Sub-Millimeter Resolved Measurement of Current Density and Membrane Resistance in Polymer Electrolyte Fuel Cells (PEFC)

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Abstract

This work is a mainly experimental study on the measurement of current density distributions in Polymer Electrolyte Fuel Cells (PEFCs). Its central competence is the development of a measurement method able to assess the current distribution on a scale smaller than one millimeter. In this way, information on local current generation across the flow field’s channels and ribs becomes available. The reliable measurement of the current distribution is a prerequisite for the determination of ionic resistance with the same spatial resolution. The behaviour of sub-mm current and resistance distributions is experimentally investigated for the first time when the method is applied on fuel cells during variation of relevant operating parameters. Eventually, results from the variation of the channel and rib dimensions open the way for developing a new kind of flow field layout at the level of single cells. This optimized design makes it possible to alleviate typical losses in PEFC by locally adapting the flow field geometry to the local conditions along the reactant flow path accounting for the respective limitations on the channel/rib scale.

Chapter 1 provides general background reading on PEFC technology, the accent being placed on relevant limitations and the conditions of their occurrence. It is emphasized that overall losses in a fuel cell eventually originate from smaller scales such as the centimeter-scale of distinguished cell regions (i.e. in- and outlet regions), and the sub-mm scale of channels and ribs. The state-of-the-art methods used for local current generation are presented and their drawbacks identified. The need for a new method to determine currents on the sub-mm scale becomes obvious.

Chapter 2 describes the conceptual approach of this new measurement principle. The current is measured by using the electron conductors in a plane perpendicular to the membrane (diffusion medium and flow field plate) as shunt resistors. The local ohmic drop is measured by filigree potential probes (gilded wires, diameter 10 µm) with a spatial resolution of 200 µm in a test cell specially developed for this purpose. The current density is finally obtained by solving Laplace’s equation in two dimensions. This principle comprises comprehensive ex-situ investigations on the electrical and mechanical properties of the shunts. The local ionic resistance is obtained by time-resolved measurement of the channel/rib current distribution during an electric perturbation. It is shown by error analysis that the measurement procedures are sufficiently accurate for qualitative and quantitative evaluation of the sub-mm current generation.

In the Chapters 3 and 4, local current and resistance measurements are successfully combined and applied to the test cell. The experiments essentially revealed that losses due to membrane drying are associated with the flow channel, while cathodic mass transport limitations are attributed to cell areas covered by a rib. Accounting for this finding, the channel and rib dimensions were appropriately varied. It could be disclosed that it is of advantage to employ different geometries for the inlet and outlet regions of technical PEFCs. Thus, an adapted flow field layout is proposed, which features variable channel and rib widths along the reactant flow path. Experimental investigations at the single cell level finally demonstrated that a homogenization of current – and in this way an improvement of cell performance – is indeed achieved.

Eventually, a synopsis and further ideas for structural optimization are provided in Chapter 5.
Zusammenfassung


Kapitel 1 geht allgemein auf die Eigenheiten der PEFC-Technologie ein, wobei relevante Limitationen und die Bedingungen ihres Auftretens erläutert werden. Es wird gefolgert, dass integrale Verluste letztendlich von untergeordneten Skalen stammen, wie z.B. von der Zentimeter-Skala entlang des Kanals, oder der Sub-mm Skala über Kanal und Steg. Die geläufigen Methoden zur lokalen Strommessung werden vorgestellt und ihre Schwiachtel identifiziert. Als Konsequenz wird die Nötigkeit der Entwicklung einer Messmethode für die Sub-mm Skala herausgearbeitet.


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Chapter 0

Motivation

Today a vast majority of primary energy demand is satisfied by fossil energy carriers. In the future, however, the foreseeable shortage of these sources and related price hikes will most likely force a radical change of the existing structures of energy supply. Decentralized generation in stationary applications and clean propulsion systems for mobile applications are major requisites to meet these challenges, even if the future shares of conventional conversion technologies and renewables are still a matter of speculation today. Nevertheless, in practically all scenarios the use of energy carriers is indispensable to offset spatial and temporal discrepancies in energy supply and demand.

A satisfactory concept for a sustainable energy supply system is based on a hydrogen infrastructure. In this option it is presumed that hydrogen as an energy carrier is produced from fossil free sources, e.g. from the electrolysis of water using carbon-dioxide-free electricity, from biomass, or by chemosynthesis using bacterial cultures. Fuel cell technology would be used for converting this energy carrier into heat and electricity on demand. Fuel cells use the principle of electrochemical oxidation, which is clearly superior to conventional combustion in terms of efficiency. Hence, hydrogen fuel cells have the potential of playing an important role in a future energy supply strategy, both in the sector of individual mobility and in stationary co-generation.

The large-scale introduction of fuel cells to particular market segments is expected in the near future. There danger exists, however, that fuel cells become a niche application, if for instance technological restraints inhibit their competitiveness. Hence, scientific research and engineering efforts are still needed to ensure application in a broad field. Today these efforts are focussed mainly on costs. Improvements of performance and lifetime will lower the operating costs, while material research aims at lowering the expenses for production and the market price of fuel cells. Optimization of fuel cell structures with respect to the above-mentioned issues requires a detailed understanding of the processes occurring on various scales. The generation of current is subject to losses at all levels, from the molecular scale right up to the level of the full system. The situation on a particular scale is thereby governed by limitations at the next lower level.

In the case of Polymer Electrolyte Fuel Cells (PEFCs), current generation at the microscopic level is a function of the reactant distribution throughout the thickness of the catalytic layer. The efficiency of reactant transport here denotes the local current generation in cell areas under a flow channel and in areas covered by a rib. Apart from diffusion processes, charge transport plays a substantial role at this level. Depending on the local resistance and the local degree of reactant depletion on this milliscopic scale, current gradients will emerge at the macroscopic
level along a channel from in- to outlet. These inhomogeneities eventually constitute a reason for overall losses in cell performance. While limitations at one of the above-mentioned levels are therefore originating from the next smaller scale, loss reduction can be achieved by structural optimization on the super ordinate scales. For example optimizing the flow channel layout on the single cell scale can alleviate loss mechanisms in the along-the-channel direction, and altering the channel and rib dimensions can improve diffusion processes on the electrode scale.

In many cases the behaviour of the fuel cell can not be correctly understood by solely considering the overall performance, since the cell voltage is the result of superposition of numerous effects. In recent years, current generation on all scales has been subject to modelling studies, while experimental investigations up to now have been limited to the scale of segmented single cells. Thus, it is necessary to develop experimental methods for investigating the current production on a scale smaller than the flow channel dimensions.

In this thesis such a measurement principle is developed for Polymer Electrolyte Fuel Cells. It allows for the assessment of the local current generation and membrane resistance resolved over the sub-millimeter scale of the flow field structure. In this way the interrelations between PEFC performance and local limitations can be more distinctly revealed. The results help clarifying the relative importance of the factors influencing local current generation, and provide a valuable comparison with model predictions. Furthermore, the method is to be employed as a diagnostic tool for the optimization of fuel cell structures, aiming at homogenizing current generation on the sub-millimeter and single cell scale. A uniform current production has a direct effect on cell performance and therefore on costs, which is a consequence of improved fuel- and catalyst utilization. Moreover, homogeneous operation may relief ageing stresses suffered by the electrochemical components, and thus contribute to lifetime improvements.

The present work was carried out in the Fuel Cell Systems Group of the Electrochemistry Laboratory at Paul Scherrer Institut (PSI) in Villigen (Switzerland). The new measurement method and the results obtained with it are used for optimizing the fuel cell systems developed in-house as well as for technology transfer to industrial organizations.
Chapter 1

Introduction

"Die weltweite Nachfrage nach Kraftfahrzeugen wird eine Million nicht überschreiten - allein schon aus Mangel an verfügbaren Chauffeuren".  
(The world’s demand for automobiles will not exceed the number of one million - alone due to the lack of available drivers.)

Gottlieb Daimler, 1885

This statement of Gottlieb Daimler elucidates the difficulty of evaluating the success of emerging technologies. Up to date fuel cells are in a similar position, ambiguous between being specialized niche products or mass application. The comprehension of the scientific background and the fundamental characteristics is therefore a major prerequisite for the success of the technology.

Fuel cells are electrochemical reactors which convert chemical energy directly into electricity and heat. In contrast to batteries the working principle is continuous, i.e. fuel and oxidant are supplied from outside of the reactor. Unlike internal combustion engines, however, they do not underlie the limitations of the CARNOT cycle. Various types of fuel cells are distinguished by the kind of electrolyte and fuel.

Besides pure hydrogen some systems are fuelled with hydrocarbons or organic liquids, depending on the kind of electrolyte, the catalyst and operating temperature. In the recent decades cell types using solid electrolytes have more and more displaced other types, since some crucial disadvantages are connected with the use of liquid electrolytes in practical applications. For high temperature fuel cells these solids are mostly metal oxides, while ion conductive polymers are used in the low temperature range.

Comprehensive considerations of the technology and science of fuel cells can be found in various text books [1, 2, 3, 4]. In this chapter solely the technology of Polymer Electrolyte Fuel Cells (PEFC) is introduced, representing the field of research at PSI and being subject to application of the measurement methodology developed in this thesis.
1.1 PEFC Fundamentals

This section describes the fundamental scientific processes in PEFC, including the working principle, thermodynamics, kinetics, catalysis and the physics of transport processes.

1.1.1 Working Principle

The electric current generated in PEFCs stems from the electrons involved in the redox reaction of oxygen and hydrogen to water. In contrast to the combustion of hydrogen, the flameless reaction requires reactants spatially separated by the electrolyte and electrons available in an electric circuit. Since the operating temperature is low (<100°C), the activation barrier has to be overcome by a catalytic dissociation of the reactant molecules.

Figure 1.1 illustrates the setup and working principle of a polymer electrolyte fuel cell. The heart of the PEFC is a proton conducting electrolyte in the form of a thin ion-permeable polymer membrane (referred to as ionomer). This allows for charge separation, since the membrane is electrically insulating and only positive ions can be exchanged. The half cell reactions take place at the catalytic sites of the porous electrodes, which are applied as thin layers on each side of the electrolyte. The catalyst therefore must provide contact to the gas- and ionomer phase and furthermore allow for electron drain at the same time, which is realized by the existence of a three-phase boundary. The Hydrogen Oxidation Reaction (HOR)

\[
H_2 \rightarrow 2H^+ + 2e^- \tag{1.1}
\]

occurs at the anode and the Oxygen Reduction Reaction (ORR)

\[
\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{1.2}
\]

Figure 1.1: Schematic drawing of the PEFC working principle: The reactants are supplied from the gas channel and dissociated at the catalyst sites. Right: Magnification of the 3-phase-boundary (catalyst, ionomer, gas).
at the cathode. Different catalysts and catalyst morphologies for each half cell reaction are reported to be of advantage [5]. In total, the oxidation of hydrogen to water is described by:

\[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O. \]  

(1.3)

Electric current in the external circuit results from draining the electrons from the active sites on the anode and supplying them to the cathode reaction sites, since unlike protons negative charge cannot pass the ionomer. Electric conduction is facilitated by the carbon support of the catalyst and the conductive material of the porous transport layers on both electrodes. These layers also allow for the transport of reactants from the gas channel to the catalytic layers. Adjacent to the porous transport layers the channel structure of the bipolar plates ensures the distribution of the reactant gases across the cell area. The plates also serve as current collectors and are typically made from a highly conductive material, e.g. graphite or metal.

1.1.2 Thermodynamics

The amount of energy converted in a chemical reaction is defined by the reaction enthalpy \( \Delta h_r \). In the case of electrochemical elements the thermodynamic cell voltage \( U^0_{th} \) can be expressed by the quotient of this enthalpy with the passed charge as follows:

\[ U^0_{th} = -\frac{\Delta h^0_r}{zF}, \]  

(1.4)

wherein \( F \) denotes the FARADAY number (charge per mol) and \( z \) the number of moles passed. \( U^0_{th} \) is calculated with the reaction enthalpies for each half cell reaction, the total cell voltage is then obtained from addition of the absolute potential differences at anode and cathode, respectively. For the reaction of \( H_2 \) and \( O_2 \) to liquid water a thermodynamic voltage of 1.481 V is obtained for a reaction enthalpy of -285.8 kJ/mol [1].

According to the second law of thermodynamics, the above expression has to be furthermore corrected for the entropic losses. The GIBBS’ free enthalpy \( \Delta g_r \) refers to the value of the reaction enthalpy \( \Delta h_r \) corrected for the product of temperature and entropy. This way the standard reversible cell voltage \( U^0_{rev} \) is obtained:

\[ U^0_{rev} = -\frac{\Delta g^0_r}{zF} = -\frac{(\Delta h^0_r - T^0 \cdot S^0)}{zF}. \]  

(1.5)

Considering standard conditions for the values of entropy and temperature, the maximum cell voltage is decreasing to 1.229 V according to Eq. 1.5. Nonetheless, operation of a fuel cell will not underlie standard conditions. The dependence of the free energy \( \Delta g_r \) on temperature and reactant activity (pressure, concentration etc.) is accounted for in the NERNST equation:

\[ \Delta g_r = \Delta g^0_r + RT \cdot \ln \prod_i \left( \frac{a_{i,products}}{a_{i,educts}} \right)^{\lambda_i}. \]  

(1.6)
Herein $R$ is the ideal gas constant, the index $i$ denotes the reactant species, $a_i$ the chemical activity and $\lambda_i$ the stoichiometric factor of the respective species. Division by the transferred charge leads to the real reversible cell voltage $U_{\text{rev}}$, also referred to as the open circuit voltage (OCV). Written in the form below, the Nernst equation yields the dependence of cell voltage on the variation of temperature and reactant concentration, the latter expressed by the reactant partial pressure $p_i$:

$$U_{\text{rev}} = U_{\text{rev}}^0 + \frac{\Delta S}{zF} \cdot (T - T^0) - \frac{RT}{zF} \cdot \ln \prod_i \left( \frac{p_i}{p_i^0} \right)^{\lambda_i}.$$  \hspace{1cm} (1.7)

In the technical range of temperature, pressure and reactant concentration the OCV is changing only slightly with a variation of these parameters. However, the calculated voltage in the vicinity of 1.23 V cannot be achieved in reality due to the effect of reactant crossover. The permeation of reactants through the ionomer on the molecular scale leads to a mixed potential at the anode and cathode, eventually lowering the OCV and thus dominating the effects of temperature and reactant activity. These crossover losses can be considered a consequence of diluted reactants, in this case a dilution with another electroactive species.

Moreover, the assumption of the exclusive participation of the reaction path as specified in Eq. 1.3 is unrealistic, since the intermediate formation of $\text{H}_2\text{O}_2$ at the catalyst is confirmed knowledge [6, 7, 8]. Contrary to the 4 electrons involved in the formation of water, the formation of hydrogen peroxide as an intermediate species is a two-electron step. Consequently, the cell voltage $U_{\text{rev}}$ is further lowered to an extent defined by the selectivity of the catalyst.

Accounting for the above-mentioned loss mechanisms, the real open circuit voltage will be in the range between 0.95 to 1.05 V, depending on the operating parameters and conditions. When the circuit is closed and current is drawn, additional types of overvoltage occur.

In the low current regime the losses are dominated by the energetic barrier involved in the charge transfer between the electrode and the reactant, these are the activation- or charge transfer overvoltages $\eta_{\text{ct}}$. With increasing cell current, the ohmic drop $\eta_\Omega$ is linearly growing and possibly superposing the kinetic losses. Mass transport limitations in the porous electrodes occur all over the load range, but become crucial near the maximum- or limiting current density. In this case the rate of reactant consumption is so high that transport of educts to the catalyst is the limiting process, and consequently the concentration at the electrode is approaching zero. This leads to a domination of the concentration overvoltage $\eta_{\text{conc}}$, which is negligible at low currents. The basic processes of these three overvoltage are discussed in the following sections.

\footnote{The word 'overvoltage' originates from the vocabulary of the galvanic industry. Losses in galvanic elements had to be countered by increasing the system voltage to keep the reaction going. The bigger the losses, the higher 'overvoltages' had to be applied. Until today, the word has been established also for the losses in electrochemical energy conversion systems, where the term 'undervoltage' would be a more appropriate expression.}
Figure 1.2: Schematic of a polarization plot of a PEFC (also referred to as U-I curve), the additive overvoltages contributing to the total losses are shown over the load range.

Figure 1.2 illustrates the regime of loss mechanisms in the open circuit equilibrium state and along the range of cell current. The plot of voltage against current (the U-I, or polarization curve) is thereby a fundamental illustration for evaluating cell performance. At a specific point of operation, the area under the graph represents the electric power, while the area above is the heat dissipated due to the loss processes.

1.1.3 Kinetics

Multiple kinetic mechanisms are proposed for each of the half cell reactions, both being subject to comprehensive research since decades [9, 10].

In the case of the hydrogen oxidation (HOR) two principles are under discussion, which are distinguished by the simultaneous adsorption of both hydrogen atoms at two catalyst sites (the Tafel-Volmer mechanism) and the one-after-another oxidation at only one active site (the Heyrovski-Volmer mechanism). It was found that the catalyst morphology (mostly Pt and Pt-alloys) may promote the one or the other mechanism, depending on the surface orientation\(^2\).

For the fine dispersed catalyst particles in technical fuel cells, the surface is showing a mixed orientation. Hence, a variable share of both mechanisms on the HOR is assumed by many authors.

