). The power change associated with a deflection of the polarization distribution is given by

\[
\Delta P = \frac{1}{L} \int_0^L \left( \int_0^\Delta \frac{\partial P}{\partial \eta} d\eta \right) dx
\]

(7.17)
When the gas flow rate is kept constant the local change of power with polarization change \( \frac{\partial P}{\partial \eta} \) may be either positive or negative, depending on flow rate, load and position along the channel. This may be seen in the local \( j/U \) curves in Fig. 6.29d to f (p. 103). In order to get an estimate on direction and magnitude of \( \Delta P \) for small deflections \( \Delta \eta \), \( \frac{\partial P}{\partial \eta} \) may be obtained from those local \( j/U \) curves as shown exemplarily for three segments in Fig. 7.3. The estimation holds only for small deflections since local \( O_2 \) depletion — and therewith \( R_{\eta}(\eta) \) — depends on all current produced upstream, which in turn changes with changed polarization distribution.

**Figure 7.3:** (a) Local and integral \( j/U \) curves with a constant flow referring to \( \lambda_{H_2} = 1.5 \) and \( \lambda = 1.2 \) at 100 A (500 mA/cm²). (b) Therefrom obtained change of local power with local polarization \( \Delta P/\Delta \eta \) as a function of \( \eta \).

Four different cases of polarization deflections are examined that way on their influence on power in Fig. 7.4. Figure 7.4a provides a sigmoidal weight function for the local polarization change of 10 mV. That is, in case 1 the polarization is raised by 10 mV at the inlet and lowered by 10 mV at the outlet. The associated power change \( \Delta P \) is given in absolute and relative measures in Fig. 7.4b and c. For cases 1 and 2, where the overall polarization is kept constant but with its distribution pivoted around the cell center, \( \Delta P \) tends in one direction on the entire polarization range. Increase of \( \eta \) at the outlet and its decrease at the inlet raises overall power (case 1) and vice versa (case 2). When \( \eta \) is kept constant at the inlet but raised (case 3) or lowered (case 4) at the outlet \( \Delta P \) depends on the polarization range. A negative slope of all local \( j/U \) curves yields increased power with increased \( \eta \). However, from a certain \( \eta \) on the slope is positive for local \( j/U \) curves close to the outlet (Fig. 7.3). Therefore, increasing polarization there lowers the overall power (case 3 with \( \eta > 0.35 \text{ V} \)).

### 7.3.1 Reaction on stoichiometry differences

The most probable cause for coupling phenomena arises from the parallel connection of the cells by the media supply. As percolation resistances may vary between the cells the reactant flow is prone to differ to some extent. The current density distribution is most sensitive to air flow and therefore coupling phenomena are investigated in the following by means of air stoichiometry differences in the two cells. Two cases are considered:

(i) For elucidating the principal mechanism as discussed in Fig. 7.2 cell 1 is kept at a
constant stoichiometry of $\lambda = 3$, whereas the other cells stoichiometry is varied from $\lambda = 3$ to $\lambda = 1.2$. The practically particularly relevant case of a certain average stack stoichiometry $\lambda_{\text{avg}}$ and some spread around that in single cells is emulated by applying $\lambda_{\text{avg}} \pm \Delta \lambda$ to the single cells with $\Delta \lambda = 0.1$ and 0.2, respectively. The fuel stoichiometry is kept at 1.5 and gas humidification is 100% and 50% relative humidity, respectively, for all feeds at a time.

The chosen 2-cell stack for examining the mentioned phenomena serves as a model system with the advantage of both individual media supply and localized diagnostic in each cell. However, the results may be generalized to larger stacks. The difference in case (i) to an extended stack is that the increased overpotential to produce the current in the anomalous cell is taken from only one cell. In an extended stack the potential distortion due to a single anomalous cell spreads out to several adjacent cells with decaying impact [82, 123]. Santis et al. [82] have shown that this decay in relative variation of the neighboring cell with respect to iso-potential operation follows a geometric sequence.

Figure 7.5 shows the current density distributions, the voltages, and the resulting in-plane current as a function of the channel length for the case with one cell at constant stoichiometry and a varied one in the other cell. As discussed above with the principal coupling mechanism, an anomalous cell with reduced stoichiometry will take more of the total polarization to produce the local current close to the air outlet and the cell voltage drops there (Fig. 7.5c+d). The driving force for the adjacent cell ($\lambda = 3$) is therefore reduced as compared with its iso-potential operation (open symbols in Fig. 7.5a+b). In turn the current density drops and couples to the current distribution of the disturbed cell (Fig. 7.5a+b). The extent of current density coupling is determined by the required potential gradient along the BPP to redistribute locally differing electrochemical performance $R_n$ by in-plane current (Fig. 7.5e+f, cf. Eq. 7.15).

When dry gases are fed (right column in Fig. 7.5) the current distribution is governed in two ways by the air stoichiometry. First, oxygen starvation reduces the current towards the outlet analogously to the saturated case. Second, decreasing stoichiometry shortens the path length until the current maximum is reached. Therefore, the anomalous cells
7.3. Results from Experiment and Modelling

Frankly, the text in the figure describes the experimental results from an electrochemical system. The key points are:

- **Figure 7.5**: Shows the along-the-channel distribution of quantities with constantly operated cell 1 (□) at \( \lambda = 3 \) and reduction of \( \lambda \) in cell 2 (○) at 100 A. Feeds are fully humidified (a, c, e) and half saturated (b, d, f), respectively. (a+b) Current distribution. (c+d) Cell voltage, measured (symbols) and calculated from Eq 7.10 ( ). (e+f) In-plane current in the BPP calculated from measured voltage (Eq. 7.9) and current density difference (Eq. 7.10).

- **Figure 7.6**: Change of local current density (a, b) and polarization (c, d) with constantly operated cell 1 (a, c) at \( \lambda = 3 \) and reduction of \( \lambda \) in cell 2 (b, d) with fully humidified feeds. Values are referenced against iso-potential operation at the respective \( \lambda \).

The text explains that the higher current level at the inlet in the case of lower air stoichiometry (Fig. 7.5b) does not mean a lower electrochemical resistance \( R_\eta \) there. It is caused by the constant current operation and does not raise cell voltage there (Fig. 7.5d).

The closely matching results for in-plane current in Fig. 7.5e and f obtained with the two described methods (Eq. 7.9 and Eq. 7.10) prove their validity. Consequently, the potential distribution obtained from the measured current density difference with Eq. 7.10 resembles the measured potential distribution (Fig. 7.5c+d).

The associated change of local current and polarization vs. iso-potential operation at the respective stoichiometry is shown in Fig. 7.6 for the case with saturated feeds (left column...
in Fig. 7.5). Note that increasing polarization means higher negative values, i.e. $\Delta \eta < 0$ means increased polarization and lower voltage. The current density of the cell with higher stoichiometry is shifted much farther from its reference value than the cell with lowered one (Fig. 7.6a and b). This is because the current-voltage curve is the steeper the lower the stoichiometry. Therefore, a certain change in polarization leads to a higher change in current density with higher stoichiometry. The polarization in the constantly operated cell 1 is slightly more increased as much at the inlet as decreased at the outlet since a higher fraction of the (constant) total current has to be carried at the inlet region, which increases all losses there (Fig. 7.6c). Lowered stoichiometry in the other cell requires successively increasing polarization along the air path as compared to iso-potential operation to carry the load (Fig. 7.6d). Although the polarization at the outlet increases yet substantially with a lowering of the stoichiometry from 1.5 to 1.2, the current density there does not grow any more.

Changes in local current and polarization are associated with local and overall power changes. How changes in the distribution of the local polarization at a certain stoichiometry change the power depends on the stoichiometry as shown in Fig. 7.7. There, the derivative of local power with respect to local polarization is drawn for various stoichiometries at 100 A. Power change with a change of local polarization is given by Eq. 7.17. Note that increasing polarization ($\Delta \eta < 0$) increases power when $dP/d\eta < 0$. The cell is still below its maximum power point at 100 A with a stoichiometry of 3. Yet, an increase of polarization does not increase power any more at the outlet segment. With decreasing stoichiometry the downstream region with falling power in response of increasing polarization expands towards the inlet of the cell. Increased polarization on the entire channel length (cf. Fig. 7.6d) leads therefore to a decreased power where $dP/d\eta > 0$. Increasingly positive values of $dP/d\eta$ towards the air outlet, where polarization increases stronger lead therefore to an integral power loss.

The consequences of this behaviour on overall cell power for the above discussed case with one cell at constant stoichiometry and a varied one in the other cell are analyzed in Fig. 7.8. The change of voltage and power is plotted as a function of stoichiometry in the varied
cell. The reference is an iso-potentially operated cell at the respective stoichiometry. The effective cell voltage

\[ U_{\text{eff}} = \int_0^L \frac{j U dx}{\int_0^L j dx} \]  

(7.18)

results from integral power and current.

Like observed in Fig. 7.6 reduced stoichiometry in one cell while keeping the other cells stoichiometry constant increases the required polarization along the channel to carry the constant total current (Fig. 7.8a+b). At the same time the polarization in the other cell decreases at the outlet and increases similarly at the inlet (Fig. 7.8c+d). In either case the effective cell voltage decreases as a result of the altered current distribution in both cells. The effect becomes more pronounced with decreasing stoichiometry in the altered cell. The results show that both increasing and decreasing polarization along the air flow path diminish the overall cell power (Fig. 7.8e+f). Already slightly decreasing polarization as observed for the unchanged cell when the other cell is operated at a stoichiometry of 2 cuts its power. To the same extent increasing polarization in the other cell does not diminish power at this combination. However, with lowered stoichiometry increasing polarization reduces power even more than decreasing one. This is in contrast to theoretical results by Senn and Poulikakos [136]. Using numerical optimization they found slightly enhanced cell power by three to five percent with growing polarization towards the air outlet. When the gases are fed with 50% relative humidity (Fig. 7.8b, d, f) instead of 100% relative humidity (Fig. 7.8a, c, e) polarization gradients and power losses are more pronounced due to additional current imbalances that stem from different path lengths for gas saturation (cf. Fig. 7.5). Cell power is substantially reduced by up to 10 and 13% for the humid and dry case, respectively.

The second above mentioned case of unequal cell operation is analyzed in Fig. 7.9. A certain average stack stoichiometry \( \lambda_{\text{avg}} \) and some spread around that in the single cells is emulated by applying \( \lambda_{\text{avg}} \pm \Delta \lambda \) to the single cells with \( \Delta \lambda = 0.1 \) and 0.2, respectively. Like before, relative feed humidities of 50 and 100% are investigated. Absolute stack power is drawn as a function of \( \lambda_{\text{avg}} \) for the two deviations in Fig. 7.9a and b, whereas the contributions to the power losses with increasing deviations are unraveled in the other graphs. Power losses due to in-plane current in the BPP (Eq. 7.12) are in either case insignificant (Fig. 7.9c+d). Losses stem from inhomogeneous polarization and reduce stack power mainly below \( \lambda_{\text{avg}} = 2 \). Losses in the order of 7% of the stack power appear for average stoichiometries as low as 1.2. The contributions of the single cells to those losses are differentiated in Fig. 7.9e and f. Thus, losses are mainly attributed to the cell with lowered stoichiometry, i.e. the cell with increasing polarization along the air flow path. Slightly increased power in the other cell might, however, lie within experimental inaccuracy and must not necessarily be attributed to polarization changes. This is, however, indicated to with the estimation above (cf. Fig. 7.4) and later on with theoretical results (cf. Fig. 7.13).
Figure 7.8: Voltage and power change with reduction of $\lambda$ in one cell and constantly operated other cell at $\lambda = 3$. Cell current is 100 A. Feeds are fully humidified (a, c, e) and half saturated (b, d, f), respectively. (a+b) Change of effective voltage and local voltage of the varied cell vs. the iso-potentially operated cell. (c+d) Change of effective voltage and local voltage of the constantly operated cell vs. the iso-potentially operated cell at $\lambda = 3$. (e+f) Power change of the cells referenced to its value at iso-potential operation and the respective $\lambda$.