\(\text{Surface orientation of metallic catalysts is denoted according to the direction of the cut section through the face centered cubic grid following the so called Miller index. A (100) orientation e.g. means a straight cut parallel to the edge of the cube, resulting in a square arrangement of neighbouring atoms at the surface. The case (111) is the angular cut through all diagonals, the atoms at this surface are packed in a dense hexagonal formation. The most uncongested arrangement is the straight diagonal cut through the cube – referred to as (110) – where a rectangular collocation is achieved. More information on the influence of catalyst surface orientation is to be read from [7] and [11].}\)
The picture is much more complex concerning the oxygen reduction kinetics (ORR). The adsorbed oxygen atoms can react to water via multiple pathways, depending on the adsorption state ($O - O_{ads}$, $O_{ads} - O_{ads}$, $O_{ads} - H$, $O_{ads} - OH^-$, a.s.o.). As mentioned in Section 1.1.2, parallel to the four-electron step

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O,$$

a series of 2 two-electron steps – involving the formation of hydrogen peroxide as an intermediate species – might occur according to

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2.$$  

Alike the HOR, ORR reaction pathways are also dependent on the catalyst morphology. Additionally the cathodic activation barrier at closed circuit is much more a function of potential as compared to the anode, it makes up the major part of the cell’s activation overvoltage.

The charge transfer from the reactant species to the electrode involves the activated complex, i.e. the adsorbate. The formation of this complex is loss prone through the process of adsorption and desorption at the catalyst surface. The reaction rate $k_i$ at one electrode $i$ is therefore connected to the potential dependent free activation energy $\Delta G^0_i$ via the surface concentration of the respective reactant $c_s$ in the Arrhenius equation:

$$k_i = c_s^i \cdot e^{-\Delta G^0_i / RT}.$$  

This rate can be expressed by the currents through the electrode-electrolyte interface $j_i^+$ and $j_i^-$, which are consequently an exponential function of the activation overvoltage $\eta_{ct}$ as follows:

$$j_i^+ = j^0 \cdot e^{\alpha \eta_{ct} \cdot zF / RT} \quad \text{and} \quad j_i^- = -j^0 \cdot e^{-((1-\alpha) \eta_{ct} \cdot zF / RT)}.$$  

The exchange current density $j^0$ thereby represent the rate of charge transfer in the equilibrium (OCV) state, it equals the value of $j_i^+ = j_i^-$ in the case of open circuit. $j^0$ is a function of reactant concentration and the catalytic reaction rate at the respective electrode. It is furthermore independent of potential since it is represented by the equilibrium reaction rate at the catalyst surface. Outside the equilibrium state anodic and cathodic charge transfer at one electrode underly different activation barriers. The charge transfer coefficient $\alpha$ denotes the partition of the anodic charge transfer losses on $\eta_{ct}$. Since it is defined between 0 and 1, the share of activation energy needed for facilitating the charge transfer in cathodic direction is expressed by $(1 - \alpha)$.

Subtraction of the equations in 1.11 finally yields the important relation between cell current $j_{cell}$ and the charge transfer overvoltage $\eta_{ct}$, which is known as the BUTTLER-VOLLMER equation:

$$j_{cell} = j_i^+ - |j_i^-| = j^0 \cdot \left( e^{\alpha \eta_{ct} \cdot zF / RT} - e^{-((1-\alpha) \eta_{ct} \cdot zF / RT)} \right).$$  

For higher activation overvoltages (ca. $\eta > 30/z$ mV) the negative exponential term in Eq. 1.12 becomes negligible, leaving a linear logarithmic relation of current and charge transfer overvoltage in the form of $y = a + b(ln x)$:
1.1. PEFC Fundamentals

This result is called the Tafel equation, it is helpful to determine the values of $j^0$ and $\alpha$ from measured polarization curves. This becomes possible since in the Tafel region (the region of validity of Eq. 1.13) the semilogarithmic plot of the current density yields a linear correlation to the activation overvoltage, where $\alpha$ is extracted from the slope and $j^0$ from the intersection with the $y$-axis. Thus, examinations on the performance of PEFC catalysts can be done sufficiently accurate with Tafel kinetics in many cases, as long as the change of surface concentration with current is negligible.

1.1.4 Charge Transport in PEFC

Charge transport in PEFC is governed by Ohm’s law. It applies for the flux of electrons in the electric conductors as well as for the transport of protons through the ionomer. The transition between these conductors is represented by the charge transfer at the catalyst sites, while the current density is compulsory constant in the entire circuit. The current density $j$ (charge transported per time and area) is expressed by

$$ j = \sigma \cdot \frac{\Delta \phi}{\delta}, $$

where $\sigma$ denotes the electric or ionic conductivity and $\Delta \phi$ the electric or ionic drop of phase potential over the conductive pathway length $\delta$. Ohm’s law is the basis of the charge conservation equation governing the distribution of potential and flux in an anisotropic three-dimensional conductor [12, 13].

Figure 1.3 illustrates the transition from electric to ionic current in the catalytic layer. The cell current density $j_{cell}$ is solely electric in the external circuit, while protons take over charge transport after the reaction at the catalyst. The electric conductivity of the polymer electrolyte is close to zero, allowing only for a technical irrelevant electric leakage besides proton conduction. The drawing further indicates that a three-phase boundary as described in Section 1.1.1 is not always provided in the catalytic layer: some gas has to permeate through a polymer film to reach the catalyst surface, and some protons may travel across the surface of the carbon support to reach the electrolyte.

**Electric Conduction.** In the case of the fuel cell’s electric conductors, the transport of electrons often underlies strong anisotropies. The resistivity of the porous transport layers and bipolar plates may vary several orders of magnitude comparing the in-plane and through-plane directions as well as the different material resistivities themselves. Additionally to the direction of the current drain from the active layer, electric conduction in a plane parallel to the electrolyte does play a significant role in terms of coupling phenomena between neighbouring cells in a stack. Here, perturbations from the failure of one cell might be either compensated or passed on as a function of the bipolar plate’s electric conductivity.
Ionic Conduction. Ionic charge transport in the electrolyte phase is a more complex process, since the charge is transported by the $\text{H}^+$ ion instead of an electron. Ionic conductors – e.g. polymers – typically accompany resistivities orders of magnitude higher than common electric conductors. The reason for this is that ionic charge carriers are limited by their mobility, which does not play a role in the case of electron conduction. The ionic conductivity is thus a function of ion concentration $c_{\text{ion}}$ and diffusivity $D_{\text{ion}}$, as well as of temperature and charge:

$$\sigma_{\text{ion}} = c_{\text{ion}} \cdot D_{\text{ion}} \cdot \frac{(zF)^2}{RT}.$$  \hspace{1cm} (1.15)

The diffusion of the proton through the polymer thereby occurs via a vacancy mechanism involving the acidic polymer end groups\(^3\). This 'hopping' process from vacancy to vacancy underlies an activation barrier $\Delta G_{\text{act}}$ according to

$$D_{\text{ion}} = D^0 \cdot e^{\frac{-\Delta G_{\text{act}}}{RT}}, \hspace{1cm} (1.16)$$

where $D^0$ is the attempt frequency of the hopping event. The activation barrier can be significantly reduced when water is present in the electrolyte matrix, since the proton travels between the vacancy sites by forming an hydronium ion ($\text{H}_3\text{O}^+$) with the surrounding water. A sufficient humidification of both reactant feeds is therefore necessary for effective fuel cell operation.

\(^3\)In the case of sulfonated polymers, e.g. NaFION®, $\text{SO}_3^-$ groups are in charge for the protonic conduction.
Most polymers used in PEFC can take up high amounts of water up to values of 14 to 20 molecules per vacancy site (SO_3^- group). As a consequence, a proton can be alternatively conducted by structural diffusion at high degrees of hydration, which is known as the Grothuss mechanism [14, 15]. In that case no acidic groups are involved in the charge transport, the proton is passing the electrolyte as a solvated hydronium ion solely through water soaked clusters. The ohmic resistance of the ionomer is therefore strongly dependent on the membrane water uptake, as well as on temperature. Figure 1.4 illustrates the linear correlation between membrane water content and ionic conductivity, which is furthermore dependent on the temperature.

![Figure 1.4: Ionic resistance and conductivity as a function of the membrane water uptake (Nafion®) for different temperatures (25, 50, 75 and 100 °C); Data derived from the experimentally found correlation \( \sigma_{\text{ion}} = (0.005193 - \lambda_{\text{H}_2\text{O}} - 0.00326) \cdot e^{(4.185 - 1268/T)} \) given in [3].](image)

Eventually, the net current through the cell is subject to be limited simply by the series connection of the discussed ohmic resistances, including the ionic fraction, the electric fractions and the contact resistances at the various interconnects in the circuit:

\[
\eta_\Omega = j_{\text{cell}} \cdot (R_{\text{ion}} + R_{\text{el}} + R_{\text{contact}}),
\]

wherein \( R_{\text{ion}}, R_{\text{el}} \) and \( R_{\text{contact}} \) are the respective area specific resistances. The resulting ohmic overvoltage \( \eta_\Omega \) is linearly dependent on the cell’s load and usually dominated by the ionic resistance.

### 1.1.5 Mass Transport in PEFC

The transport of reactants and product in fuel cells is characterized by a number of diffusive processes and convection. Generally, the transport of gas in the channel, from the channel to the active sites and the transport of ions and water in the electrolyte are considered separately. All domains are thereby subject to two-phase flow.

Figure 1.5 elucidates the different mass transport processes in the various domains of the fuel cell. Gas is transported from the channel to the catalyst layer by convective flow (reactants and inert gas) and diffusion (only reactants), while liquid product water is removed from the electrode. Proton transport in the electrolyte is driven by concentration- and potential fields,
Figure 1.5: Scheme of the mass transport processes in a PEFC. Convective and diffusive processes occur inside the porous transport layers. The catalyst layer implicates pore- and thin film diffusion; electroosmotic drag and migration effects have to be additionally considered in the domain of the polymer electrolyte.

while water is dragged with them or also follows concentration gradients. Since the proton diffusion is considered as a charge transport process, mainly the transport of reactants to the active sites is dominating the mass transport- or concentration overvoltage.

Eventually the concentration of the reactive species at the catalyst surface is critical for the concentration overvoltage $\eta_{conc}$. A lowered concentration will on the one hand affect the Nernst potential, since the theoretical voltage obtained with the concentration in the gas channel $c^{chan}$ is not the same as the one obtained with the concentration at the catalytic layer $c^{cl}$:

$$ \eta_{conc} = U_{rev}^{chan} - U_{rev}^{cl} = \left( U_{rev}^{0} - \frac{RT}{zF} \cdot \ln \frac{1}{c^{chan}} \right) - \left( U_{rev}^{0} - \frac{RT}{zF} \cdot \ln \frac{1}{c^{cl}} \right), \quad (1.18) $$

or summarized as:

$$ \eta_{conc} = \frac{RT}{zF} \cdot \ln \frac{c^{chan}}{c^{cl}}. \quad (1.19) $$

On the other hand also the kinetic performance will be affected, since the exchange current density and the rate constants are as well a function of reactant concentration. Considering the Tafel kinetics in Eq. 1.13, the charge transfer coefficient $\alpha$ is introduced to obtain a comprehensive description of the mass transport related overvoltages [3]:

$$ \eta_{conc} = \left( 1 + \frac{1}{\alpha} \right) \cdot \frac{RT}{zF} \cdot \ln \frac{c^{chan}}{c^{cl}}. \quad (1.20) $$

It becomes obvious that $\eta_{conc}$ is logarithmically dependent on the concentration ratio across the diffusion media domain. When the transport through this domain is solely diffusive, the process is governed by Fick’s first law, where the mole flux $\dot{n}$ (mol per time and area) can straightforwardly be converted into electric flux $\dot{j}_{cell}$ (charge per time and area) via the specific mole charge $zF$ at a particular stoichiometric ratio $\lambda$ of the reactant $i$ (dimensionless excess ratio):

$$ \dot{n}_i = \dot{j}_{cell} \cdot \lambda_i = D_{eff} \cdot \frac{\Delta c^{chan,cl}}{\delta}. \quad (1.21) $$
The concentration gradient between channel and catalyst layer $\Delta c^{chan,cl}$ is thereby depending on the consumption ($j_{cell}$) and effective diffusivity through the porous medium ($D_{eff}$). With high consumption and/or low diffusivity the achievable current density might be limited by reactant transport. In this extreme case the concentration at the catalyst layer becomes zero, leading to the definition of a limiting current density $j_{lim}$, derived from Eq. 1.21:

$$j_{cell} = zF \cdot D_{eff} \cdot \frac{c^{chan} - c^{cl}}{\delta} \quad \rightarrow \quad j_{lim} = zF \cdot D_{eff} \cdot \frac{c^{chan}}{\delta}. \quad (1.22)$$

With this expression for the limiting current density the ratio of the reactant concentration in the gas channel to the concentration at the catalyst layer $c^{chan}/c^{cl}$ may be expressed as $j_{lim}/(j_{lim} - j_{cell})$. As done already in the sections dealing with kinetics and charge transport, also the concentration overvoltage can now be written as a function of the cell’s current density:

$$\eta_{conc} = \left(1 + \frac{1}{\alpha}\right) \cdot \frac{RT}{zF} \cdot \ln \frac{j_{lim}}{j_{lim} - j_{cell}}. \quad (1.23)$$

**Convective Mass Transport from Channels to Electrodes.** Convective transport is driven by pressure gradients in the gas phase. These gradients occur most prominently in the along-the-channel direction of a fuel cell, but also from the channel towards the catalytic sites. The convective mole flux may be calculated according to

$$\dot{n}_{i}^{conv} = Sh \cdot D_{ij} \cdot \left(\frac{\rho^{chan}_{i} - \rho^{cl}_{i}}{d_{hyd} \cdot M_{i} \cdot RT}\right). \quad (1.24)$$

Thereby the Sherwood number $Sh$ represents the ratio of the overall mass transfer rate to the diffusion rate, it is dependent on the flow channel geometries and might be obtained experimentally. Although the flux is only considered over one channel wall – the interface to the diffusion medium – the channel dimensions and the shape of the cross section impact the Sherwood number and the hydraulic diameter $d_{hyd}$ \(^4\). A triangular channel cross section e.g. shifts the core flow closer to the diffusion medium interface, allowing for increased convective penetration. Generally, convective flow in this medium is only dominating reactant transport in the case of pressure gradients between neighbouring channels or in bends. The flow field layout is therefore an additional influence factor besides the channel geometries. More reading on this impact factor is provided in Section 1.2.4.

Eq. 1.24 further shows that convective transport is also dependent on the molar mass $M$ and the diffusivity of the component $i$ in the mixture with the component(s) $j$. Diffusion driven by concentration gradients is a process occurring in the channel as well as in the diffusion media, hence it is always participating in mass transport. Diffusion is the dominating process in areas remote from the channel.

---

\(^4\)The hydraulic diameter is defined as four times the cross section area divided by the cross section perimeter.
Diffusive Mass Transport in the Porous Layers. The diffusive transport of gas from the channel to the active sites in a concentration field is hindered by interactions of gas molecules with each other and with the porous structure of the diffusion medium. In macroporous domains – e.g. the channel or the gas diffusion layer (GDL) – diffusive limitations are due to collisions of molecules in the mixture of reactant, product and inert gas. In microporous layers, however, collisions with the pore walls are limiting effects prior to intermolecular friction.

The depletion of a reactant species along the diffusion pathway length is the central issue in terms of diffusive flux. However, Fick’s law holds only true for simple cases involving a binary mixture. As indicated in the above section, fuel cells operated with air involve the presence of three species in the gas distributing structures (O$_2$, N$_2$ and H$_2$O). A more comprehensive description of the multicomponent diffusion process is therefore provided by the Stefan-Maxwell equation:

$$\frac{dx_i}{d\delta} = \sum_{i \neq j} \frac{x_i \cdot n_{ij}^{df} - x_j \cdot n_{ji}^{df}}{c^{chan} \cdot D_{eff}^{ij}}.$$  \hspace{1cm} (1.25)

Herein, $dx_i/d\delta$ is the derivate of the diffusing species’ mole fraction along the diffusion pathway, $n_{ij}^{df}$ are the diffusive mole fluxes of the species $i$ and $j$, $c^{chan}$ is the reactant concentration in the channel and $D_{eff}^{ij}$ the effective diffusivity for the binary transport of species $i$ in $j$. For reactants, the mole flux $\dot{n}$ is expressed by $j_{cell}/zF$. The species $i$ is considered the diffusing species, while all other components in the mixture appear individually as respective species $j$ in an additional sum expression. Since the molar fraction $x_i$ is appearing on both sides of Eq. 1.25, numerical methods are required to solve the problem [16, 17].

A key parameter for mass transport in porous media is the effective diffusivity $D_{eff}^{ij}$. It is a parameter depending on both, the geometrical structure of the diffusion medium and the species properties. Generally, the effective diffusivity equals the binary diffusivity of a species in a gas mixture (Eq. 1.27) corrected for a geometrical factor involving tortuosity $\tau$ (real diffusion pathway/direct pathway) and porosity $\epsilon$ (pore volume/total volume), which is known as the Bruggemann correction. Comprehensive examinations on this geometrical factor have been carried out for many special cases [18, 19, 20], a common expression providing sufficient accuracy is however defined as:

$$D_{eff}^{ij} = \frac{\epsilon}{\tau} \cdot D_{ij}. \hspace{1cm} (1.26)$$

The form factor $\epsilon/\tau$ is a measure for the geometrical obstacles in the porous structure diminishing the nominal- or binary diffusivity $D_{ij}$, which describes the transport of the species $i$ in an environment of $j$. This value is unique for every binary gas mixture and has to be considered for the calculation of the effective diffusivity in a multi component system regarding Eq. 1.25. It may be obtained from the Slattery-Bird relation accounting for the thermophysical properties of the single gas species [21]:

$$D_{ij} = \frac{1}{p^{chan}} \cdot a \left( \frac{T}{T_{c,ij} \cdot T_{c,j}} \right)^b \left( \frac{p_{c,i} \cdot p_{c,j}}{p_{c,ij}} \right)^{\frac{1}{2}} \cdot (T_{c,i} \cdot T_{c,j})^{\frac{5}{12}} \cdot \sqrt{\left( \frac{1}{M_i} + \frac{1}{M_j} \right)}. \hspace{1cm} (1.27)$$

$T_{c,ij}$ and $p_{c,ij}$ describe the critical temperature and pressure of the respective species, $p^{chan}$ the
absolute gas pressure in the channel and $M_{ij}$ the species molar masses. The coefficients $a$ and $b$
are determined empirical.