Figure 7.9: Power and power change associated with stoichiometry deviations $\Delta\lambda$ from average stoichiometry $\lambda_{\text{avg}}$. Cell current is 100 A. Feeds are fully humidified (a, c, e) and half saturated (b, d, f), respectively. (a+b) Stack power. (c+d) Change of stack power vs. stack with equally operated cells and power loss due to in-plane current in the BPP. (c+f) Contributions of the single cells to the power change.

7.3.2 Electrical/thermal coupling in end cells

A commonly encountered phenomenon in fuel cell stacks is that the performance of cells located in the periphery of the stack (i.e. first or last cell) may differ from the average performance of the rest of the cells. These cells can experience increased thermal losses because of their peripheral location in the stack which makes them more susceptible to temperature variations which could affect their performance in relation to other cells in the stack. Other than in the case of stoichiometry differences as discussed above current distribution differences are likely to occur due to undersaturated gases when the cell temperatures differ.

The experiment shown in Fig. 7.10 emulates the end of a stack, where the one cell is at
7.3. Results from Experiment and Modelling

Figure 7.10: Electrical/thermal coupling at stack end cells with isothermal inner cell and thermally open end cell. Current density distributions at different humidifications (a), the respective local cell voltages (b), and relative power vs isothermal and humid reference against gas dew point. $\lambda_{\text{H}_2/\text{air}} = 1.5/1.5$ and $T_{\text{cell}} = 70^\circ\text{C}$ (inner cell).

The temperature of inner cells in the stack and the other cell encounters a lower temperature due to heat losses over the endplate. Both reactants are fed with a dew point of 70, 50, and 35 °C, respectively, at a cell temperature of $T_{\text{cell}} = 70^\circ\text{C}$ in the inner cell, 500 mA/cm² average current and stoichiometries of $\lambda_{\text{H}_2/\text{air}} = 1.5/1.5$. The cell temperature of the end cell was 5 °C lower than of the inner cell. The differences in current density (Fig. 7.10a) are attributed to the different effective inlet humidities; the cooler end cell favours therefore current production at the inlet, which becomes more pronounced with decreased gas humidity. An even stronger effect is observed in terms of cell voltages as shown in Fig. 7.10b, where the voltage distributions of both cells are drawn. Notably the inner cell suffers from electrical coupling to the end cell as the latter one forces higher current through the inlet region. The inner cell polarizes therefore strongly to meet this current (see inlet region, filled symbols in Fig. 7.10b). The effect on power density relative to fully humidified operation at $T_{\text{cell}} = 70^\circ\text{C}$ is shown in Fig. 7.10c. Thus, even slight temperature differences between cells may have strong influence on cell power when gases are undersaturated. This influence exceeds the effect of stoichiometry differences. However, in this experiment the air stoichiometry was forced in both cells. In practical situations the air flow through the first cell may be hampered due to e.g. increased liquid water or flow conditions in the manifold.

7.3.3 Influence of cell size and plate conductivity

The model is used to explore the influence of plate conductivity and geometry on the effects of coupling, which are experimentally costly to obtain. The base case conductivity of the BPP in the simulations is with $2 \times 10^3$ S/m roughly one tenth of its conductivity in the experiment. Furthermore the stack is operated at constant polarization of -0.7 V instead of constantly 5000 A/cm² as in the above experiments.

The current distribution, the overpotentials between current collector and the center of the BPP, and the in-plane current for the case of one constantly operated and one disturbed cell
are shown in Fig. 7.11. Due to the low plate conductivity the current densities couple much closer as compared to the experiments in Fig. 7.5. This is because only smaller current differences can redistribute in the plate with the resulting voltage drop (cf. Eq. 7.15). The total local polarization partitions therefore between the two cells in a way that both cells have more similar local current. Their differences are merely confined to the air outlet region, which is also reflected in the in potential distribution (Fig. 7.11b) and in-plane current (Fig. 7.11c).

Figure 7.11: Simulated results for the 2-cell stack as depicted in Fig. 7.1 but roughly one tenth the conductivity as in the experiment. \( \lambda_{\text{cell}1/2} = 3 \) (dashed lines), \( \lambda_{\text{cell}2} = 3\ldots1.1 \) (full lines). Total polarization is -0.7 V. (a) Current distribution in the two cells, (b) the local overpotentials at the CL/membrane interfaces and (c) the resulting in-plane current.

Figure 7.12 compares the effect of the same anomaly as before in cells with 0.4 and 0.05 m channel length, respectively. The current density change relative to a stack operated at \( \lambda_{\text{cell}1/2} = 3/3 \) is shown for reduced stoichiometry in cell 2. Results for the cell with 0.4 m channel length correspond to the data in Fig. 7.11. In the case of the short channel length the in-plane current is sufficiently large to redistribute current differences and therefore weaken the coupling.

Figure 7.12: Simulated current density change against \( \lambda_{\text{air}, \text{cell}1/2} = 3/3 \) for lowered \( \lambda_{\text{air}, \text{cell}1} \) (bold lines) for (a) 0.4 m and (b) 0.05 m cell length.

According to Eq. 7.10 possible current differences grow with increasing BPP conductivity as shown in Fig. 7.13a for constant operation with \( \lambda_{\text{cell}1/2} = 3/1.1 \). This allows both cells to produce current where it is favorable in terms of local \( R_i \). Consequently, when the conductivity is low, the cell with higher stoichiometry forces current through the outlet region of the other cell by applying high polarization, where \( R_i \) is high. Increasing polarization
7.3. Results from Experiment and Modelling

Figure 7.13: (a) Local current difference for $\lambda_{\text{air, cell } 1/2} = 1.1/3$ and varied BPP conductivity ($\sigma_{\text{BPP}}$) at constant total polarization of -0.7 V. (b) Power in the two cells at -0.7 V total polarization vs. conductivity of the electron conductors referenced to $\lambda_{\text{air, cell } 1/2} = 3/3$ and $\sigma_{\text{BPP}} = 2 \times 10^3$ S/m.

in regions, where $R_\eta$ is high increases losses there. In turn increased polarization at the inlet region of cell 1 ($R_\eta$ small) and its decrease at the outlet can raise cell power slightly as compared to the iso-polarization case. Both effects are shown in Fig. 7.13b, where the single cell power with $\lambda_{\text{cell } 1/2} = 3/1.1$ as a function of BPP conductivity is referenced to a cell with $\lambda = 3$ and homogeneous polarization. At low conductivities both cells suffer from their strong coupling and therefore unfavorable current distribution with respect to the distribution of $R_\eta$. At high conductivities both the polarization of cell 2 is only little increased at the inlet and reduced at the outlet, which leads to slightly higher power in cell 1 ($\lambda = 3$) and lower power in cell 2 ($\lambda = 1.1$).

7.3.4 Local EIS in fuel cell stacks

The experiments are carried out as before with base case conditions and individual air feed in both cells. Local EIS spectra are measured simultaneously for all 10 segments of a cell and one cell at a time. The current distributions for combinations of $\lambda$ in cell 1/cell 2 of $\lambda = 2.5/2.5$, $\lambda = 2.5/1.2$ (both cells individually measured), and $\lambda = 1.2/1.2$ are given in Fig. 7.15a. The corresponding integral spectra are shown in Fig. 7.15b. A low frequency capacitive arc starts to evolve at a modulation frequency of $f_{\text{mod}} = 7.9$ Hz for all air stoichiometries. The low frequency arc has in the literature been attributed to gas phase mass transport limitations in the backing and its size was found to be sensitive to air flow rate [91, 95]. However, finite diffusion in the backing layer as generally assumed in previous work as reason for this arc was disproved together with SCHNEIDER as shown in Section 6.5 and published in [96]. A comprehensive explanation of the underlying physical processes could be given. All further discussion given here is based on that paper.

Figures 7.15a to d show the local impedance spectra for the four mentioned combinations of $\lambda$. Equal flow rates in both cells of $\lambda = 2.5$ and $\lambda = 1.2$, respectively, were used in Figs. 7.15a and d yielding spectra like in appropriate single cells (cf. Section 6.5, Fig. 6.29,
Figure 7.14: (a) Current distributions for combinations of $\lambda$ in cell 1/cell 2 of $\lambda = 2.5/2.5$, $\lambda = 2.5/1.2$ (both cells individually measured), and $\lambda = 1.2/1.2$. Stoichiometries are indicated for the measured/adjacent cell. (b) The corresponding integral spectra of the single cells in the stack.

Figure 7.15: Simultaneous localized impedance spectroscopy in the 2-cell stack with independently controlled gas flow rates. (a-d) The local impedance spectra corresponding to Fig. 7.14b for the four combinations of $\lambda$ with segment numbers as indicated.

p. 103. The low frequency negative resistance loop, which is observed for segments near the air outlet at low air stoichiometry has earlier been shown by Brett et al. [97]. Its intercept with the real axis near dc was correlated with the slope in the equilibrium point of the local $j/U$ curves obtained at constant gas flow, which was proven in Section 6.5 as published in Schneider et al. [96] for any given air flow. Therefore, the local $j/U$ curves
obtained with the stoichiometry combination in cell 1/cell 2 of \( \lambda = 2.5/1.2 \) and shown in Fig. 7.16 are used for discussing the appropriate local spectra measured in the individual cells (Figs. 7.15b and c). When the measured cell is operated on \( \lambda = 1.2 \) with the other one having \( \lambda = 2.5 \) electrical coupling causes the single segments to have strongly differing voltages. This in turn causes both the local and integral spectra to change slightly in the low frequency part as compared to pure operation at \( \lambda = 1.2 \). A totally different behaviour is observed for the inverse stoichiometry combination. The adjoining cell with much lower stoichiometry provokes the local \( j/U \) curves of segments near the outlet to have a narrow bend back to higher voltage and lower current (insert in Fig. 7.16a). As the voltage deflection during EIS measurement is not in a linear regime in these segments both the local and integral spectra are heavily disturbed (Fig. 7.15a+c). More detailed studies on the underlying mechanism of this disturbance by in-plane current are subject to future work.

![Figure 7.16: Local \( j/U \) curves of the 2-cell stack at constant flow. Flows correspond to stoichiometries of (a) \( \lambda_{\text{H}_2/\text{air}} = 1.5/2.5 \) in cell 1 and (b) \( \lambda_{\text{H}_2/\text{air}} = 1.5/1.2 \) in cell 2 at 500 mA/cm\(^2\). The equilibrium points of the corresponding spectra in Fig. 7.15c and 7.15e are highlighted by filled symbols. See Fig. 6.29d+e (p. 103) for local \( j/U \) curves in a single cell at \( \lambda = 2.5 \) and \( \lambda = 1.2 \).](image)

### 7.4 Conclusions

In this Chapter cell interaction phenomena were comprehensively investigated using a specialized test stack with advanced in-situ diagnostic capabilities and a fuel cell model based on a commercial CFD-code. Equations for calculating in-plane current and the related power losses out of measured potential and current distributions were derived. The degree of coupling and power changes due to non-uniform polarization are rationalized. Individual media supply and localized current and voltage measurement in each cells enabled to investigate mechanism and effect of electrical cell coupling.