In order to examine the influence of binary diffusion in different inert gases, experiments with
oxygen diluted in helium instead of nitrogen are often of advantage. Table 1.1 hence provides
the critical gas properties and empirical coefficients for ternary cathodic gas mixtures containing
O$_2$, H$_2$O and N$_2$ or He, respectively.

<table>
<thead>
<tr>
<th>Species</th>
<th>critical temperature $T_c$ [K]</th>
<th>critical pressure $p_c$ [bar]</th>
<th>empirical parameters $a / b$</th>
<th>binary diffusivity $D_{ij}$ [cm$^2$/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>155.4</td>
<td>5.1</td>
<td>diffusion of O$_2$ in:</td>
<td>diffusion of O$_2$ (H$_2$O) in:</td>
</tr>
<tr>
<td>N$_2$</td>
<td>126.1</td>
<td>3.4</td>
<td>0.000274 / 1.823</td>
<td>0.295 (0.416)</td>
</tr>
<tr>
<td>He</td>
<td>5.3</td>
<td>2.3</td>
<td>0.000274 / 1.824</td>
<td>2.300 (1.300)</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>647.1</td>
<td>22.1</td>
<td>0.000363 / 2.334</td>
<td>0.398 (–)</td>
</tr>
</tbody>
</table>

Table 1.1: Thermophysical and empirical constants of O$_2$, N$_2$ and H$_2$O [21], the binary diffusion coefficients are
obtained according to equation 1.27.

However, the calculation of effective diffusivity using the binary constant from equation 1.27 is
only valid for macroporous structures and free gas volumes. In microporous domains pore walls
may dominate the transport limitations. The regime of pore diffusion allows for neglecting other
gaseous species in the multicomponent mixture. Now, instead of $D_{ij}$, the KNUDSEN diffusion
coefficient $D_K$ is inserted into Eq. 1.26 [20, 22, 23]:

$$D_K = \frac{3}{2} r \cdot \sqrt{\frac{8}{\pi} \cdot \frac{RT}{M_i}}.$$  (1.28)

Herein $r$ denotes the radius of an approximately round and straight pore, and $M_i$ the molar mass
of the diffusing species. The KNUDSEN criterion (or KNUDSEN number) $Kn$ is defined as the
ratio of the mean free path of a molecule and the pore diameter, it denotes the regime of pore
diffusion when $Kn >> 1$. The mean free path of a diffusing molecule is thereby a function of gas
pressure, temperature and molecule size.

Possible pore diffusion domains are found in the microporous layer (MPL) of the GDL and
the catalytic layer (CL). These are usually made from a fine carbon powder and feature mean
dore radii of around 0.1 to 1 µm, which is in contrast to the coarse void volumes of most GDL
materials with quasi radii of 10 to 50 µm. The reactant species travel through these domains to
eventually reach the catalyst surface at the three-phase boundary, where the connection to the
proton conducting ionomer and the electron conducting carbon support is assured.

In recent years the comprehension of this interface has been extended. Agglomerate models for
the catalytic layer [24, 25] showed that the reaction rate is not significantly affected when a
reactant from the gas phase has to cross a thin film of electrolyte covering the catalyst surface.
This step of solid state- or thin film diffusion is also governed by Fick’s first law. However, the
concentration of the dissolved reactant in the ionomer film is – according to HENRY’s law – lower
than the concentration in the gas phase at the CL interface, expressed by the partial pressure $p_L$:
\[ c_i^{cl} = \frac{1}{H} \cdot p_i^{cl} \quad \Rightarrow \quad \dot{n}^{tf}_i = D_i^{tf} \cdot \frac{\left( \frac{1}{H} \cdot p_i^{cl} \right) - c_i^{cs}}{\delta^{tf}}. \] (1.29)

Herein \( H \) denotes the Henry constant, which is a measure of the solubility and temperature dependent. Following the diffusion equation, the mole flux of reactant through the thin film \( \dot{n}^{tf}_i \) is eventually depending on the diffusivity of the reactant \( D_i^{tf} \) and the film thickness \( \delta^{tf} \). The driving force for the thin film diffusion is the concentration gradient between the interface to the gas phase \( c_i^{cl} \) and the concentration in the solid phase at the catalyst surface \( c_i^{cs} \).

**Mass Transport in the Electrolyte.** The charge transfer reaction at the catalyst surface requires the supply or removal of ionic species in the electrolyte. The displacement of protons can be driven by both, concentration gradients (diffusion) and potential gradients (migration). Convective effects are however unlikely to occur in a solid electrolyte. Thus, the Nernst-Planck equation is used to describe the area specific flux of the transported proton \( \dot{n}_i^{H^+} \):

\[ \dot{n}_i^{H^+} = D_i^{H^+} \cdot \frac{\Delta c_i^{H^+}}{\delta} + (c_i^{H^+} \cdot u_i^{H^+}) \cdot \frac{\Delta \phi}{\delta}. \] (1.30)

The first summand involving the species diffusivity \( D_i^{H^+} \) represents the diffusive transport according to Fick’s first law, while the second summand describes the migration in the potential field. The product of the proton concentration \( c_i^{H^+} \) and its mobility \( u_i^{H^+} \) corresponds to the term \( \sigma_{ion}/(zF) \), accounting for the charge transport aspect of ion conduction as shown in equation 1.15. However, for low currents or electrolytes with high conductivity the potential gradient \( \Delta \phi \) converges zero, and only the diffusive term governs the ionic mass transport in the membrane. The diffusivity of the ionic species \( (D_i^{H^+}) \) thereby obeys the relation displayed in Eq. 1.16.

Another aspect of mass transport in the electrolyte is the electroosmotic drag of water. When a proton is transported through the membrane, the water present in the polymer matrix forms a solvation shell around the ion. The number of water molecules attached to a proton is obviously depending on the membrane water content \( \lambda \), it is referred to as \( x_{\text{drag}}(\lambda) \). This number can range from values below 1 (dry membrane) to ca. 2.5 for a saturated ionomer [26, 27]. The area specific molar flux of water through the membrane can be related to the cell’s current density corrected with \( x_{\text{drag}} \).

Since this transport process is directed from the anode to the cathode, water accumulations consolidated with the product water may occur leading to considerable humidity gradients across the electrolyte. Hence a back diffusion process occurs towards the anode, which has to be considered when evaluating the net transport of water. It is depending on the concentration and diffusivity of water in the polymer, as well as on the specific water content \( \lambda \) and its gradient from anode to cathode \( \Delta \lambda \). The overall expression for the water transport therewith reads as

\[ \dot{n}_{\text{H}_2O}^{net} = j_{\text{cell}} \cdot \frac{x_{\text{drag}}(\lambda)}{F} - D_{\text{H}_2O}(\lambda) \cdot \frac{c_{\text{H}_2O}}{\lambda} \cdot \frac{\Delta \lambda}{\delta}, \] (1.31)

where the water diffusivity in the polymer \( (D_{\text{H}_2O}) \) is itself a function of the water uptake \( \lambda \) (the diffusivity increases with the water content), and \( \delta \) denotes the pathway length through the
electrolyte. In this equation the first expression represents the osmotic water drag (anode → cathode), and the second term the back diffusion (cathode → anode).

Recalling the considerations from Section 1.1.4, water gradients across the membrane cause local variations of conductivity. Accounting for the increased water drag at high currents, the ionic conductivity must not necessarily rise, although the water production at the cathode is increased. Due to anode drying induced by the drag effect, the integral cell resistance is observed to increase, especially with the use of thick membranes [28, 29, 30].

**Two-Phase Flow in Porous Media.** Since PEFC are generally operated below 100°C, condensation of product water or water from the external humidification may occur, especially at high current densities. The transport of these liquid accumulations through the porous electrodes can be described by Darcy’s law [21, 31]. Herein, the volume flux of a liquid through a porous medium is proportional to pressure gradients over the length of the flooded domain δ:

$$
\dot{V}_{\text{H}_2\text{O}}^{\text{liq}} = -\kappa \cdot \frac{A}{\mu_{\text{H}_2\text{O}}} \cdot \frac{\Delta p}{\delta}.
$$

(1.32)

The term involving the permeability of the porous medium ($\kappa$), the cross section area available for the flow ($A$) and the fluid’s dynamic viscosity ($\mu_{\text{H}_2\text{O}}$) thereby represents the mobility of water. This equation is valid in regions where convective gas flow drives the two-phase transport, i.e. in the GDL near the interface to the channel. In regions where no hydraulic pressure gradient can serve as driving force, i.e. near the CL, transport of liquids is driven by the capillary pressure $p_{\text{cap}}$ as described by the Young-Laplace equation:

$$
p_{\text{cap}} = \frac{2\sigma}{r} \cdot \cos \Theta.
$$

(1.33)

Herein, $\sigma$ denotes the surface tension of the water agglomerate, $r$ the pore radius and $\Theta$ the contact angle to the pore wall.

Although there are many unknowns for two-phase transport in fibrous media, inspection of Equation 1.33 reveals that the pore size distribution and the hydrophobicity – both design parameters of diffusion media – have a crucial influence on water management via the pore radius and the contact angle.

Moreover, also superordinate cell structures are of particular significance: the velocity of the gas flow will affect the removal of liquid water accumulations such as droplets or films by contributing to the critical removal pressure [32]. Consequently, positions in the diffusion medium with only little share of convective flow might suffer from poor water removal, which entails electrode flooding and hence reactant starvation. These limitations might be overcome by optimizing the flow field dimensions and -layout.
1.2 PEFC Components

This section briefly describes the typical components used in PEFC from a technical point of view. The material properties which enable the application in fuel cells are discussed, as well as the disadvantages and bottlenecks connected with them.

1.2.1 Polymer Electrolyte

A very common polymer electrolyte for PEFC – which is the one used in all experiments presented in this thesis – is produced by DuPont under the trade name Nafion®; it is a perfluorated copolymer (back bone with side chains). The back bone consists of a Polytetrafluoroethylene-like chain (PTFE, a.k.a. Teflon®), comprising around 1000 CF₂ and CF groups. Every 10 to 20 monomers a side chain of variable length is attached, facilitating proton conduction by means of sulfonic acid groups (SO₃⁻). Perfluorated membranes in general are known since years to qualify well for electrochemical applications [33]. The chemical structure of Nafion® comprising the back bone, the side chains and the acidic end group is shown in Figure 1.6a.

As mentioned in Section 1.1.4, protonic conduction requires the presence of water to ensure the transport of protons in form of hydronium ions between the acidic groups⁵. This is assured by the existence of water filled clusters in the polymer structure, exploiting the hydrophilic properties of the side chains and the hydrophobic character of the PTFE back bone (see Fig. 1.6b). These clusters have been found to expand upon increasing water content, eventually forming channels, resulting in an improvement of ionic conductivity [34].

![Figure 1.6: a) Molecular and b) Microscopic structure of the Nafion® copolymer. Proton conduction is assured by the sulfonic end groups which extend in water filled clusters or -channels containing the solvated proton.](image)

Nafion® is changing its mechanical properties during water uptake as a function of temperature. The expanding water clusters lead to a swelling of the polymer film, which goes along with the loss of mechanical integrity [35, 36, 37]. Vice-versa, the application of mechanical stress might impair the ion conductive properties by hampering the formation of said clusters.

⁵Ionic conductivity is obviously a function of the number of available sulfonic groups and membrane thickness. The notation of Nafion® membranes follows these two parameters: the equivalent weight (EW = polymer mass in g per mol acidic group) divided by 10 + the membrane thickness in mil (1 mil = 1/1000 in = 25.4 µm). The common product Nafion® 112 has therefore an EW of 1100 g/mol and a dry thickness of ca. 51 µm.
1.2.2 Electrodes and Catalysts

The Catalytic Layer (CL) of PEFCs is typically a microporous structure of carbon particles impregnated with electrolyte (ionic phase). The carbon represents the electric phase and carries the finely dispersed catalyst particles, as can be seen from Figure 1.7 b. The CL is either applied to the polymer membrane or to the side of the gas diffusion medium contacting the electrolyte. In the latter case hot pressing is required to ensure a good ionic contact between the ionomer in the CL and the membrane.

![Figure 1.7: Structure of a PEFC catalytic layer; a) SEM-micrograph of the impregnated carbon structure (adapted from [38]). b) TEM-micrograph of the carbon support with dispersed catalyst agglomerates.](image)

**Electrode Structure.** For achieving a higher catalytic performance, increasing the layer thickness or the catalyst loading seems to be effective. However, thin electrodes with a minimum of catalyst loading are desired, since both of the above options are disadvantageous.

As a consequence of the impregnation with electrolyte, the electric resistance is comparatively high and lays in the range of the ionic resistance. Increasing the thickness would therefore noticeably effect the cell’s ohmic overvoltage [39, 40]. An even more dominant limitation is the transport of reactants inside the active layer, an increased thickness would thus be associated with using only part of the catalyst sites [41, 25].

It is furthermore mainly the cost issue asking for a reduction of the catalyst loading, since mostly noble metals are used in PEFC. The mass of catalyst used for a specific electrode area has thereby drastically reduced from 4 mg/cm² in the 60ies to less than 0.1 mg/cm² today [42]. This became possible through a finer dispersion of the metal particles and a concomitant increase of the specific surface of the electrode structure.

Electrode preparation may be done using conventional impregnation methods [43] or microemulsion techniques using anorganic precursor materials with a high specific surface [44, 45]. In both cases the catalyst is incorporated via a solution of the respective metal salt, cluster diameters below 10 nm are state of the art [46]. The adsorptive surface (BET) of the electrode can thereby
be increased by controlled nano-structuring of the carbon support. A non-dispersed catalyst (‘metal black’, only used in model systems) exhibits a specific surface of 30 to 40 m$^2$/g, while a fine dispersed catalyst on a microporous carbon support achieves a BET-surface of 100 to 300 m$^2$/g. With nanostructured electrodes however, e.g. carbon nanotubes or similar filigree support structures, specific surfaces of more than 1000 m$^2$/g BET are possible [47, 48].

**Catalysts.** The measure for catalytic activity is the exchange current density $j^0$. Although this value is order of magnitudes smaller in the case of the ORR compared to the HOR, the same group of metals show the best catalytic performance for both reactions. Generally, the catalytic activity of a reaction can be correlated to the position of the catalyst metal in the periodic system (Sabatier principle). This relation can be plotted in a so called volcano curve, where platinum shows the highest performance (see Fig. 1.8a). Extensive studies on the ORR have however shown that a higher activity compared to pure Pt can be achieved with the use of several platinum alloys as shown in Figure 1.8b. The reason for this is the modified surface orientation of the crystalline grid, which denotes the activity and selectivity.

![Volcano Curve for Catalytic Activity](image.png)

Figure 1.8: Exchange current densities $j^0$ for different catalysts: a) Volcano plot for the catalytic activity of metals for the HOR in acidic electrolyte, b) Catalytic activity of pure noble metals and platinum alloys for the ORR in acidic electrolyte; all data compiled from [49, 50, 51].

Platinum based catalysts only tolerate small amounts of carbon monoxide up to 10 ppm. The CO has a higher affinity to the catalyst as H$_2$ or O$_2$, and therefore blocks the adsorption sites by forming a covering monolayer [52]. Hence, a lot of research is currently focussing on the manipulation of the catalyst surface structure in order to increase the tolerance against impurities in the reactant feeds [53].

In general, the use of noble metals is disadvantageous. This is not just because of their costs, but because of their scarcity, i.e. in the case of platinum. Research to find appropriate non noble catalysts has therefore come up in the recent years. Promising candidates are macrocyclic complexes containing transition metal based sulfides and selenides. Such molecular-level assemblies are based on cheap metals as Fe, Cu, Co or Ni, whereby heat treatment and nano structuring of the support are prerequisites for stability and sufficient performance [54, 55].
1.2.3 Gas Diffusion Layers

The Gas Diffusion Layer (GDL) fulfils mainly two tasks: allowing for access of gaseous reactants to the catalytic layer under the flow field land and facilitating the electric connection between the electrode and the external circuit in the flow field channel. The material thus requires a porous structure and good electric conductivity. All presently available materials consist of carbon fibres or filaments, either woven in a cloth structure or randomly arranged in a carbon felt or paper (see Fig. 1.9 or [56]). The porosities in the uncompressed state range from 70 to 80% [57].

In addition to this function, removal of liquid water is an important characteristic. GDLs are therefore normally PTFE-impregnated to 10-50% of their weight. Consequently, water films or droplets cannot clog the hydrophobic structure and are removed towards the gas channel.

To improve water removal and the electric interconnect of GDL and CL, a Micro-Porous Layer (MPL) is applied on one side of the GDL [58]. This carbon powder layer exhibits a similar pore size distribution as the catalyst support in the CL, which is about 2 to 3 orders of magnitude lower than the pore sizes of the GDL bulk (see Fig. 1.10). The thickness of the MPL varies from less than 10 up to 50 µm or more, since it penetrates bigger pores of the GDL.

**Figure 1.9:** SEM micrographs of different GDL materials without microporous layers: a) E-Tek woven carbon cloth (adapted from [59]), b) TORAY carbon paper, non-impregnated.

**Figure 1.10:** SEM micrographs of a) Microporous layer (MPL) on an impregnated carbon paper, b) Magnification of the MPL, the carbon clusters are visible on a fibre of the bulk material.

An important feature concerning most of the GDL materials is the strong anisotropy regarding the mechanical – and therewith connected – the electrical properties. Due to fibre orientation, the in-plane and through-plane electrical conductivities can vary about one order of magnitude. These parameters are furthermore subject to change when the medium is compressed, which is a consequence of the increasing number of contact sites between the fibres. Additionally, the high compressibility of the porous structure has a strong influence on the gas permeability since the void volume decreases with compression [60]; typically tortuosities changes from 1.2-1.5 to ca. 3.
1.2.4 Flow Field Plates

The Membrane-Electrode-Assembly (MEA = GDL + CL + Membrane) is sandwiched between flow field plates. These components ensure the drain of electrons and heat from the single cells in a stack, respectively. Furthermore they separate the reactant gas fluxes and provide mechanical stability. Good electric conductivity, low gas permeability, mechanical- and chemical stability at low volume and weight are therefore the key properties. Another important issue is the layout of the flow field structure, which governs the quality of the gas distribution across the cell area.