The impact of various practically relevant anomalies was studied: (i) a single anomalous
cell next to a constantly operated cell, (ii) certain deviations of single cell stoichiometries from the average stack stoichiometry, (iii) thermal effects in cells close to the end of the stack. The influence of plate conductivity and cell size is for case i is studied using the model.

Results show that the degree of coupling is governed both by BPP resistivity and electrochemical performance. For practically relevant conductivities of carbon made BPP cells with anomalous local performance drops, e.g. caused by low stoichiometry, cause neighboring cells to couple closely in terms of current density distribution. Consequently, the voltage and power density distribution is distorted significantly. Both increasing and decreasing polarization along the air flow path has been shown to reduce cell power significantly in general cases. Spreading stoichiometry in single cells around the average stack stoichiometry causes therefore power losses both in cells with higher and lower flows. High plate conductivities and small cell sizes were shown to reduce the impact of anomalous cells.

Furthermore, simultaneous localized EIS was used to scrutinize EIS in fuel cell stacks in general. We have revealed that low frequency features of stack spectra or single cell spectra in a stack are heavily error-prone. Virtually homogeneous operation of all cells is vital to meaningful spectra.
Chapter 8

Development of a PEFC System for Vehicle Propulsion

In a collaborative project between Conception et Développement Michelin SA, Michelin's research center in Givisiez, Switzerland, and PSI's Electrochemistry Laboratory a car with pure electric power train, Hy-Light, was realized between 2002 and 2004. PSI developed the fuel cell system and the electrochemical double layer capacitor (super capacitor, SC) unit. Michelin was responsible for the overall concept and all other components and systems. Within this work mainly the cell and stack development, assembly and test as well as the integration into the fuel cell system were accomplished in cooperation with other members of the Electrochemistry Laboratory and Michelin. After a short overview on the general concept of the car selected insights into the cell, stack and system development are outlined in Section 8 as far as nondisclosure concerns allow for.

The concept of Hy-Light was presented by Dietrich and Laurent in [137]. Without the constraints of the integration of a fuel cell system in an existing car platform numerous possibilities of a car with pure electric power train were exploited. The power train is based on a H2/O2 fuel cell system. Oxygen as oxidant was chosen to increase power density and efficiency. The main benefits in using O2 vs. air are enhanced specific power and the greatly reduced parasitic power in the balance of plant as pointed out by Buchi et al. [138]. Besides that the use of O2 also provides outstanding fuel cell dynamics [139]. Extreme power rises of up to 0 to 0.85 A/cm² within 20 ms have been shown. To profit from the electrical power train the fuel cell power of 30 kW is designed for covering the expected continuous load at peak velocity. Peak power demand for acceleration and breaking energy recuperation is provided by the SC unit. The unit can deliver or recover 32 (45) kW for 20 (15) s, which is sufficient to collect most of the breaking energy and to boost peak power for acceptable vehicle acceleration. The vehicle is equipped with two brushless wheel motors with a nominal/peak power of 30 kW/60 kW each. Additional electric motors in each wheel provide the electric suspension and damping which can also be used for anti-
roll and anti-pitch control (MICHELIN ACTIVE WHEEL™). Fuel is stored in pressurized compartments partly integrated into the vehicle frame [140].

8.1 Requirements of the Cell on the Fuel Cell System

The FC system has to provide all operation conditions in a range that allows the PEFC to work at maximum efficiency. These conditions include gas stoichiometry, pressure, and humidification and the cell temperature. At a time the optimum conditions may vary with current. In order to define the operation conditions the FC system has to deliver cell characterization as summarized in Fig. 8.1 has been undertaken using a single cell. During conceptual design of the FC system a power density of 0.625 W/cm² at a current density below 1 A/cm² has been fixed. Figure 8.1a shows the \( j/U \) curves of the cell for the variety of operation conditions as covered in Fig. 8.1b to d. This reveals the rated power density to be achieved above 0.9 A/cm² for all tested conditions. Figures 8.1b to d provide the dependence of cell voltage with changing cell temperature, gas humidification and gas pressure with base case conditions otherwise (cf. caption Fig. 8.1). The progression of cell voltage with cell temperature reflects the superposition of facilitated reaction with increasing temperature and at a time growing membrane resistance with declining relative feed humidity. Maximum voltage is obtained around 75 °C, which was chosen to be the base case temperature. Although even higher cell temperature leads apparently to reduced power due to membrane dehydration, optimum humidification is not at saturation temperature but around 40 °C as shown in Fig. 8.1c. The pressure dependence of the cell voltage is plotted in Fig. 8.1d, which shows that the rated power is reached for a pressure of 3 bar or above.

The above results have revealed the preferred range of operation conditions. However, due to constraints in system architecture not all of these conditions may be achieved equally easy. Particularly the feed gas humidification remains to be delicate to stack power, i.e. gas flow rates, and the heat management in the system components. Since pure reactants are used, feed humidification in the present system is accomplished by mixing the recirculated exhaust gas stream from the stack with the fresh gas. Therefore, feed humidity is limited by the humidity of the respective exhaust gas. Water balance in the MEA governs the partitioning of product water between anode and cathode exhaust. Figure 8.2 shows results from water balance measurement as a function of current density and \( \text{O}_2 \) stoichiometry. According to Fig. 8.2a, \( \text{H}_2 \) leaves the exhaust widely dry above 4000 A/m² irrespective of its inlet humidity. This is because electro-osmotic drag transports the water from the anode side into the cathode side. The effect becomes stronger with growing current density. Figure 8.2b shows that the cathodic exhaust transports vast amounts of liquid water which reach some ten times the amount the saturated gas could transport in the vapour phase. The effect shows no significant dependence on the stoichiometry of \( \text{H}_2 \) which leaves the
8.1. Requirements of the Cell on the Fuel Cell System

Figure 8.1: Performance of the single cell. (a) $j/U$ and power curves and the appropriate iso-power curves for both plots at 0.625 W/cm². Dependence of the voltage at 0.9 A/cm² on temperature (b), O₂ humidification (c), and O₂ stoichiometry (c). Base case conditions are $T = 74 \, ^\circ C$, $T_d, H_2/O_2 = 40 \, ^\circ C$, $p_{H_2/O_2} = 3.5 \, \text{bar}$.

Figure 8.2: (a) Effective drag (water flux relative to protonic current) vs. current density. (b) Saturation of the exhaust gases relative to the vaporous transport capacity of the exhaust. Values are plotted vs. O₂ stoichiometry for two H₂ stoichiometries at 7500 A/m².

The previously shown characteristics of the single cell did not point out particularly high demands on reactant stoichiometries since pure gases are used. Stoichiometries of $\lambda_{H_2} \geq 1.05$ and $\lambda_{O_2} \geq 1.15$ did not lead to significantly enhanced power. However, the parallel percolation of the single cells in a stack by the reactants is prone to evoke flow variations among the cells as it was discussed in detail for air fed cells in Chapter 7.
influence of both $\lambda_{\text{H}_2}$ and $\lambda_{\text{O}_2}$ on cell voltage and spreading of the single cell voltages during operation in a short stack is shown in Fig. 8.3. The data point out that $\lambda_{\text{H}_2} \geq 1.3$ and $\lambda_{\text{O}_2} \geq 1.3$ is required to keep the single cell voltages within narrow limits. The demand in $\lambda_{\text{O}_2}$ increases with growing current slightly to a value of 1.4, which is no particular problem as the efficiency of the realized recirculation system increases with increasing gas flow.

![Figure 8.3: Behaviour of the cell with operation in a stack. (a) Average cell voltage as a function of $\text{O}_2$ stoichiometry. (b) Voltage divergence at a $\text{H}_2$ stoichiometry of 1.3. $p_{\text{H}_2} = p_{\text{O}_2} = 3$ bar. (c) Average cell voltage and its divergence as a function of $\text{H}_2$ stoichiometry at 9500 A/m$^2$.](image)

8.2 Constructive Measures to Improve Power Density and Lifetime

A central point of the cell, stack, and system development for Hy-LIGHT was superior power density both in terms of volume and mass. Moreover, the rated power of 30 kW had to be achieved with limited stack size due to constraints in available room within the car body. In particular the stack length was limited which led together with the rated power per cell to a limited thickness of the repetitive unit comprising the cell and the bipolar plate (BPP).

For the sealing of the BPP a similar design to that developed by Ruge and Schimid [85, 84] for POWERPAC was used. It uses a foil of expanded graphite (Sigraflex, SGL carbon group) that covers the entire area of the BPP. The design described in [85] uses two identical coolant flow fields machined into both back parts of the BPP. However, the coolant channels are separated into two parts by the graphite sealing as shown in the left part of Fig. 8.4a. Since the coolant channels have a depth (0.3 mm in POWERPAC) similar to the thickness of the graphite sealing (0.35 mm) integration of coolant channels into the

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1The improved sealing design presented here was patented in:

sealing may save considerable plate thickness. This is shown in the right part of Fig. 8.4a.
Therewith plate thickness \( d_{\text{plate}} \) equal to the sealing thickness \( d_{\text{graphite}} \) is saved. In order to maintain the rigidity, bridges were left in the sealing at the coolant in-/outlets and at corners of the channels. The percolation cross section is maintained by an additional channel as shown in Fig. 8.4b.

**Figure 8.4:** (a) Comparison of earlier and improved sealing design by integration of cooling channels into the 0.35 mm thick expanded graphite sealing of the two part BPP. (b) Bridges at corners of the cooling channels to maintain rigidity.

Operation with pure \( O_2 \) imposes a harsher environment to the materials than air does. For the MEAs, which were provided by umicore (Hanau, Germany), a preparation method was chosen where the CL is applied to the membrane and the GDLs attached to either side during cell assembly. Tolerances in CL application and swelling of the membrane during operation caused occasionally the CL to overlap the GDLs. On this sites the CLs have very poor thermal connection to the cooled flow field plates but still are accessible by the reactants and to some extend electronically connected. The electrochemical reaction there causes therefore strongly elevated temperature and eventually membrane damage and cell failure. A typical hole at the border of the active are due to overlapping catalyst is shown in Fig. 8.5b. In order to avoid this failure mechanism first overlapping of the GDLs over the CL was assured (cf. Fig. 8.5a) and second additional reinforcement of the open membrane using polyimide films was applied by the MEA manufacture umicore (cf. Fig. 8.5c).

**Figure 8.5:** (a) Possible membrane defects due to CL that overlaps the GDL area (right) and improved layout by a CL safely overlapped by the GDL (left). (b) Leak in the membrane at overlapping portions of the CL close to the GDL edge. (c) Protection of the open membrane portion by an enforcement with polyimide film (Kapton, DuPont) which reaches slightly under the GDL.
8.3 Integration into the Fuel Cell System

The fuel cell system and its electrical regulation were developed by Tsukada, Paganeli, and Tobler. In this work, system and regulation requirements were defined and tested in cooperation with them based on the cell and stack characterization described so far.