**Materials.** There are three main types of plate material available: those based on graphites, composite materials and metal plates. Table 1.2 provides an overview on these types and their properties.

<table>
<thead>
<tr>
<th>Type:</th>
<th>Metal</th>
<th>Graphite</th>
<th>Composite</th>
</tr>
</thead>
<tbody>
<tr>
<td>MATERIAL:</td>
<td>stainless steel</td>
<td>sintered carbon</td>
<td>carbon based</td>
</tr>
<tr>
<td></td>
<td>noble metal coated Al, Ni, Ti</td>
<td>flexible graphite</td>
<td>(raisin w. carb. filler, fibre backing)</td>
</tr>
<tr>
<td>ADVANTAGE:</td>
<td>low resistance</td>
<td>chemical stable</td>
<td>chemical stable</td>
</tr>
<tr>
<td></td>
<td>mechanical stable</td>
<td>low contact resist.</td>
<td>low density</td>
</tr>
<tr>
<td>DISADVANTAGE:</td>
<td>corrosive (uncoated)</td>
<td>unstable, brittle</td>
<td>low conductivity</td>
</tr>
<tr>
<td></td>
<td>expensive coatings</td>
<td>high permeability</td>
<td>expensive and complex machining</td>
</tr>
</tbody>
</table>

Table 1.2: Types, materials and properties of flow field plates for PEFC; compiled from literature [61, 62, 63, 64].

Metal plates feature the advantage of comparably high electric conductivity at high mechanical strength, even with low plate thickness. Media separation is also assured due to the very low gas permeability of metals. However, non-coated plates suffer from passivation or corrosion, whereby the corrosion products can contaminate the electrochemical components of the cell. Coatings to prevent corrosion – mostly noble metals – are expensive since vast amounts are necessary as compared to the catalyst loading of the electrodes.

An alternative are graphite based plates, which are available as sintered carbon materials or layered, flexible sheets. They accompany chemical stability, good electric conductivities at low weight as well as a low contact resistance to the GDL, since the group of material is the same. A crucial drawback is however the relatively high gas permeability of these materials. Furthermore, the mechanical stability is not sufficiently guaranteed neither for the brittle carbon plates nor flexible graphite.

A promising type of plates are composite materials. Besides a few metal based compounds, the majority of composite materials is based on carbon, dissolved in a polymeric binder. To improve mechanical stability, a framework structure of synthetic fibres can be introduced. Composite materials are chemically inert, mechanical stable and provide a good media separation. In recent time also improvements have been made concerning the electric conductivity [65], which was typically one order of magnitude below pure graphite and two orders below metal plates. One issue with these materials is however the yet insufficient chemical stability.
Flow Field Layout. An issue not less important than the choice of material is the quality of reactant distribution across the active cell area, which is defined by the flow field structure. The dimensioning of channels and ribs is thereby a delicate balance between maximizing the gas accessibility and the contact area for electron drain. The ratio of gas channels to current lands as well as their dimensions and shapes strongly influence the distribution of potential and current on the millimeter scale and below, which will be subject of discussion in Chapters 2 and 4.

On the single-cell scale, however, the layout of the flow field structure across the cell area influences the current generation through the kind of gas transport process from the channel to the active site. Thereby the enforcement of convective transport is of advantage, since the reactant concentration gradient may decrease throughout the GDL and liquid accumulations may be removed more easily. Figure 1.11 clarifies the influence of flow field layouts on GDL gas transport.

The most unconstrained gas flow is obtained with straight channel- or pin-type layouts as depicted in Figure 1.11 a). Only marginal convection is facilitated in the porous transport layer, resulting in low limiting current densities. The occurrence of 'dead zones' with low flow in the gas channel is another issue with the use of pin-type flow fields. Therewith connected, severe flooding is the...
reason that these kinds of flow fields are for the most part used for academic studies and are not relevant for technological applications.

In order to force convection in the GDL, often bends are introduced in the channels. This leads to curved flow field layouts or serpentines as shown in 1.11 b). The intention behind this principle is to create a pressure gradient between neighbouring channels, leading to a compensating flux of gas underneath the land. The deeper penetration of the gas flow into the GDL allows for higher limiting currents, although the diffusion process is not completely superseded by convective flow. Serpentine layouts are state of the art in fuel cells for technical applications.

An extreme case regarding the enforcement of convection is the principle of the interdigitated flow field layout (see Fig. 1.11 c). Here, the gas channels are not continuously conducted from inlet to outlet rather than being dead ended. This way the gas reaches the outlet channels solely by convection through the porous medium, theoretically leading to the highest possible limiting currents. However, high expenses for reactant pumping power to compensate for the enormous pressure drop and insufficient water management lead to the inapplicability of interdigitated layouts in technical PEFC applications.

1.2.5 Component Degradation

The durability of PEFC performance depends on the degradation of the fuel cell components, which is caused by chemical or mechanical stress during operation. It can be distinguished between membrane degradation, loss of catalytic surface area and corrosive effects. Degradation is measured in terms of voltage loss over time at a specific current density, typical rates are in the range of 10 to 60 \( \mu \text{V/h} \) with operation on mean cell currents [67, 68].

Loss of Sulfonic Groups. Over time, the chemical structure of the membrane is suffering from the loss of side chains with the sulfonic groups attached. Fluoric and sulfonic species can therefore be detected in the product water as a consequence of this decomposition process.

There are various reasons proposed for triggering the decay, involving \( \text{H}_2\text{O}_2 \)-radicals from crossover permeation of reactants [69, 70] and metal ions dissolved from the flow field plates [71]. These mechanisms are promoted predominantly under high voltages, i.e. OCV.

However, it can be shown that sub-optimal operating conditions also accelerate membrane degradation. Chemical stress is applied from the flux of ionic current and water through the polymer, leading to gradients in membrane degradation from inlet to outlet positions [72] as well as from channel- to rib covered areas [73].

Loss of Catalytic Surface. The loss of active catalyst area is also due to various kinds of degradation. The most prominent forms are the catalyst dissolution and agglomeration, whereby parts of the metal catalyst move across the carbon support and sinter to bigger agglomerates with a smaller specific surface, or become completely removed with the gas- or liquid flow [74]. The presence of water thereby substantially facilitates the mobility of the metal particles.

Catalytic surface can also be forfeit by reactions with impurities contained in the reactant feed. Irreversible adsorption of carbon monoxide or organic species thus leads to a cumulative loss of catalyst activity over time.
Mechanical Integrity. Finally, mechanical failure is responsible for additional degradation of cell performance. On the one hand, corrosion of carbon to CO₂ occurs at high potentials, resulting in the decay of the catalyst’s carbon support. This leads again to a loss of active area, this time chemically triggered by the decay of the support structure.

On the other hand, recurring mechanical stress due to changing conditions is imposed by the current lands, especially upon dynamic operation. Thereby the membrane is permanently swelling and shrinking due to humidity cycling, resulting in material fatigue and the possible formation of pinholes. Such temperature- and humidity cycles also facilitate the structural decay and the delamination of the electrode. Especially frost heave under sub-zero conditions is known as a failure cause [75].

Furthermore, corrosion of metallic bipolar plates or the forming of a passivation layer might with time increase the contact resistance between the plate and the GDL [76].
1.3 Local Current Generation in Fuel Cells

Current generation in fuel cells is for the most part not uniform across the active area. Inhomogeneous operating conditions and design parameters result in locally discriminated distribution of ionic resistance and reaction rate, which co-actively entails non-uniform current generation on the scale of the respective limitation. This section provides an overview on the measurement and the origin of these current gradients in PEFC. The relevant diagnostic methods are introduced and a review of the recent literature concerning current gradients on various scales is provided.

1.3.1 Diagnostic Methods for PEFC

**Integral Performance and Resistance Measurement.** The accurate measurement of current and resistance is an important prerequisite for evaluating losses and understanding processes in fuel cells. The most simple diagnostic method to evaluate the performance of a fuel cell is to record the behaviour of the cell voltage during alteration of the integral current density (the U-I plots have been discussed in Figure 1.2).

In analogy to this, the ohmic cell resistance can be determined during operation with transient methods. Besides stationary data acquisition, often temporally resolved measurements are carried out to analyze the system answer during transient operation of the fuel cell. Information on various phenomena can be returned this way, depending on the frequency of the current transient. The fraction of ohmic resistance is identified by the dynamic response of cell voltage on very fast current transients, whereby the application of current interruptions, pulses or steps represent the most simple techniques [77].

As shown in Figure 1.12, the sudden perturbation of the stationary point of operation triggers a reaction of cell voltage. Two regimes are thereby identified regarding the behaviour in the time domain: an immediate voltage rebound and a much slower relaxation to the new stationary point. These regimes correspond to overvoltages stemming from different processes in the fuel cell. The ohmic overvoltage connected to the cell current $j_{cell}$ is the only one changing instantaneously with the load. All other factors, e.g. the diffusion overvoltages, are noticeably slower and may even balance out in the magnitude of seconds after the current transition.

![Figure 1.12](image-url)  
**Figure 1.12:** Principle of the current interrupt/pulsing technique for measuring ohmic resistance in PEFC: the voltage response on a current perturbation shows an instantaneous rebound followed by a slow relaxation (magnification), the instantaneous response is a measure for the ohmic cell resistance.
The perturbation is often realized by interrupting the cell current for a defined period of time (current interrupt technique), allowing for a relaxation of cell voltage towards OCV. Alternatively, steps or short current pulses to a value different from zero might be applied, entailing a voltage rebound towards positive or negative values depending on the direction of the current transient. Possible reversion of cell voltage may thereby be avoided by adapting the pulse length or the step amplitude.

As another option, continuous pulsing [78] or sinusoidal current modulation with a constant high frequency (HFR resistance) is applied during dynamic operation, allowing for the temporally resolved assessment of the ohmic resistance. The polarization curve can then be corrected for the resistance and information on mass transport and kinetics is gained.

A more intricate extension of this principle is the application of Electrochemical Impedance Spectroscopy (EIS), where modulation of current or voltage is pursued inside a wide scope of frequencies, ranging from a few mHz up to 10 kHz or more. In this way quantitative information on a number of loss mechanisms is gained, according to the time constants of the different phenomena [77].

Impedance measurements generally exploit the effect that different passive elements in an electric circuit show a distinguished response on an AC signal. A PEFC always involves circuits consisting of passive elements in various connections, a resistor represents e.g. the electric or ionic conductors while a capacitor describes the behaviour of the electrochemical double layer and adsorption processes. When perturbing PEFC operation with a sinusoidal signal of shifting frequencies, impedance spectra allow for a quantification of resistances in terms of kinetics, ohmic loss and mass transport processes. Models based on equivalent circuits are consulted to explain measured impedance data. However, this procedure has to be carried out with care since different circuits might generate the same spectrum and inductive effects might corrupt the data.

Localized Current and Resistance Measurement. All above-mentioned measurement methods can only return information on the integral- or cumulative performance over the whole cell, not accounting for non-uniform current generation across the active area.

As a consequence of reactant depletion and product formation, the current generation in PEFCs is far from being differential along the reaction pathway from gas inlet to outlet. The separate measurement of current in distinguished regions along the flow path is therefore required to allow for statements on loss mechanisms. Such locally resolved current measurements are typically realized by segmented current drain. Figure 1.13 illustrates this principle involving current collectors behind one flow field plate, which are segmented with the single segments isolated against each other.

To reduce compensating in-plane currents, the flow field plate can additionally be segmented. This makes however sense for academic interests rather than using the setup as a diagnostic tool for technical fuel cells, since the cell behaviour might be disturbed. In order to avoid the use of shunt resistors, the current is eventually measured by means of HALL sensors\(^6\) connected to the segments’ drain.

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\(^6\) The sensor exploits the HALL effect, where a force is experienced by a charged conductor in a magnetic field. It comprises a magnetic coil inducing a flux as a measure of the current signal.
This method can be extended to local resistance measurement by combining it with impedance spectroscopy (EIS). A sinusoidal signal is thereby applied to the cell, the signal response can be analyzed for every segment. Changes of ohmic, kinetic and mass transport resistance across the cell area can be detected by comparing the spectra from the different cell regions. This principle is called LEIS for Localized Electrochemical Impedance Spectroscopy.

The segmented approach described here is however limited in resolution to cell structures larger than the channel/rib scale, no state-of-the-art alternative approach is available yet. The measurement of current and resistance at this sub-mm level is however subject of this thesis, the development of a sufficient method is described in Chapter 2. Also other research groups have undertaken efforts for finding alternative methods with increased resolution. Imaging methods thereby appear to be of some significance for investigations of local current generation.

Out of these methods, a direct measurement of current density is only possible with Magneto-Tomography (MT) as proposed by WIESER and HAUER [79, 80]. This principle exploits the magnetic field surrounding electric currents by measuring its induction with an array of magnetic loops, or with a scanning procedure. Common drawbacks are the relatively coarse resolution (in the range of centimeters) and the undefined depth of measurement, accounting for the varying quality of current distribution comparing the GDL plane and the current collector plane.

Other imaging methods with sub-cell resolution are not capable of returning measure for current generation, they are aiming for the examination of the water distribution at the level of single cells and at the level of cell structures in the range of a millimeter and below. They are nevertheless useful tools for finding explanations for the quality and behaviour of local current generation.

Neutron Radiography (NR, [81, 82, 83]) exploits the high absorption rate of neutrons in water, enabling the visualization of two phase flow in a fuel cell without disturbance opposed by carbon or metal materials. A lot has been learned from NR studies concerning water clogging along the channel in serpantines [84, 85], or the preferred occurrence of liquid accumulations in the channel or rib covered regions [86] depending on geometry, operating conditions and diffusion.
material properties. However, the position of liquid water detection does not necessarily comply with the position of water generation. Drawing conclusions on the local current generation from the liquid distribution is therefore problematic.

Finally, high resolution X-Ray Computer Tomography ($\mu$-CT, [87, 88]) provides valuable 3-D information on the behaviour of diffusion material under compression liquid flow in porous media. Similar to NR measurements, the transmitting radiation is detected after penetrating the sample, the exposition is thereby altered with various angles between 0 and 180°. The large number of X-Ray images (radiograms) is in the following reconstructed to a 3D visualization (tomogram) with sub-$\mu$m resolution. The three dimensional mapping of the pore structure (uncompressed and under different states of compression) allows for quantitative fluid dynamic computations of the effective permeability for gas and liquids, a parameter strongly influencing the current generation on the sub-mm scale. Furthermore, experiments involving the GDL liquid water penetration at various capillary pressures are able to clarify the influence of hydrophobicity on two-phase flow.

1.3.2 Efforts in Research on Local Current Generation

After providing insight into the measurement tools, this subsection tends to give an overview on the state of research concerning the measurement and modelling of local current generation in PEFC. The production of current has to be considered non-uniform on all scales, starting at the thickness of the active layer up to the series connection of cells in a stack. Locally resolved simulations and measurements are therefore necessary to understand and possibly counterbalance the losses connected to these phenomena.

Electrode Scale. On the smallest scale, variations of reaction rate occur inside the catalytic layer. The utilization of catalyst might be ineffective due to the forming of a main reaction zone, essentially diverging from the idealized illustration in Figure 1.3. In-situ measurement of rate distribution inside the catalytic layer has not been accomplished yet, to date only modelling studies are available on this scale [23, 25].

The authors find that cathodic starvation effects inside the thickness of the catalytic layer are depending on the reactant concentration (see Fig. 1.14). When mass transport limitations are the dominating losses in the cell, the reaction zone moves with the front of the reactant penetration into the catalyst layer thickness. The existence of regions in the CL starving of reactant supply accompanies inefficient operation, since catalyst sites are unutilized. The diffusivity – or penetration – of reactant gas in the CL is therefore of importance for the significance of mass transport limitations. The authors point out that under the regime of other limitations than mass transport a more uniform distribution of reactant and catalytic reaction rate throughout the CL thickness can be expected.

Thus, losses on this scale are directly coupled to the operating conditions (cell current) and the quality of the gas distribution. The latter parameter is influenced by the structural properties of the diffusion medium as well as by flow field design and -layout, which are defined on the next larger scales, respectively.
Chapter 1. Introduction

Figure 1.14: Schematic cut-out of the active layer: The local current generation along the thickness of the CL is depending on the reactant concentration. A main reaction zone is shifting along the CL thickness when mass transport limitations are the dominant losses in the cell.

Figure 1.15: Sketch of parameter gradients across a repetitive channel/rib unit: The local current is eventually a function of charge- and mass transport limitations. The also inhomogeneous temperature distribution will affect the cell’s water management regarding condensation.

Channel/Rib Scale. The sub-mm level is characterized by the dimensioning of the flow field plate’s channel/rib structure. Transport of reactant, electrons, heat and liquid is significantly distinguished when cell area covered by a rib is compared to area under the gas channel. The varied conditions give rise to considerable current gradients at the active layer, as shown in Figure 1.15. Explicitly, these inhomogeneities are a consequence of transport limitations along the different pathways from the gas channel to the active sites (mass transfer), or from the active sites to the flow field plate (heat and electron transfer). Due to a lack of sufficient experimental techniques, resulting current gradients on this sub-mm scale could up to now only be postulated in modelling studies [89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102], or by comparison of integral cell performance for different channel/rib dimensions [103, 104, 105, 106].