The mentioned durability concerns due to the use of pure O₂ suggest to reduce the operation pressure to the minimum required value to reach the power demand. Therefore, a pressure ramp from 1.5 bar at low load to 2.5 bar at full load is introduced. Figure 8.6 provides a comparison of j/U curves obtained at constant and variable pressure and the associated influence on the homogeneity of the cell voltages. Clearly, cell voltage obtained with the pressure ramp crosses the respective curves at constant pressure (Fig. 8.6a). Increasing voltage spreading a growing current with low pressure requires the increase of pressure that leads to an equally homogeneous cell voltage on the entire current range.

![Figure 8.6: Influence of the pressure regulation on the j/U characteristics (a) and the voltage spreading (b).](image)

In Hy-Light hybridization by supercaps provide part of the dynamic capabilities required. However, also outstanding fuel cell power change is possible in Hy-Light [139] owing to the operation with pure O₂. The dynamic capabilities of the stack in the fuel cell system are emphasized with an extreme power change from zero to a rated power of 30 kW in 20 ms, as shown in Fig. 8.7a. That is, current is raised from zero to 0.85 A/cm². The power jump was performed current-controlled with a constant pressure of 2.5 bar.

The limiting factor for dynamic response in air fed systems is the response time of the air compressor, which takes several 100 ms to accelerate [141]. The limiting factors in O₂-fed systems become the pressure regulator valves and the recirculation system, when pumps are employed for that purpose. In Hy-Light, however, static injectors are used for recirculation at high loads, which show instantaneous response. Therefore, highly dynamic power change is can be achieved with minimal pressure excursions as shown in Fig. 8.7b and c. In- and outlet pressures of both gases are drawn during the current step, which corresponds to a gas consumption change from zero to 300 and 150 standard liters per
Figure 8.7: (a) Current, voltage, and power during a jump from zero to full nominal power. Appropriate progression of gas pressures at stack in- and outlet for H₂ (b) and O₂ (c).

minute of H₂ and O₂, respectively. Inlet pressure does not deviate more than 0.1 bar from the steady state value. Outlet pressure decreases according to the increased pressure drop due to increased gas flow rate.

A major advantage of the use of pure O₂ as oxidant is the superior cell and system efficiency as compared to air systems (cf. BüCHT et al. [142]). The outstanding fuel efficiency of HY-LIGHT has been proved on the occasion of the 2004 Bibendum Challenge [143]. Obtained data were published in [139] and [144, 142]. Figure 8.8 shows exemplarily stack and system efficiency vs. the respective power as obtained during a random driving cycle. It can bee seen that the system efficiency, as calculated with respect to the lower heating value (LHV) is higher than 60% for the power range of 5 to 27 kW (8 to 80% of rated power.) [142].

Figure 8.8: Stack and system efficiency based on current integration, calculated for the lower heating value of hydrogen. Data obtained in vehicle [137] in random driving profile. Adopted from [142].
8.4 Concluding Remarks

In this Chapter some vertices of cell, stack, and system development and characterization for the automotive power train of Hy-LIGHT were outlined as far as nondisclosure concerns allowed for. The cell and short stack was characterized thoroughly in order to derive requirements for the operating system. Power density and lifetime issues were successfully addressed by constructive measures with MEA configuration and the bipolar plate design. Key features of the realized power train are outstanding dynamic capabilities and system efficiency.
Overall Conclusions and Outlook

Throughout this thesis both mathematical models and experimental techniques have been developed and applied to capture essential physics behind power generation in PEFC. These are the fundamental transport mechanisms of charge, mass and heat, which determine the required driving force, i.e. voltage loss, for current generation and ultimately power generation. The most general conclusion from this work is that phenomena governing the behaviour of complex systems are best elucidated by stepping back into less complex subsystems with less superpositions of the phenomena involved. The ultimate goal of this work was the development of a fuel cell system for automotive propulsion. The integral characteristic of this fuel cell system results from a complex superposition of the local characteristics on all scales from material properties up to the stack level. The phenomena on all of those scales have to be analyzed in order to develop a detailed understanding of the integral characteristics. Therefore, this work employed a stepwise approach with increasing complexity of the investigated systems.

From the system point of view constraints on operation conditions are imposed by issues of parasitic power consumption of auxiliary aggregates. Therefore, optimum conditions for cell operation such as humidification, gas flow rates, and cooling flow cannot be applied. Altogether, we face system efficiency concerns that limit the coolant flow rate, restrict the energetically costly gas humidification to an extent well below cell operation temperature, and allow only for stoichiometric ratios that are not capable of completely removing product water as vapour. Moreover, limited coolant flow causes inhomogeneous temperature that might impair cell power.

As a basis for improvement the loss mechanisms have to be understood most comprehensively. Both theory and experiment was used to gain understanding.

Achievements in Methodology and Understanding

Chapter 3 started with the assessment of membrane models and the measurement of gas transport properties of gas diffusion media. Both a reliable membrane model and valid diffusivity data are prerequisites for the analysis and optimization of fuel cells by
computational simulation. The analysis of transport models for charge and water in the membrane revealed significant differences in terms of voltage drop and water transport, which suggests considerable influence of the used model on simulations of entire cells. Measured effective diffusivities of usual GDL materials have shown that models available in the literature underestimate the tortuosity factors.

Theoretical work in the literature has identified mass transport losses on the scale of channels and ribs to be crucial for performance under high load operation. However, no current measurement method was available so far to corroborate these findings. By introducing a new principle, a method has been developed in a joint effort with Mathias Reum in Chapter 4 that enables measurement of the current density distribution in PEFC with sub-millimeter resolution for the first time. The validity of the novel method was demonstrated by applying it successfully to a test cell under air and oxygen operation. The results show that electrical and ionic resistances govern the current distribution at low current regimes, whereas mass transport limitations locally hamper the current production at high loads. Future work is focused on further understanding of the physical processes involved on that scale and the optimization of channel and rib structures based on the gained insight.