In general, most authors dealing with multiphysics simulations find very low oxygen molar fractions with the use of air at the catalytic layer under a rib, resulting in a significant attenuation of local current generation in particular at high loads [107, 108, 109]. Not only the prolonged diffusion pathways but also the non-uniform compression of the GDL are causing this starvation effect. In addition, high levels of reactant humidification do also participate on the decrease of oxygen partial pressure, which is associated with a higher concentration overvoltage. The above-mentioned effects are promoted when the condensation of product water is taken into account, which preferably obstacles the gas transport in the rib covered areas. Neutron imaging studies have revealed that liquid accumulations start in the GDL in rib regions, and eventually extend inside the channel upon increasing the load or external humidification [110].
In the case of low cell currents and high oxygen fractions in the cathodic reactant, a distribution controlled by electron transport – associated with higher rib currents – is proposed by other publications [12, 111]. This is because the areas under a rib take advantage of the short electron pathways and lower resistance in the compressed GDL, when mass transport limitations are not dominant. The authors herein account for the electrical properties of the gas distributors, whereby additionally a transition state with promotion of areas under the rib edges is predicted at moderate current densities as a consequence of increased reactant consumption. Another modelling study confirms these findings by accounting for the relation between locally resolved ohmic and concentration overvoltage as the leverage on local catalytic activity on the channel/rib scale [112].

An interesting study on heat transfer at the sub-mm level is provided by Hottinen and Himanen [113]. The authors model the temperature distribution across the channel and rib domain in CL, GDL and FFP and postulate significant inhomogeneities. It is found that a notable portion of heat produced in the CL under a gas channel has to be transferred in the in-plane direction under a rib to be passed on into the GDL, which is a consequence of the lower thermal contact resistance in the compressed region. Accounting for the low heat conductivities of the CL and the microporous layer, temperature gradients of up to 15 K are proposed. This findings elucidate that – depending on the flow channel dimensions – the formation of hot spots is a realistic assumption, which will strongly influence the cell behaviour regarding the condensation of liquid water.

Accounting for gradients of temperature, pressure and species concentration along a flow channel, the group of Djilali has presented a comprehensive three-dimensional model earlier [114, 115]. This simulation is capable of predicting a load current dependent shifting from a resistance- (rib currents promoted) to a mass transport controlled (channel currents promoted) distribution at different locations along the channel. These results clearly show that understanding the current gradients in the along the flow channel direction is not possible without accounting for the conditions on the channel/rib scale.

**Single Cell Scale.** Most research efforts on inhomogeneous current generation have indeed been dedicated to the understanding of gradients along the channel of a single PEFC. Broad examinations by modelling as well as by experiments with varying degree of comprehensiveness are found in the literature [116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126]. As seen in Figure 1.16, reproducing experimental results by a computational model at least requires the involvement of the two most important effects to govern the current production along the channel: reactant depletion and water management.

Concerning the composition of oxidant gas, Brett et al. [127] observed a significant decrease of local current production near the cell outlet, especially with air and low flow rates. Later, Kulikovsky et al. confirmed these findings and correlated the local performance to the upstream consumption of the cell [128, 129]. The authors could provide a simple analytical model, which is capable of explaining the observations only by accounting for the two effects causing a low reactant partial pressure: gas diffusion processes and depletion by upstream consumption. Reactant diffusion in the GDL is thereby identified as a process on the next smaller scale, which is influenced by the design of the channel/rib structure. Another excellent overview of modelling
efforts concerned with this type of limitation is provided by Weber and Newman [130].

The influence of water management on current profiles has been described first by Berg et al. [131]. It was found in experiments that particularly under dry conditions a strong decline of local performance occurs near the inlet, which is attributed to insufficient membrane hydration at this position. The observed behaviour was found reproducible by computation, when accounting for the water balance of the cell and the increasing hydration by product water in regions towards the outlet. Buchi et al. could experimentally correlate the dew point of the feed gas to inhomogeneities in the current profile. The authors showed that severe variations of local performance will occur at any stoichiometry, as long as dry conditions are applied [132]. However, even operation with saturated gases can not compensate for humidity gradients along the channel, which noticeably influence the local current generation.

In a technical fuel cell a superposition of the before-mentioned effects is most likely to occur. Analysis of losses due to local limitations thus requires a breakdown of the single factors achieved by applying locally resolved impedance spectroscopy (LEIS), a principle followed by several research groups [133, 134, 135, 136].

All authors are able to locally identify losses caused by membrane drying (high frequency impedance) and reactant starvation (low frequency impedance), which could be attributed to the cell inlet- and outlet regions, respectively. In recent time, combined studies applying LEIS during neutron radiography have been carried out at PSI [137], confirming the connection of local water content to drying of the inlet regions and outlet flooding. The authors agree that the regime of a single limitation, as well as factors which determine said regime, can not be identified by analysis of integral cell performance only.

Only few efforts are dedicated to experimental examinations to correlate flow field layout and along-the-channel performance [138, 139, 106]. Similar to the channel/rib scale, mostly models are employed to estimate the influence of different designs on the local generation across the active area, often neglecting one or more factors in the complex interplay of parameters. Also the above-mentioned experimental approaches are only restricted to the comparison of integral performance for modified flow field layouts, correlating the results to local data is not pursued.
**Stack Scale.** The distribution of process media in a multicell stack is – in contrast to the electric pathway – realized in a parallel connection, gradients of reactant concentration are therefore not occurring along the stack coordinate. The disturbance of performance is typically expressed in the parameter of cell voltage, since the current is the same through all cells in the common series connection. Inhomogeneities and losses will occur due to unequal current density distributions in adjacent cells caused by temperature differences, condensation of water and therewith connected differences in reactant mass flow through individual cells.

An often observed phenomenon is lowered performance of cells near the stack in- or outlets (see Figure 1.17), which is in the most cases due to temperature effects. Heat dissipation over the end plates entails gradients in operating temperature of a few degrees, which noticeably influences the performance of the affected cells [140, 141]. Additional rim effects (disturbances in cells near in- or outlet) can be caused by suboptimal design of the medium manifolds, where some cells are not sufficiently supplied with process gases or coolant [142].

In general, perturbated performance of a particular single cell – stemming e.g. from a disturbance of reactant supply or electrochemical failure – will spread out to the neighbouring cells by electrical or thermal coupling phenomena, which is attributed to the limited electric and thermal conductivity of the bipolar plates [143, 144]. These cell interaction phenomena are able to compensate or amplify the inhomogeneity of an along-the-channel current distribution in an individual cell, when the adjacent cells exhibit different current distributions [145].

Consequently, uniform distribution of performance in a stack can be achieved by structural and material design on the single cell scale, as well as by controlling the flow of media in the single cells in terms of co- or counter flow mode [146, 147, 148].
1.4 Summary Chapter 1

This chapter gave an overview on the science and technology of polymer electrolyte fuel cells. Furthermore, the most prominently used diagnostic methods were described, and the literature on local current generation on various scales was reviewed. The most important facts are summarized below:

- Thermodynamic and kinetic factors often allow for the neglect of anode processes. Almost all severe performance limitations in a PEFC stem from the cathode side reaction (ORR) and oxygen mass transport processes.
- Charge transport is governed by the ionic resistance in the polymer electrolyte, whereby the proton conductivity is strongly dependent on humidification. Furthermore, the mechanical properties of the polymer are changing on water uptake, which might additionally influence the ohmic resistance.
- For the evaluation of mass transport processes, diffusive and convective transport have both to be considered. Diffusion through the porous material is governed by the structural properties of the GDL (compression → porosity), and therefore also by the *dimensioning* of gas channels and current lands. The share of convection is depending on the *layout* of the flow channels across the active area.
- Liquid water accumulations need to be avoided, since pore- or even channel clogging might occur. The removal of droplets may be realized by increasing the fraction of convective transport in the GDL, or the degree of impregnation.
- Structures on a particular scale cause losses on the next smaller scale. Current generation suffering from losses on the scale of the catalyst layer thickness might therefore be optimized by adapting structures at the channel/rib level. To achieve homogeneous current generation across channel and rib, the flow channel layout might be altered.
- Significant current gradients are found on the channel/rib scale and in the along-the-channel direction. Although numerous models are available for both scales, experimental examinations are up to date only possible at the level of single cells.

With respect to the improvement of performance and durability of PEFC, homogenization of current generation on the above-mentioned scales is expected to be worthwhile. The development of a measurement method for current density on the scale of the channel/rib distribution – as done in this thesis – is therefore a necessary task to understand and counterbalance current gradients on the single cell scale.
Chapter 2

Method Development

"Any sufficiently advanced technology is indistinguishable from magic."

Arthur C. Clarke, 1973

This chapter describes the development of a method for the measurement of current density with sub-mm resolution. At the time of its introduction in 2006 [149, 150], the principle was unique in the fuel cell literature and has been exploited for comprehensive investigation of current density distributions on the channel/rib scale since then [151, 152]. Thereby the extension to transient measurements also allows for the determination of local membrane resistance with the same spatial resolution.

2.1 Concept

Only few concepts of how to measure the current distribution resolved over channel and rib covered cell area are proposed in the literature, and after all the classical methods for local current measurement are difficult to apply on a scale smaller than a millimeter.

As indicated before in Section 1.3.1, imaging methods such as Magneto-Tomography fail due to a lack of resolution and depth of focus. The conventional measurement method for local current density – involving segmentation of the current drain – is obviously not applicable on this scale, since the exclusive collection of current from the channel area is impossible. The principle is restricted to segmentation into repetitive units, consisting of a rib and the respective half of the adjacent channels. As Figure 2.1 a) shows, the achievable resolution only allows for comparison of different channel/rib units instead of channel and rib in a particular unit.

A modification of this approach would be possible by filling of the channel with a porous and
Conductive material. This highly invasive interference would allow for localized current drain, but at the same time considerable changes of the cell behaviour in terms of GDL compression, gas transport, and electron pathways have to be expected. The information gathered with this setup would hardly be useful for diagnosis of technical fuel cells.

Similar drawbacks are to be expected with the use of the partly catalyzed approach illustrated in Figure 2.1b), as proposed by Wang et al. [153]. Herein, a cell operated with electrodes exclusively catalyzed under the rib covered area is compared to a cell with electrodes exclusively catalyzed under the channel. However, by altering the interaction between channel- and rib covered areas in terms of reactant consumption and electron transport only falsified conclusions on limitations are drawn.

Consequently an indirect method has to be developed, with an indicator representing a reliable measure for the local current density. This indicator was found with the distribution of voltage at the catalyst layer–GDL interface, the measurement of local current thus 'simplifies' to the measurement of the local voltage drop between active layer and current collector with a sufficient spatial resolution.

This concept relies on the assumption that the current collector on the back side of the flow field plate (FFP) is equipotential in contrast to the active layer, where the potential is inhomogeneous and a function of the rate distribution across channel and rib. The electric conductors in the plane perpendicular to the membrane (GDL and FFP) thereby serve as shunt resistors to eventually obtain the current density distribution.

Figure 2.2 elucidates the modus operandi of the principle. It becomes obvious that the use of these shunt resistors entails extensive examinations on the potential field inside the relevant domain. Although the kernel of the method is the in-situ measurement of local potential \( \phi_i \) by means of thin voltage probes, ex-situ studies of the electronic resistors and their behaviour upon cell compression are required.

Since the electric resistance \( R_{el} \) is a function of the cell’s compacting pressure \( s \), theoretical studies on the structural mechanics inside the shunt domain are carried out in the first place, in order to obtain the local electric conductivity. The required distribution of compressive stress...
is obtained from FEM modelling applying linear elasticity theory. The diffusion layer’s Young modulus $E_{GDL}$ is thereby extracted from stress strain curves, which are obtained from material characterization experiments.

Based on the resulting 2-dimensional field of resistance, the $x$- and $y$-current fluxes throughout the domain are eventually obtained solving the charge conservation equation (OHM’s law applied on LAPLACE’s equation in 2D) with the measured potential distribution as the boundary condition. The distribution of current density at the active layer ($y$-direction) thereby represents the flux causing the measured function of local potential.

Concludingly, the method allows for in-situ determination of local current density with channel/rib resolution, even though it is a model supported approach. In the following, a section is devoted to each module specified in Figure 2.2.

**Figure 2.2:** Conceptual design of the method used for sufficient measurement of the channel/rib current distribution: The current at the active layer is obtained from solving the Laplace equation with the in-situ measured voltage boundary conditions. The distribution of resistance in the shunt domain is determined by calculation, accounting for the compression dependence of the 2-dimensional electric conductivity of the GDL and the distribution of compressive strain.
2.2 \textit{In-Situ} Potential Measurement

Besides characterization of the shunt resistors, the determination of the local potential distribution at the active layer ($\phi_i$) is one of the major questions comprised in the current density measurement method. The simplest way to obtain the local potential at the active layer is to employ potential probes.

The idea of introducing filigree voltage probes into an operating cell origins from earlier work at PSI, at that time aiming to measure the transversal function of ionic resistance throughout the polymer electrolyte \cite{29}. To transfer this principle on the sub-mm current measurement method, a specialized test cell had to be developed, which is operated in combination with a customized data acquisition system.

2.2.1 Development of a Specialized Test Cell

The insertion of the voltage probes is done best at the interface of the GDL to the catalytic layer. This excludes the use of electrodes with the CL attached to the GDL, since measurement at the ionic boundary is unreliable. Thus, catalyst coated membranes (CCM) and separate GDL with or without microporous layers (MPL) are applicable.

Figure 2.3 illustrates the measurement setup in a PEFC. The voltage probes are inserted between the CL and the MPL and connected with the data acquisition and the current collector on the back side of the flow field plate (FFP). Generally, the measurement is possible on both electrodes. To avoid errors by polarization of the electrode, however, the anode side was chosen in all experiments since the insertion of the probes is expected to be least disturbing there.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{setup_diagram}
\caption{Schematic drawing of the setup for the \textit{in-situ} measurement of local potential in PEFC; The voltage probes (gilded W-Re wires of 10\,$\mu$m diameter) are inserted between the CCM and the GDL. They measure the voltage drop against the equipotential current collector. Directions are defined as follows: $x$-direction – cross channel coordinate, $y$-direction – through-plane coordinate, $z$-direction – along-the-channel coordinate.}
\end{figure}
The voltage probes used to date are thin gilded Tungsten wires containing 4 wt. % of Rhenium to ensure flexibility at high robustness. They exhibit a diameter of 10 $\mu$m and constitute the third generation of probes used for the sub-mm current measurements. In the beginning, carbon fibres of 12 $\mu$m diameter were employed, but found to be chemically unstable in the fuel cell environment. Alternatively gold wires with a diameter of 25 $\mu$m served for the probing, which failed due to the soft metal’s inability to sustain the mechanical stress in the compressed cell.

Figure 2.4 shows SEM micrographs comparing the insertion of a 25 $\mu$m gold wire (a) or a 10 $\mu$m gilded W-Re wire (b) to the interface of MPL and CL, regarding invasiveness at the catalytic layer. It is seen that the thinner W-Re wire is disturbing the contact of these layers less compared to the Au-probe.

Figure 2.4: SEM micrograph of a) a 25 $\mu$m gold wire, and b) a 10 $\mu$m gilded W-Re wire at the interface of CL and MPL. The GDL is visible as the coarse structure in the upper left corners, the membrane is identified as the material on the right.

Thirty wires with a spacing of 200 $\mu$m are mounted on a frame made from a fibre-composite material (STESALIT®), assuring parallel alignment along the channel. This allows for covering 6.0 mm cell area, which makes up several repetitive channel/rib units of common flow field geometries. The wires are insulated outside the active area by means of sub-gaskets to prevent electrical perturbations. Every probe is connected to a contact pin, passing the voltage signal to the test bench control station where it is read by the data acquisition device.

Figure 2.5 provides constructional details of the specialized test cell. Part a) shows a scaled drawing of the shunt resistor domain, consisting of the flow field plate (FFP) and the gas diffusion layer (GDL) with a microporous layer (MPL) attached. The probe wires are placed between the MPL and the catalyst coated membrane (CCM, = membrane + CL), they cover more than two repetitive units of an exemplary flow field with channel and rib widths of 2.0 mm, respectively. The $y$-coordinate is defined zero at the back side of the flow field plate, which is used as the equipotential counter pole. The local potential is measured at $y = y_{cl}$.

Part b) of Fig. 2.5 displays the construction drawing’s side and top view of the specialized test cell’s anode plate. It is seen that the wire frame is completely incorporated in the vacuity, which is surrounded by a gasket tongue. The active area of the size of the flow field plate (14.0 x 9.0 mm) is thereby considerably smaller than the area of the vacuity. Inlet and outlet chamber are separated by the flow field plate and adjacent branches of the gasket system. Thirty connector pins are
Figure 2.5: Constructional details of the specialized test cell (anode plate); a) Scaled drawing of the shunt domain including the catalyst coated membrane (CCM), the GDL with MPL attached, the FFP, and the 30 probe wires, all measures in mm. b) Side view (upper drawing) and top view (lower drawing) of the test cell, the wire frame is mounted over the 1.3 cm$^2$ flow field plate, the wires are connected to contact pins incorporated in the frame.

Figure 2.6: Photographs of the specialized test cell: a) The wire frame is mounted over the active area, the end plate, the frame and the gasket surrounding the vacuity is seen, the wires are recognizable as the shivering array above the flow field plate, their connections to the contact pins on the wire frame are seen; b) Magnification of the 30 probe wires over a flow field structure, 5 wires cover a channel or rib with 1.0 mm width each.

leading outside the cell through a gas-tight electrically insulated inset in the endplate, fifteen on each side of the active area. The contacts of the wire frame are plugged into these pins for the measurement during operation.

The reason for keeping the active area small is the necessity for differential operation. To avoid current gradients along the channel the test cell is operated with excessive stoichiometries, representing a differential cut-out of a technical sized fuel cell with no change of channel/rib current distribution in the along-the-channel direction ($z$-coordinate, see Fig. 2.3). The channel may furthermore not feature bends or serpentines, since only short and straight distances can be overcome with the probe wire setup.