Inhomogeneities in the along-the-channel direction were addressed in Chapter 6. Theoretical and experimental tools for that were developed in Chapter 5. Additionally, experimental techniques developed by coworkers at PSI were employed: Localized electrochemical impedance spectroscopy with Schneider and neutron radiography with Kramer. Possibilities to beneficially counteract the drying and flooding in a technically feasible way were explored. The relative flow direction of all media in the cell turned out to be crucial for cell performance. Internal humidification both in a passive cell internal device and within the active area by counter flow arrangement of the gases was assessed as well as the effect of in-plane temperature gradients. Further on, inhomogeneous catalyst loading was investigated theoretically and was found to be able to homogenize the current density distribution but not to increase power. Finally, a comprehensive picture of the role of electro-osmotic drag, water diffusion through the membrane and liquid water transport through the GDLs for the cell's water balance could be developed from the application of complementary sophisticated experimental and theoretical tools on a cell at different loads.

In Chapter 7 cell interaction phenomena in PEFC stacks that arise from inequalities between adjacent cells were investigated in detail experimentally and theoretically. The impact of various practically relevant anomalies was studied. Results have shown that non-uniform polarization is detrimental for cell power in general. Furthermore, simultaneous localized EIS was used to scrutinize EIS in fuel cell stacks in general.

Chapter 8 has summarized contributions of this work to the collaborative project between Conception et Développement Michelin SA, Michelin's research center in Givisiez, Switzerland.
land, and PSI's Electrochemistry Laboratory in course of which a car with pure electric power train, HY-LIGHT, was realized between 2002 and 2004. Some vertices of cell, stack, and system development and characterization were outlined as far as nondisclosure concerns allowed for. Requirements for the operating system were derived from thorough characterization of single cells and short stacks. Power density and lifetime issues were successfully addressed by constructive measures with MEA configuration and the bipolar plate design. Key features of the realized power train are outstanding dynamic capabilities and system efficiency.

Directions for Future Work

Two major directions for future work emerge from the insights gained so far:

- The pursued way to step back with characterization into less and less complex sub-systems holds promise to further unveil eminent loss mechanisms. Information from high resolution current measurement and detailed material analysis points in this direction. Insight gained fosters understanding of yet required investigations on more complex systems. Experimental characterization of key processes open the route for truly predictive simulations on all scales.

- Ultimately take advantage of the insights to make a better performing and more durable cell.

As long as there are no substitutes for aqueous-based polymer electrolytes water management, mass and heat transfer remain the foremost issues in optimization of component design and cell operation in terms of performance. Intimately connected with performance – and cost – is degradation, which becomes an increasingly evolving area of fuel cell research. Moreover, the dynamic behaviour plays a crucial role in practical fuel cell operation due to its impact on system layout and eventually reliability and degradation. Those issues call for further advancement in methodology and eventually cell design:

Material characterization.— Both to unveil weak points in particular duties of materials and as an input for simulation vacancies in the knowledge of material properties need to be closed. Direction and compression dependence of GDL conductivity as well as contact resistance became required for the high resolution current measurement method described in this work. Likewise, the distributions of gas and liquid transport properties need to be determined for the assembled and compressed GDL rather than assuming a homogeneous material. As a first step effective diffusivities in the dry media were commenced to be measured.
Characterization of the catalyst layer in a simplified, well determined system.— Extensive theoretical studies have been performed to optimize the composition of the CL in terms of void, carbon, and ionomer fraction and to rationalize the polarization behaviour (e.g. [29, 14, 30]). A prerequisite, however, for the function of the CL is an optimized supply with reactants, removal of product and heat, and electrical connection to the current collector. All of this is governed by the interplay of GDL, channels and ribs. Experimental complement (e.g. [26, 27, 28]) to such theoretical studies suffer therefore from this additional complication. It is desirable to characterize the performance of the CL with uniform and well determined conditions at the CL-GDL interface.

Deepen understanding on the scale of channels and ribs.— Our results in Chapter 4 have shown that the performance of the CL is to a great extent not alone decisive for charge transfer losses. In fact O₂ supply through the GDL is a major bottle-neck. Localized EIS in the single cell [96, 116] have shown to be able to separate polarization losses due to local and upstream processes. Consequently, LEIS with sub-mm resolution remains a desirable yet extremely challenging goal. Current step techniques might be a first approach. Ultimately, the combination with liquid detection should be strived.

Dynamic response. — The dynamic behaviour of cells has been studied theoretically both on the channel rib scale and in along-the-channel direction. Experimental studies are, however, chiefly restricted to the integral cell due to difficulties with in particular rapid current changes. The fast local current measurement of the developed large scale cell and the unique capability of our lab for high resolution current mapping suits this goals. The large imbalance in small-scale current distribution is thereby expected to translate in high impact on the full cell dynamic response.

Degradation.— Degradation phenomena are largely current and humidity dependent and also related to dynamic operation [145]. Therefore, all localized methods mentioned above may serve to get insights in degradation as it is likely to occur rather locally confined than uniformly distributed. In addition to steady and transient electrical techniques analysis of decomposition products is desirable.

Translate insights to better cells designs.— This is certainly the ultimate goal behind every effort towards understanding. Besides the examined way of employing beneficial thermal gradients (Section 6.3), optimization of CL supply via optimized channel and rib structures hold promise for the most improvement. Thereby, both local humidity and O₂ depletion have to be accounted for. This means a tailoring of these structures to local conditions along the flow path. Truly validated and predictive computational models are necessary tools hereby. At the same time models often open access to significantly deeper insights from experimental studies on all scales (e.g. Section 6.6).
Bibliography


[54] Datasheet SGL Diabon, SGL carbon group.


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Selected Talks and Poster Presentations

Talks


**Posters**


Curriculum vitae

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