For the sake of clarity, Figure 2.6 a) shows a photography of the wire frame mounted in the test cell, the parallel alignment with the channel structure (in this example a geometry with channel and rib width 1.0 mm each) is seen in b). In an operating cell, however, a piece of GDL would sit in between the wires and the FFP. The CCM is then placed on top of the wire frame, separating the anode and cathode vacuity. The active area is restricted to a window of ca. 1.3 cm$^2$ in thin sub-gaskets (Mylar-foil, thickness 12 $\mu$m) placed on both sides of the CCM. This way the probe wires only contact the CCM and MPL in the active area.
2.2.2 Test Equipment and Data Acquisition

The *in-situ* potential measurement is carried out on an in-house built test bench, providing a customized environment for operation of the specialized cell. A schematic of the test bench is provided in Figure 2.7, illustrating the installations used for gas conditioning and electronics.

![Figure 2.7: Schematic of the test bench to operate the specialized test cell for the sub-mm current density measurements.](image)

**Reactant Conditioning.** The reactant feed is regulated by mass flow controllers (*Brooks 5850 TR*), on the cathode side connected with a mixing device (*Brooks Model 5878*) to modify the gas composition (oxidant and inert gas). The flow controllers and the mixer are controlled via the software *LABVIEW®* (*National Instruments*). The gas flow is passed through bubbling type humidifiers, the anodic and cathodic dew points are thus defined by the temperature of the water reservoir, which is controlled via electric heating cartridges. The reactant gas pressure is adjusted by back pressure regulator valves of *Swagelok* (KBP series), integrated in the anodic and cathodic gas outlet.

**Electronics and Data Acquisition.** The control of cell current, voltage and potential signals from the 30 probe wires is fully automated via a graphical user interface, programmed using the GUI-builder of the *MATLAB* software package. This control interface actuates the electronic load (*Höcherl & Hackl ZS 506-4*) and triggers four data acquisition devices (*National Instruments PCI6250M*). The concomitant use of several synchronized multiplexing devices enables a high sampling rate of 110 kSamples/s for all 30 channels plus cell voltage and current. The necessity of an acquisition frequency of this magnitude is explicated in Section 2.6, where the transient measurement of the *in-situ* potential measurement is discussed.
2.3 Ex-Situ Characterization of the Shunt Resistor Materials

To obtain the local current density from the voltage distribution at the active layer, the 2-dimensional field of electric resistance in the domain of the shunts needs to be determined. This data is obtained by *ex-situ* material characterization before operation of the test cell.

The simplest principle would be to measure the electron pathways *in-situ* during operation. This way the distribution of compressive stress is not needed to obtain the distribution of electrical conductivity. However, inducing current flux over the very voltage probes used for the measurement of $\phi$, entails the occurrence of additional contact resistances at the interconnection of the probes with the shunt, which would falsify the inference on the local resistance. Hence, the approach involving extensive *ex-situ* resistor characterization was chosen.

The shunt in the measurement domain is composed from four items: the resistance of the MPL, the GDL bulk resistance, the contact resistance of the GDL to the current land, and the bulk resistance of the FFP itself. While the FFP material used in the experiments is incompressive and shows isotropic conductivity, it has been learned from Chapter 1 that the GDL material exhibits highly anisotropic electrical properties, which is a consequence of its fibrous structure.

Moreover, particularly the through-plane electric resistance is strongly depending on cell compression, requiring the measurement of bulk resistivity as well as of contact resistance as a function of compressive stress. Therewith the GDL is the cell component requiring the most comprehensive examination with respect to its mechanical and electrical properties.

2.3.1 GDL Structural Mechanics

The mechanical characterization of the GDL material aims to predict the distribution of stress inside the compressible domain of the shunt resistor, which in turn defines the distribution of electrical resistance. Cell compaction is realized by adjusting a particular distance between the two flow field plates. To gain information on the stress affected to the anodic GDL only (which is part of the shunt resistor for the potential measurement), stress-strain curves are measured for all components in the cell, including the cathodic GDL and the CCM. This is because their compaction upon cell compression also defines the force applied on the anodic GDL. Computation of the local stress distribution – to obtain the local resistance – does however not require the consideration of the cathodic GDL and the CCM, since they are not part of the shunt resistor.

The GDL material used is a 20 wt.-% PTFE-impregnated carbon paper of the type TORAY TGP0H-060, comprising a microporous layer on one side. The thickness of the cathode GDL ($230 \pm 5 \mu m$) thereby exceeds the one of the anode side ($217 \pm 5 \mu m$), which is predominantly a consequence of different intrusion depth and granularity of the MPL. The CCM is purchased from Umicore and comprises the NAFION® 112 polymer membrane coated with catalytic layers on each side (anode CL thickness: ca. 10 $\mu m$; cathode CL: ca. 20 $\mu m$).

**Measurement of Stress-Strain Curves.** Stress-strain experiments were carried out for both GDL and the CCM at the Swiss Federal Laboratories for Material Testing and Research (EMPA) in Dübendorf. A material testing machine of Zwick-Roell equipped with an inductive extensometer (resolution 0.1 $\mu m$), allowing for accurate measurement of the sample’s strain, was used.
Figure 2.8 a) shows a sample of GDL on the testing machine. To avoid the necessity of large compressive forces, the samples were kept small with areas of less than 1.0 cm². A further reduction in size would entail the danger of changing the mechanical properties, since the carbon fibre length is in the magnitude of several millimeters.

The obtained stress-strain curves are shown in Figure 2.8 b). It can be seen that anode and cathode side GDL differ by less than 10% strain at a maximum stress of 20 MPa, whereby the carbon paper is compressed about half of its initial thickness $d^0$. The CCM exhibits a higher mechanical strength. The compression of 30% of initial thickness at 20 MPa is attributed mainly to the porous structure of the catalytic layer.

The most important value for the calculation of the stress distribution is the Young’s modulus $E_{GDL}^{y}$, which is defined as the ratio of dimensionless strain $u$ and stress $s_y$ (Hooke’s law) and is thus represented by the slope of the curves in Figure 2.8 b) at a particular compression. As a consequence of the asymptotic behaviour observed in the diagrams it is possible to see that Young’s modulus in the $y$-direction $E_{GDL}^{y}$ is dependent on compression rather than being a constant:

$$E_{GDL}^{y} = \frac{s_y}{u} = \frac{F_y}{A^0} \cdot \frac{d^0}{\Delta d}.$$  \hspace{1cm} (2.1)

Herein $F_y$ is the applied clamping force, $A^0$ the sample’s cross sectional area, $d^0$ the initial sample thickness and $\Delta d$ the sample’s strain in $\mu m$ upon compression. The theory of linear elasticity requires a linearization of $E_{GDL}^{y}$ for small increments of compression, which has been realized by discretization of the data in Figure 2.8 b) in steps of 2.0 MPa.

**Modelling of the Compressive Stress Distribution.** The calculation of the stress distribution in the GDL domain is however a 2-dimensional problem, accounting for stress components in $x$- and $y$-direction. This means that all strain and shear in the along-the-channel direction is per definition zero. To describe the interconnection of both planes in the 2-dimensional formulation...
of Hooke’s law, $E^{GDL}$ is replaced by the flexibility matrix $\mathbf{\mathcal{E}}$, which is the ratio of stress and strain in their vector notations, respectively. Its inverse can be expressed as:

$$
\mathbf{\mathcal{E}}^{-1} = \begin{bmatrix}
\frac{1}{E_x} & -\nu_{xy} & 0 \\
-\nu_{yx} & \frac{1}{E_y} & 0 \\
0 & 0 & \frac{1}{G_{xy}}
\end{bmatrix}
$$

with $\nu_{xy} = \nu_{yx}$ and $G_{xy} = \frac{1}{2} \cdot \frac{E_x}{1 + \nu_{xy}}$. (2.2)

Table 2.1 provides the input parameters for cell components considered in the 2-dimensional model. The behaviour of the GDL in $x$-direction $E^{GDL}_x$ is assumed highly elastic, referring to the tensile strength. Poisson’s ratio $\nu^{GDL}$, describing the $x$-deformation upon a particular strain in $y$-direction, needs to be assumed from literature values [37, 154]. The shear modulus $G^{GDL}_{xy}$ is obtained from the ratio of Young’s modulus and Poisson’s ratio as shown in Equation 2.2. The implementation of the parameters and the set up of the numerical equations can be read from textbooks on the linear elasticity theory, e.g. [155].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus diffusion layer,</td>
<td>$E^{GDL}_x$ 10000 N/mm²</td>
</tr>
<tr>
<td>Young’s modulus flow field plate,</td>
<td>$E^{FFP}$ 17.5 N/mm²</td>
</tr>
<tr>
<td>Young’s modulus catalyst coated membrane,</td>
<td>$E^{CCM}$ 125.0 N/mm²</td>
</tr>
<tr>
<td>Poisson’s ratio diffusion layer,</td>
<td>$\nu^{GDL}_{xy}$ 0.30</td>
</tr>
<tr>
<td>Poisson’s ratio flow field plate,</td>
<td>$\nu^{FFP}_{xy}$ 0.30</td>
</tr>
<tr>
<td>Poisson’s ratio catalyst coated membrane,</td>
<td>$\nu^{CCM}_{xy}$ 0.35</td>
</tr>
</tbody>
</table>

Table 2.1: Mechanical parameters of the cell components used for the 2-dimensional model to obtain the stress distribution in the GDL.

The numerical solution of Equation 2.1 with respect to Equation 2.2 is realized using the commercial finite elements software Ansys®. The program code, involving the linearization of the measured function for $E^{GDL}_y$, has been developed in cooperation with Tribecraft AG, Zürich. A more comprehensive consideration of the errors induced by grid generation and linearization are hence provided in the first publication of the method [150] as well as in [13].

The model is able to produce results for multiple states of cell compression, an example for 90 µm compaction of the anode GDL ($\approx 40 \%$ of initial thickness) is given in Figure 2.9. The standard flow field geometry of the experiments is chosen for the computation, which involves a channel and rib width of 2.0 mm each. The deformed domain of one repetitive unit (half channel + half rib) is shown in 2.9a), the greyscale code is representing the absolute values of displacement in $y$-direction. It is seen that the GDL is bending around the rib edge, hence the thickness in the middle of the channel remains virtually uncompressed.

Figure 2.9b) illustrates the pressure at the contact interface of rib and GDL. Its maximum, exceeding 20 MPa, is located at the rib edge, which is due to the stiffness of the fibrous material bending around the edge. A minimum of pressure is therefore to be observed in short distance towards the middle of the rib, caused by the following delamination of diffusion layer and FFP. According to the stress-strain behavior of the anode GDL shown in Figure 2.8b), the mean compressive stress for achieving a deformation of 40 % of thickness is in between 11 and 12 MPa.
This value matches the mean value of the contact pressure distribution across the current land with sufficient accuracy.

Finally, the distribution of compressive stress in the undeformed GDL domain is plotted in Figure 2.9c). The position of the rib edge is easily identified by the peak of compressive stress. Inside the material stress is eventually compensated, and only slight differences of between 0 and 5 MPa are visible at the GDL-CCM interface comparing the virtually uncompressed domain under the channel and the compressed domain under the land.

Figure 2.9: Calculation of the compressive stress distribution: a) Deformed domain of the MEA (2 GDL + CCM) upon cell compression of 195 µm (therefrom 90 µm of anode GDL, ≈ 40% of initial thickness), the GDL is bending into the channel; b) Distribution of contact pressure across the GDL-rib interface, due to the bending a maximum of pressure is observed at the rib edge followed by a minimum attributed to delamination of the stiff fibres; c) Distribution of compressive stress throughout the undeformed GDL domain, the peak of stress at the rib edge is compensated across the bulk material to the GDL-CCM interface.

This 2-dimensional map of compressive stress (Fig. 2.9c) is eventually converted into local bulk resistance, having the data on GDL conductivity available as a function of compression. Furthermore, the stress-dependent measurement of contact resistance is combined with the calculated distribution of contact pressure (Fig. 2.9b) to obtain the local contact resistance across the GDL-rib interface.
2.3.2 Electric Properties

Measuring the electric resistance of the shunts resistors includes the consideration of the FFP, of the GDL in two planes plus the contact resistance between GDL and FFP, and of the MPL. Due to the characteristics of the four-probe setups used, the acquisition of resistance data is not always straightforward and requires additional computation efforts, i.e. in the case of GDL through-plane measurements.

Flow Field Plate Material. The measurement of the FFP resistance is generally unproblematic. The material used is the sintered graphite DIABON NS 2® purchased from SGL Carbon Group. It is incompressible inside the range of forces applied in fuel cell applications and shows isotropic electrical properties as a consequence of no structural orientation in the material bulk. Several samples were tested by passing a current through the material and probing the voltage drop over a particular distance \( \delta \), similar to the sketch in Fig. 2.10. The equipment used comprises a DC Power Supply of Agilent (E 3633 A) and a high precision multimeter of Hewlett Packard, type 3468 A.

Independent of the \( x \)-, \( y \)- or \( z \)-direction a relatively high electrical conductivity of 110'000 S/m (= 0.91 mΩcm) could be determined, which is about one order of magnitude above the typical values for carbon composite FFP materials. The number has been implemented as the value for \( \sigma_{\text{xx}}^{\text{FFP}} \) and \( \sigma_{\text{yy}}^{\text{FFP}} \) in the flow field plane domain.

In-Plane Resistance of the GDL. The setup for measuring the conductivity of the GDL in the \( x \)-\( z \)-plane (in-plane) direction is illustrated in Figure 2.10. Clamping pressure is applied by two plates made from insulating material, which include embedded voltage probes in contact to the surfaces of the GDL. Since the resistivity of the GDL is depending on compression, the probing of voltage drop \( \Delta \phi^{\text{Sample}} \) is arranged inside the compacted domain while the current flux \( j^{\text{Sample}} \) is induced from outside the clamps.

![Figure 2.10: Setup for the in-plane measurement of GDL conductivity; The voltage drop \( \Delta \phi^{\text{Sample}} \) is probed over the distance \( \delta \) in the compressed region of the GDL, the conductivity \( \sigma_{\text{xx}}^{\text{GDL}} \) calculates according to Ohm’s law as formulated in Eq. 1.14 using the current density \( j^{\text{Sample}} \) and \( \Delta \phi^{\text{Sample}} \).](image)

Probing of the voltage drop is arranged by copper wires integrated into both clamping plates on the interfaces to the GDL, grinded and polished to an even level. The obtained data is
averaged over both sides, since only GDL without microporous layers are measured here. The MPL has to be considered independent of the GDL bulk, due to its strongly deviant properties. The electronic equipment used is the same as in the case of the flow field plate measurement, combined with the application of a hydraulic press (0 to 100 kN, P.O. Weber, Germany).

Figure 2.11 provides the results obtained for the in-plane measurement of GDL conductivity $\sigma_{xx}^{GDL}$, calculated in the undeformed state. Since the carbon fibres of the paper-like material are orientated in-plane, the conductivity is one order of magnitude higher compared to the through-plane direction. $\sigma_{xx}^{GDL}$ remains in the range of 20'000 S/m (= 5.0 mΩcm) throughout pressure variation. The slight decrease upon compression is assumed to be due to the breaking of fibres, increasing the number of 'bottlenecks' along the electron pathway.

The error bars shown in the figure exhibit partitions on the x- and y-axis. The force applied on the sample (x-axis) underlies the error of the pressure gauge connected with the press, it is assumed to be ± 0.5 MPa at maximum. The error of the voltage measurement (y-axis) is defined by the accuracy of the multimeter (in the range of µV) and structural parameters of the setup. The error bars given in Figure 2.11 thus represent a standard deviation of 6 %, determined from repetitive measurements with partly different current densities $j^{Sample}$. Accordingly, 68 % of all reproduced data was found to be in this trust range.

**Through-Plane Resistance of the GDL and Contact Resistance to the FFP.** For measuring the through-plane conductivity $\sigma_{yy}^{GDL}$ a modified setup has to be used, which additionally allows for the assessment of contact resistance $R_{cr}$. Hence, it involves the flow field plate as a part of the electric circuit.

Figure 2.12 shows the measurement setup for GDL through-plane conductivity $\sigma_{yy}^{GDL}$ and contact resistance $R_{cr}$, whereby the required instrumentation is the same as used for the in-plane measurements. The assessment of the voltage drop across the GDL requires the acquisition of the potential at the opposite GDL surfaces, which is a tedious task regarding the layer thickness.
of ca. 220 µm. The potential probes are therefore integrated into the FFP, similar to the in-plane setup, but have to be insulated against the surrounding material at the same time.

This is realized by incorporating straight grooves (width 200 µm) into the FFPs by means of microsaw machining. Subsequently, the grooves are filled with raisin, and an insulated copper wire with a diameter of 125 µm is introduced. After hardening the plate is ground and polished until exposure of the copper strand, as shown in the magnification of Figure 2.12. This way the current conduction through the interfacial planes of the FFPs are interfered only by a 0.2 mm disturbance. The voltage drop measured over these two insulated probes \( \Delta\phi_{\text{GDL}} \) represents the resistance over the GDL from surface to surface. The contact resistance is obtained from the voltage drop \( \Delta\phi_{\text{cr}} \) measured between an insulated probe and the surrounding FFP.

Since the disturbance induced by the probe insulation is in the same magnitude as the GDL thickness, a substantial error is added by the measurement itself: the potential at the insulated probe significantly differs from an undisturbed position. The measured value needs therefore to be corrected for the disturbance in the GDL potential field, which is realized by solving Laplace’s equation with flux boundary conditions.

![Figure 2.12](image1.png)

Figure 2.12: Measurement setup for the through-plane measurement of GDL conductivity comprising insulated voltage probes; The voltage drop \( \Delta\phi_{\text{GDL}} \) represents the resistance in the GDL from surface to surface, the voltage drop \( \Delta\phi_{\text{cr}} \) the interfacial resistance to the FFP.

![Figure 2.13](image2.png)

Figure 2.13: Correction of the voltage drop measured with the through-plane setup; a) Potential field with disturbance induced by the probe insulation; b) The calculated (real) voltage drop differs about 20% from the measured value.
For this simple rectangular domain the potential field inside the GDL is supposed to show a linear decrease between the boundaries upon a constant current density. A discontinuity is induced when the electric flux is set zero for the x-positions of the 200 µm insulation. This perturbation exhibits its minimum at the position of the voltage probe, representing the measured value for \( \Delta \phi \). Of interest is however the potential at an undisturbed position, which can not be measured, but which is needed for the calculation of the conductivity \( \sigma_{yy}^{GDL} \).

Figure 2.13 illustrates the situation arising from the measurement of potential drop over the GDL using insulated voltage probes. The potential field throughout the GDL domain, including the disturbance induced by the insulation, is shown in 2.13 a). The plot of the voltage drop as a function of the x-position is given in b), distinguishing the measured from the real value.

The real values for \( \Delta \phi_{GDL} \) are hence obtained by calculation, reproducing the measured values at the position of the probe by iteration over the conductivity \( \sigma_{yy}^{GDL} \). Repeating this procedure for different states of compression yields the correlation shown in Figure 2.14 a).

![Figure 2.14: a) Through-plane conductivity \( \sigma_{yy}^{GDL} \) as function of compressive stress, the increase is due to new contacts between fibres; b) Contact resistance \( R_{cr} \) between GDL and FFP, the interfacial conductivity shows an asymptotic increase with compression.](image)

It is seen that the conductivity increases by more than 400% starting from ca. 350 S/m in the uncompressed state. The asymptotic behaviour upon compression is attributed to the forming of new contacts between the carbon fibres, converging to a maximum value of ca. 2000 S/m (= 50 mΩcm) for compressive stress higher than 20 MPa. The error bars in y-direction again represent the standard deviation of four independent experiments, while the trust range on the stress axis is again assumed as ±0.5 MPa.

Besides the calculation of \( \Delta \phi_{GDL} \), the voltage drop from the GDL surface to the FFP \( \Delta \phi_{cr} \) also uses the corrected potentials to obtain the interfacial contact resistance to the plate \( R_{cr} \). The graph in Figure 2.14 b) clearly shows the dependency of \( R_{cr} \) on the compressive force, a decrease of interfacial resistivity by a factor of 5 is observed for compressions between 0 and 20 MPa.

Eventually, the data obtained from these measurements is converted into local resistance. A simple grid mapping algorithm programmed in MatLab is used to assign in-plane (\( \sigma_{xx}^{GDL} \)) and through-plane (\( \sigma_{yy}^{GDL} \)) conductivities to every coordinate in the material bulk, which is characterized by the local compression at this position as obtained in Section 2.3.1. The contact resistance at the GDL-rib interface – which is later converted into interfacial conductivity –
is obtained likewise in 1 dimension, the local resistivity is obtained according to the contact pressure distribution as given in Figure 2.9 b).

The results of this procedure are shown in Figure 2.15, where in-plane (a) and through-plane (b) conductivities are plotted over the GDL domain (without MPL). Figure 2.15 c) shows the resulting function of contact resistance on the GDL-FFP interface. The range of x-position represents the smallest symmetric repetitive flow field unit, comprising one channel in the middle and two adjacent half ribs.

![Figure 2.15](image_url)

**Figure 2.15:** a) In-plane ($\sigma_{xx}$) and b) Through-plane ($\sigma_{yy}$) conductivities mapped over the cut-section through the GDL, c) Contact resistance along the rib surface (x-direction) of this cut section; The domain represents the smallest symmetric repetitive channel/rib unit.

Generally, the distribution of in-plane conductivity plotted in Fig. 2.15 a) varies only slightly throughout the domain. Accounting for the behavior of $\sigma_{GDL}^{xx}$ upon compression, the electric conductivity is lowest at coordinates with the highest stress. In contrast, the distribution of through-plane conductivity $\sigma_{GDL}^{yy}$ is qualitatively identical with the distribution of compressive stress. It varies almost over the entire range of values when comparing different positions inside the GDL, showing high peaks at the rib edges and relatively low values in the middle of the channel area (see Fig. 2.15 b).
### 2.3. Ex-Situ Characterization of the Shunt Resistor Materials

**Resistivity of the Microporous Layer.** In contrast to the *ex-situ* material characterization experiments, a GDL with an MPL is used in the *in-situ* measurements with the specialized test cell. Its electrical properties are expected to be significantly different from the GDL bulk material and have therefore to be evaluated as a part of the shunt resistor domain.

However, the assessment of the MPL properties is difficult since it strongly interpenetrates the GDL bulk material. The application on a non-conducting carrier instead on the GDL, which would allow for determining the layer thickness and the electrical conductivity of the microporous layer, is unfortunately not possible. Hence, examinations based on microscopy are carried out to get a picture of the situation.

Figure 2.16 a) illustrates the ratio of thickness between GDL and MPL in an LM micrograph of a polished cut-section of a raisin-prepared sample. It is seen that the interpenetration of the microporous layer into the fibre bundles of the GDL bulk varies strongly along the $x$-coordinate. The layer thickness ranges from less than $5 \mu m$ up to $50 \mu m$, in parts of the GDL (not shown in image) MPL material was even found all through the diffusion layer thickness. Based on statistic evaluation of the micrographs, the mean MPL thickness is implemented into the calculations as $20 \mu m$ on the anode and $30 \mu m$ on the cathode side.

The SEM micrograph shown in Figure 2.16 b) provides a close-up of the MPL structure. It is possible to deduce an isotropic conductivity of the MPL from a lack of particle orientation. The resistivity is assumed independent of compression and significantly higher as the GDL bulk.

However, a quantification of $\sigma^{MPL}$ is not possible without having the separate material available. The implementation of this value in the computation of the shunt resistor’s potential field is therefore carried out by treating it as a fitting parameter, ranging between 80 and 150 S/m. The existence of a contact resistance between fibres and MPL is not assumed, since it is expected to be in the range of the interfacial resistance of a fibre-fibre contact.
2.4 Model Development and Validation

The ex-situ data of the resistance distribution in the shunt domain is used to calculate the respective potential field upon particular boundary conditions measured using the in-situ setup described in Section 2.2. As mentioned previously, the potential- or current distribution is obtained by solving LAPLACE’s equation for the considered domain.

It is seen from the conductivity maps in Figure 2.15 that the distribution of electric resistance varies significantly as a consequence of inhomogeneous compression between channel and rib covered areas. The accurate implementation of the electric properties is therefore of prime importance for the calculation of the potential field and the current distribution, and thus requires validation experiments using a setup of test circuits.

2.4.1 Calculation of the Potential- and Current Field

The two-dimensional distribution of electric resistance in the shunt domain (FFP, GDL and MPL) defines the potential field and the local current flux inside the shunt domain. With all boundary conditions known, the continuum of flux or potential inside these boundaries is governed by the charge conservation equation (an expression of the LAPLACE equation based on OHM’s law):

\[- \nabla \cdot (\sigma \nabla \phi) = 0 \quad \longrightarrow \quad \frac{\partial}{\partial x} \left( \sigma_{xx} \cdot \frac{\partial \phi}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma_{yy} \cdot \frac{\partial \phi}{\partial y} \right) = 0, \tag{2.3}\]

with \( \phi \) being the electric potential and \( \sigma_{xx} \) and \( \sigma_{yy} \) the electric conductivities in \( x \)- and \( y \)-directions. Since the considered domain does not include the catalytic layer, no source term needs to be accounted for on the right side of the equation. It is furthermore an elliptical partial differential equation, which means that the boundary conditions can be either a given current flux (NEUMANN problem) or – as in this case – a given electric potential (DIRICHLET problem).

Since the shunt resistor domain represents a repetitive unit, the current flux and therewith the change of potential across the domain boundaries in \( x \)-direction is per definition zero:

\[ \frac{\partial \phi}{\partial x} = 0. \tag{2.4}\]

In the \( y \)-directions, however, the boundary to the current collector \( (y_{cc}) \) is considered holding the reference potential, while the opposed boundary to the catalytic layer \( (y_{cl}) \) exhibits the measured wire potentials \( \phi_i \) at the GDL-CL interface:

\[ \phi \big|_{y_{cc}} = 0 \quad \text{and} \quad \phi \big|_{y_{cl}} = \phi_i(x). \tag{2.5}\]

Equation 2.3 is solved using the numerical capabilities of the MATLab software package. The calculations are done in the undeformed shape, but with the local conductivities being corrected for compression. This is unproblematic because all conductivity data given in Figures 2.11 and 2.14 a) and b) are also referred to the uncompressed shape, i.e. the change of GDL thickness was
not accounted for in deducing the values for $\sigma$ from the measured voltage drops $\Delta \phi^{\text{Sample}}$ in the \textit{ex-situ} experiments.

While the implementation of $\sigma_{xx}$ and $\sigma_{yy}$ becomes thus straightforward, the contact resistance has to be converted into interfacial conductivity $\sigma_i$ by formally introducing a thin layer with a specified thickness $d_i$, which is considered in the calculation as:

$$ j = \sigma_i \cdot \frac{\Delta \phi_{\text{interface}}}{d_i}. $$

(2.6)

Herein $j$ denotes the current flux and $\Delta \phi_{\text{interface}}$ the potential drop over the interface, the latter is given by the contact resistance data in Figure 2.15(c). The boundaries of this 'contact layer' conductivity to $\sigma^{\text{FFP}}$ and $\sigma^{\text{GDL}}$ are implemented via a formulation yielding the harmonic mean between the conductivities rather than the arithmetic average, as described in [156].

The solution of Eq. 2.3 is shown in Figure 2.17 for an exemplary boundary condition chosen to $\phi \mid_{y=0} = 5.0 \text{ mV}$ independent of the $x$-position (see 2-D diagram in a). The 3-D plot of Fig. 2.17 a) illustrates the voltage drop over the different materials as indicated along the $y$-axis. It is seen that the flow field plate contributes least to the total drop, the three significant resistors in the shunt domain are the contact resistance to the GDL (expressed by the strong slope of voltage drop between the FFP and GDL), the GDL bulk resistance and the bulk resistance of the MPL (with an assumed conductivity of 100 S/m, realistic estimate).

Figure 2.17: Solution of the LAPLACE equation for an artificial boundary condition $\phi_i$ of 5.0 mV at the CL-MPL interface. a) The potential field shows the drop of potential over the different materials; b) The field of current density ($y$-component) exhibits peaks at the corners of the channel domain, the function of current density at the CL-MPL interface $j_i(x)$ (2-D diagram) is not constant due to the distribution of electric resistance.
The result regarding the distribution of current density is shown in part b) of Figure 2.17. The 3-D plot thereby shows only the \( y \)-component of current density, since the desired result is the distribution of current entering the domain from the CL-MPL interface in \( y \)-direction. This function is plotted in the 2-D graph on the left, illustrating the promotion of current in the rib areas due to shorter electron pathways and the locally higher through-plane conductivity \( \sigma_{yy} \) in the GDL for the case of the artificial constant boundary condition shown in part a).

The field of current density in the three-dimensional illustration furthermore shows sharp peaks at the four corners of the channel. These are attributed to the electric flux circumventing the insulating channel, rather than being numerical artefacts. However, to avoid singularities entailing infinite height of these entities, careful grid optimization at interfaces and corners has been conducted.

### 2.4.2 Validation in a Test Circuit Setup

In order to confirm the quality and quantity of the results obtained from the solution of Equation 2.3, a replica of the specialized test cell (as introduced in Section 2.2.1) without active electrochemical components was developed. Its heart is a substitute of the catalyst layer, consisting of a segmented current feed capable of simulating a particular current distribution at the CL-MPL interface, similar to the situation in an active cell under operation. With the local current density given, the error from the calculation of the current distribution by means of local potential measurement (\( \phi_i \)) can be evaluated.

![Figure 2.18: Principle and setup of the validation cell; a) Schematic drawing of the cell setup, the current is inducted via 15 segmented plates insulated against each other; b) Components of the validation cell, GDL and FFP are the same as used in the active test cell; c) Measurement setup, the current distribution is modulated by means of 15 potentiometers, the voltage drop is measured against the current collector.](image)

Figure 2.18 illustrates the setup of the validation cell, it comprises the same electric components as used in the \textit{in-situ} measurements. Electric current is fed via the edges of 15 gilded copper plates insulated against each other. This way a specific current distribution can be adjusted by a set of potentiometers connected to the plates. The current through every electric pathway in the test circuit setup is determined by the voltage drop over the respective potentiometer. The
potential distribution across channel and rib is measured directly between the segments of the current feed and the back side of the current collector, eluding the need of probe wires. Since Laplace’s equation is elliptic, local potential is calculated from a given current distribution (Neumann boundary condition). This way $\phi_i$ can be compared with the measured values from the validation cell, obtained for an adjusted ‘artificial’ current distribution. This distribution was modified for Case a) as a constant current density across channel and rib at 2.0 A/cm$^2$, Case b) as a distribution with the maximum of current under the ribs and Case c) with the maximum of current in the channel area, both with integral currents also at 2.0 A/cm$^2$.

Figure 2.19 shows this artificial current distributions for all three cases (dotted lines) and compares for each case the measured voltage distribution with the results from the calculation. The experiment was conducted with only one cell compression of 6.25 MPa, which is in accordance with an anode GDL compaction of 35 % of initial thickness.

![Figure 2.19: Adjusted current distributions and comparison of measured and calculated potential distributions from the validation experiments (cell compression 6.25 MPa, MPL conductivity 80 S/m); Case a) Constant current across channel and rib; Case b) Current distribution with maxima under rib covered area; Case c) Current distribution with maxima under channel.](image)

A good agreement of the potential distributions is obtained, indicating that the absolute values as well as the quality of the pressure- and conductivity distribution in the shunt resistor domain are implemented correctly. The calculated potential distributions are obtained using the resistance field as discussed in Section 2.3.2. Since the conductivity of the microporous layer is not known, it served as a fitting parameter to conform the absolute values. The correlation seen in the figure is accomplished assuming the realistic value of 80 S/m for the isotropic $\sigma^{MPL}$.

However, the implementation of MPL conductivity will not change the quality of the channel/rib inhomogeneity, since the shape of this distribution is defined by the distribution of stress and electric resistance in the GDL bulk only. According to the electron pathways, the Cases a) and c) produce higher voltage drop in the channel area, which is in contrast to Case b). This shows that the electron pathways have been understood quite well, since the quality of the potential distribution is reproduced without substantial error. The observed deviance of measured and calculated potential data of ca. 10 % is assumed to be attributed to non-uniform electrical or mechanical GDL properties, such effects are discussed in the following section.
2.5 Reliability and Reproducibility

Reliability and reproducibility of sub-mm current measurements depend on multiple factors. Before all other considerations the reliability of the in-situ potential measurement needs to be evaluated, in particular regarding the invasiveness of the probe wires. Another major criterion concerning reproducibility is the shunt resistor GDL. Here, the significance of small variations in conductivity and mechanical properties need to be clarified. Furthermore, exact replication of the GDL compression is the most striking feature in terms of reproducing results from one cell to another.

2.5.1 Invasiveness of the Potential Probes

When inserting voltage probes in an active fuel cell, a possible disturbance of cell operation needs to be traded against mechanical and thermal robustness of the wires. Considering a CL thickness of 10 to 20 μm, the wire diameter can easily become a critical factor regarding the contact between catalyst and gas diffusion layer. Using a tungsten-rhenium alloy as described in Section 2.2.1 enables a decrease of the wire diameter to 10 μm, which offers a satisfactory trade-off. Since the wires penetrate the CL and MPL for equal parts, the active area is only disturbed on ca. 5% of its surface assuming a wire spacing of 200 μm. In general, a decrease of performance upon wire insertion was not observed.

However, it is likely that the quality of wire penetration into CL and MPL is different comparing channel and rib, according to the pressure distribution. The LM-micrograph in Figure 2.20 indeed indicates that the contact of CL and MPL is somewhat disturbed in the channel area.

Figure 2.20: LM-micrograph of the probe wire impression marks in the anodic catalyst layer; The rib covered areas (upper and lower parts) can be identified by the stronger imprints of the GDL fibres and probe wires.
It is seen for this typical cell compression of 10.0 MPa that the impression marks after operation are weaker in the channel area, whereas even the imprints of the GDL fibres can be seen in areas formerly covered by a rib. Thus, there is the danger that the wires serve as a spacer between the CL and the GDL, collecting the current from the delaminated layers. In this case, the voltage signals would be falsified in the channel area since the probes are serving as current drain and change the potential field in the shunt.

To gain more insight on this problem, Figure 2.21 provides a closer analysis by means of REM micrographs. The depth of penetration can be identified by means of the width of the impression mark, which is the diameter of the wire at maximum intrusion.

![Figure 2.21](image)

**Figure 2.21:** Impression marks of the probe wires in the anodic CL (attached to the polymer membrane) and in the anodic MPL (attached to the GDL): a) Rib covered area of CL; b) Rib covered area of MPL; c) Channel area of CL; d) Channel area of MPL. Different intrusion depths can be deduced comparing channel and rib.
The Figures 2.21 a) and b) elucidate that equal penetration into MPL and CL holds true for the case of a rib covered area, both impression marks have the width of the wire diameter. In c) and d) however, showing the middle of the channel area, the imprints have a width of 6 to 7 µm only. According to a simple geometrical calculation, the penetration depth can be determined between 1 and 2 µm, leaving an interspace of ca. 6 µm between CL and MPL with the wire serving as a spacer.

Despite this observation a negative impact on cell performance could not be observed upon wire insertion. There is however the danger of adding a systematic error on the measured potential data in the channel area, stemming from the current collecting effect of the wire in the interspace between GDL and CL. After all, the quality of a current distribution can be evaluated by its integral value, which has to match the cell current. This criterion would disclose errors induced by the delamination effect, it is discussed in Subsection 2.5.3.

2.5.2 Variance of the Shunt Resistors

The GDL is not a precision resistor. In particular the electric conductivity of the carbon paper and its behaviour under compression are sources of error. The following ex-situ studies show that, due to the carbon fibre macro-structure, the GDL properties on the scale of channel/rib dimensions are far from homogeneous. Variations of GDL thickness, density and transport properties are occurring all over its area, leading to variations in the measured voltage distribution.

Thereby two scales have to be considered: First, the mean values of the material properties (e.g. thickness) of a GDL used in the test cell (area = 1.3 cm²) will vary when comparing pieces of carbon paper used for different cells. The results obtained might thus be of limited reproducibility. Second, the properties are non-uniform inside one piece of GDL used in a particular cell assembly, considerable gradients of electric conductivity and thickness are hence expected to affect the local current on the sub-mm scale.

Variations on the Sub-mm Scale. In order to verify the variance of GDL properties on the scale of channels and ribs, five round samples with a diameter of 3.0 mm (area 0.071 cm²) were stamped at random positions from an unused piece of anode GDL of the size 1.3 cm², including a microporous layer as used in the active test cell. The sample thickness and the weight were compared. While the sample weight showed relatively low variations between 13.6 and 13.8 mg, it has been found that the thickness of all five samples exhibits a more considerable variance between 198 and 215 µm. All values are thereby smaller than the mean value for the original 1.3 cm² piece with 217 µm. A standard deviation of ± 6.7 µm (± 3.5 %) has been determined, while the highest difference between two samples was 17 µm (8 % of thickness). This number indicates significant gradients of GDL thickness even inside a piece of 1.3 cm².

Since the compression in the specialized test cell is realized by adjusting a particular distance between anode and cathode plates instead applying a particular pressure, these thickness variations result in a non-uniform compressive strain of the diffusion layer (expressed in percent of initial thickness). The distribution of electric conductivity as calculated in Section 2.3.2 is thus somewhat falsified, and also its mean value may be too high since parts of the GDL are less compressed in reality.
To elucidate the significance of these inhomogeneities, a virtual GDL with non-uniform thickness was implemented into the calculation of the potential field. The current density distribution obtained with this modified shunt resistor is compared to the one obtained with a uniform GDL, which does not consider inhomogeneous thickness.

Figure 2.22 shows in a) the design of this non-uniform anode GDL construct with a maximum thickness of 215 $\mu$m as measured for the 1.3 cm$^2$ piece. The GDL is divided into 12 domains representing areas with lower thickness (e.g. large macropores with less fibre density). This artificial distribution resembles a more realistic picture of the fibrous material structure, it arises from the statistics of the five small samples (0.071 cm$^2$) where the biggest difference is 17 $\mu$m.

The modified distribution of compressive stress with the non-uniform GDL is obtained from structural mechanics calculations, it is used to map the electric resistance onto the GDL domain. Compared to a uniform GDL with constant thickness of 215 $\mu$m the non-uniform shunt entails a non-uniform potential field, and therewith a non-uniform current distribution. This correlation is shown in Figure 2.22 c) for the case of a constant potential of 5.0 mV (diagram b).

In theory, domains with lower thickness decrease the local electric conductivity upon compression. Thus, less current is necessary at these positions to cause a voltage drop of 5.0 mV. Comparison of the two current distributions in Figure 2.22 c) indeed shows this effect. While the integral value of the current distribution is only slightly decreased (0.02 A/cm$^2$), the local currents are
more than 5\% lower in regions with the highest reduction of GDL thickness. As a consequence, fluctuations in the current distributions of this magnitude can not be considered reproducible and might be eliminated by statistic data treatment (e.g. smoothing splines), or averaging of the distributions from one experiment with several independent cells.

**Variations on the Centimeter Scale.** The considerations above show that variations of GDL properties inside the cell area of 1.3 cm\(^2\) are unavoidable. However, also the mean properties on a larger scale are expected to underlie statistic fluctuations. To evaluate the deviation from cell assembly to cell assembly, 25 samples of GDL were stamped from a 200 cm\(^2\) carbon paper sheet purchased from Umicore, which is used in the in-situ test cell. The sample size was 3.8 cm\(^2\) and therewith ca. three times the size of the GDL pieces used in the active cell.

Even with this size strong variations of mean thickness and density are found. Inspection of the mean sample thickness in Figure 2.23 a) shows that the same magnitude of deviation occurs as it is found on the sub-mm scale. Also the variations of material density revealed in diagram b) indicate differences in the sample’s structural mechanics (e.g. tensile strength).

![Figure 2.23](image)

**Figure 2.23:** Variation of a) GDL thickness and b) GDL density for 25 samples of the size 3.8 cm\(^2\); both properties show a strong variance which might entail differences in electron and mass transport.

Similar to the scale below one millimeter, a maximum difference in mean thickness of 18 \(\mu m\) was observed comparing two random samples (see Figure 2.23 a). This high deviation is assumed to be attributed to different positions on the 200 cm\(^2\) GDL sheet, e.g middle or rim, respectively. These variations might be a consequence of the production process of the GDL sheets and are expected to have a noticeable influence on reproducibility of the in-situ measurement results. Since thinner samples inherit a higher density (compare diagrams a) and b), two cells equipped with GDL pieces which exhibit such deviations might show different behaviour in terms of mass transport as a consequence of an altered porosity.

The above findings elucidate the necessity of manual selection of cell components to be used in the experiments. When GDL thickness and density vary for more than 8\% in two assumed identical cells, the results are assumed to be of limited reproducibility. The GDL thickness is therefore used as a selection criterion for choosing GDL pieces with similar properties. In general, the achievement of the best possible reproduction of cell compression is of high importance regarding the reproducibility of sub-mm current density distributions.
2.5.3 Statistic Data Treatment and Quality Criterion

It is possible to deduce from the above considerations that a precision resistance – other than the commercial GDL used here – would be necessary to increase the reliability and reproducibility of the sub-mm current measurements. However, with the exclusive use of non-commercial components the measurement principle would lose its qualification as a diagnostic tool. Careful statistic data treatment is hence applied to eliminate quantitative and qualitative uncertainties contained in the results.

Figure 2.24 a) shows typical potential distributions measured in-situ with the 30 probe wires in the test cell at various currents (H₂/air, rh = 0.4, cell compression = 35% of initial thickness). As it is seen, the standard flow field dimensions (channel- and rib width 2.0 mm each) allow for covering 6.0 mm of the x-coordinate, which is more than two repetitive channel/rib units (2.0 mm), and more than one symmetric unit comprising a channel and two adjacent half ribs (4.0 mm). As anticipated, the distribution of potential exhibits variations comparing the two repetitive 2.0 mm units. This variance arises from differences in electron conduction (see Figure 2.22) and differences in local pore distribution (locally altered reactant and water transport).

The calculated current for the domain of one channel and two half ribs (4.0 mm) is plotted in Figure 2.25 a), it represents the real flux of current in y-direction from the catalyst layer into the GDL, as it caused the measured potential drop. Due to the symmetry of the domain, there is no reason for discussing the differences between the left and the right half of the 4.0 mm domain since their channel/rib distributions should be identically.

![Figure 2.24: a) Original and b) Symmetrised potential data φᵢ for a cell operated on H₂/air, rh = 0.4, GDL compression = 35% of initial thickness; Distributions are shown for increasing cell current.](image1)

![Figure 2.25: Current density distributions at the active layer jᵢ obtained from a) Original and b) Symmetrized potential data from the cell in Figure 2.24; Distributions are shown for increasing cell current.](image2)
Therefore, the data points for $\phi_i$ at corresponding coordinates in both 2.0 mm half-channel/half-rib units are averaged and plotted over the 4.0 mm repetitive unit as done in Figure 2.24 b), data outside this domain is ignored. Furthermore, the symmetric function is fitted with a smoothing spline to prevent the occurrence of artefacts and to ensure the condition of zero slope at the boundaries of the repetitive unit. Conversion into current density (Figure 2.25 b) thus also yields symmetric distributions, whereby most of the fluctuations attributed to material inhomogeneities are eliminated.

The quality criterion for the calculated current is the integral value of the distribution. It has to match the load current, which is applied to the cell during an experiment. Possible reasons for not fulfilling this criterion would be a wrong implementation of the shunt resistors, or a different magnitude of current generation outside the wire covered cell area (the mean current of the distribution on the 4.0 mm domain is extrapolated to the entire active area).

Figure 2.26 shows the behaviour of cell voltage and integral currents for the cell from Figures 2.24 and 2.25. It is seen for this typical example that a sufficient agreement between the cell’s load current and the mean value of the distributions is found. Furthermore, it is possible to deduce from the small differences between the mean values from the original data (●) and the mean values from the symmetrized data (○) that the procedure of symmetrization does not add a substantial error on the integral of the distribution.

![Figure 2.26](image)

**Figure 2.26:** Polarization curve and match of load and integral current for a cell operated with $H_2/air$, $rh = 0.4$, GDL compression = 35% of initial thickness; In general the quality criterion is sufficiently fulfilled, deviations can be explained with membrane swelling and thermal effects. The symmetrization of potential distributions has only a marginal effect on the integral of the current distribution.

However, a systematic deviation between load and mean current can be observed in the diagram, which is qualitatively reproducible in other cells. At low load, the calculated current underestimates the real value while higher integrals are found when decreasing cell voltage towards limiting current.

The underestimation seen between 0.2 and 0.6 A/cm$^2$ may be a consequence of membrane swelling. It is known from literature that NAFION® 112 can change its thickness by 10 to 12% upon water uptake from $rh = 0.4$ to saturation [35, 37]. Due to the fixed plate distance additional pressure is applied from inside the cell, which has to be compensated by the component with
the lowest Young’s modulus: the GDL. Thus, a higher conductivity than implemented into the
calculation might apply, leading to lower currents from a measured potential distribution.
The reason for the departure from linearity in the high load range is only speculation. Besides
thermal effects, a possible explanation could be the delamination effect discussed in Subsection
2.5.1. Upon water production, the swelling of the membrane does not only affect its thickness,
but also its in-plane dimensions. As a consequence, the crumpling of the swelling polymer in the
channel area could affect the CL-MPL interface and the quality of the potential measurement.
A delamination of these layers corrupts the contact of the probe wires to the CL. This way
they might serve as current conducting bridges between CL and MPL. Higher potentials are
consequently measured in the channel area, leading to higher calculated currents.
While such systematic errors can not be quantized, stochastic errors attributed to the variance
of the component properties (e.g. in the GDL, see Figure 2.23) can be identified and eliminated
by averaging results of one experiment over several independent cells, equipped with identical
components. In this context, the measurement of current distributions shown in Figures 2.24
and 2.25 is repeated with two other cells using hand-picked pieces of GDL assorted for equal
thickness. This procedure is a consequence of the considerations in Subsection 2.5.2.
Figure 2.27 a) provides the distributions of these cells obtained at an integral current of 0.8 A/cm²,
the circles mark the arithmetic average of the three data sets. It is seen that the shape of the
distributions varies most in the channel area, where a single peak in the center or two smaller
peaks near the rib edges can be observed for measurements with identical operating parameters.
Thus, a trust range is identified inside which the shape of the distribution may randomly vary
as a consequence of material inhomogeneities or insufficient potential measurement.

This trust range was defined as the length of the error bars representing the standard deviation of
the measured distributions (see Figure 2.27 b). Hence, 68 % of the measured data will be in this
range. The current distribution plotted through the trust range is a spline fit of the arithmetic
averaged data points shown in diagram a). It can be concluded that a stochastic error of about
±15 % has to be taken in account for channel and rib covered areas. According to the Figure,
no evidence for less reliable measurement in the channel (due to delamination) is found.
2.6 Measurement of Local Membrane Resistance by Current Pulsing

Current density distributions as shown in Figure 2.25 can be obtained during stationary or transient operation. This opens up the possibility for expanding the sub-mm current measurements to sub-mm resistance measurements: if \( j \) is measured with a sufficient temporal resolution during an electrical perturbation (i.e. a current pulse or step), its behaviour contains information on the local ohmic resistance \([151, 157]\), similar to the context described in Chapter 1.3.1.

Considering the high aspect ratio of membrane thickness (NAFION® 112 ca. 50 \( \mu \)m) and channel/rib dimensions (typically 1.0 mm), a non-uniform membrane hydration is expected for a wide range of operating conditions. The distribution of ionic resistance – coupled to the water uptake – is hence assumed to strongly influence the shape of the current distribution, its measurement is thus of great value for understanding the local losses on the sub-mm scale.

2.6.1 Principle of Local Resistance Measurement

Essentially, two methods for membrane resistance measurements are available: those based on DC-perturbations (i.e. current interruption \([158]\) and current pulses \([78]\)), and those based on AC-techniques, i.e. high frequency resistance measurements at constant frequency \([134]\) and electrochemical impedance spectroscopy at varied frequency with model based fitting of the data \([159]\). For the sake of much simpler instrumentation and data processing, the option of DC-perturbations with current pulses was chosen.

When applying integral current steps or pulses, the dynamic local current changes are governed by the different compositions of local overvoltages. Since ohmic resistance has an infinitely short time constant, comparing the local current distribution immediately before \( j_1 \) (stationary state) and after \( j_2 \) (disturbed state) the perturbation allows for calculating the local cell resistance \( R \) at the position \( i \). With this principle, the degree of freedom is the local current density distribution instantly after the perturbation. Current interrupt measurements are thus not applicable, because they enforce a fixed distribution when the integral current is cut off. Consequently, a step to a value different from zero needs to be made to obtain a current distribution \( j_2 \), which emerges only from the change of ohmic overvoltage directly after the current transition.

Fig. 2.28 illustrates the principle of recording the potential distribution \( \phi \) across channel and rib during a current step. The relaxation of cell voltage and local potential across the two repetitive channel/rib units can be observed after the current transition.

According to the principle of resistance measurement with a current step/pulse technique – as illustrated in Figure 1.12 – the ohmic resistance is obtained from the instantaneous response of voltage \( \Delta U \) divided by the change of current \( \Delta j \). In analogy, the calculation of local cell resistance is obtained from the division of the local drop of cell voltage at a position \( i \) by the change of local current at a position \( i \) during the perturbation:

\[
R_i = \frac{|U^{t2}_i - U^{t1}_i|}{|j^{t2}_i - j^{t1}_i|} = \frac{\Delta U^{t1,t2}_i}{\Delta j^{t1,t2}_i},
\]

(2.7)
2.6. Measurement of Local Membrane Resistance by Current Pulsing

The local cell voltages $U_{cell}^{t_1}$ and $U_{cell}^{t_2}$ before and after the step are obtained from correcting the respective integral cell voltage $U_{cell}$ at $t_1$ and $t_2$ for the measured electronic potential drop over GDL and FFP, which is provided by the measured values of $\phi_i$. Due to the use of identical components for the anode and cathode side electrodes, the potentials $\phi_i$ measured on the anode are assumed valid also for the cathode. Therefore, the local cell voltage at the time $t_1$ or $t_2$ is defined by

$$U_{cell}^{t_1,t_2} = U_{cell}^{t_1,t_2} - 2 \cdot \bar{\phi}_i^{t_1,t_2}.$$  \hspace{1cm} (2.8)

In order to minimize the error, the cell voltage $U_{cell}^{t_1}$ and the local potential $\phi_i^{t_1}$ – both stationary state – are averaged over time before the perturbation. For the values at $t_2$ averaging can not be applied, since this data has to be identified as the values directly after the end of the current transition. Therefore, a critical factor for the resistance measurement is the resolution in the time domain, which needs to be in the order of a few microseconds [78]. Failure to achieve a sufficiently fast current switching time or data acquisition rate will result in current distributions $j(t)$, which are influenced by other processes than ohmic loss.

Accounting for the correction of cell voltage with $\phi_i$, the resistance distribution obtained from Eq. 2.7 very closely represents the ionic membrane resistance. With the cell components used (membrane and electric components) the ionic fraction makes up ca. 90 % of the total ohmic drop in the fuel cell. However, since the electric fraction of ohmic drop is known from the local potential measurement, subtraction of these values is expected to leave only the ionic fraction and the fraction of electric drop from the CL.

The sum of the calculated local resistances according to Eq. 2.7 needs to match the measured integral cell resistance. The latter value may be obtained from simply dividing the instantaneous voltage drop $\Delta U_\Omega$ (corrected for $2 \cdot \Delta \tilde{\phi}$) by the integral current step:
\[ R_{cell} = \frac{\Delta U_{t1,t2}^t - 2 \cdot \Delta \phi_{t1,t2}^t}{\Delta j_{cell}^t}, \quad (2.9) \]

while the calculated cell resistance equals the sum of the local resistances \( R_i \) from the parallel circuit:

\[ R_{cell} = \left( \sum_i \frac{1}{R_i} \right)^{-1}. \quad (2.10) \]

If the quality of the current measurement is good enough, the integral values of the current distributions \( j_{i}^{t1} \) and \( j_{i}^{t2} \) match the cell’s load at \( t_1 \) and \( t_2 \). In that case, the integral resistance calculated in Eq. 2.10 will co-actively match the measured resistance obtained from Eq. 2.9. It is worth mentioning that due to the parallel nature of the resistors on the channel/rib domain the integral resistance is dominated by the lower values and does not match the arithmetic average.

The local current distributions \( j_i \) from an exemplary set of data (H\(_2\)/O\(_2\), 0.4 A/cm\(^2\), \( rh = 1 \)), obtained for the stationary \((t_1)\) and disturbed state \((t_2)\), can be seen in Figure 2.29-a). In the next step, the locally resolved distribution of ohmic resistance is calculated according to Equations 2.7 and 2.8, it is plotted in Fig. 2.29-b) together with the integral resistances obtained from Equations 2.9 and 2.10.

![Figure 2.29](image)

**Figure 2.29:** a) The local difference of the current distributions \( j_i \) at \( t_1 \) and \( t_2 \) leads to b) The locally resolved membrane resistance \( R_i \); representative data for operation on H\(_2\)/O\(_2\), 0.4 A/cm\(^2\), \( rh = 1 \).

The local resistances are obtained with the same spatial resolution as the current density distributions. It is seen that even in this case (operation under saturated conditions) the membrane resistance is not uniform across channel and rib.

### 2.6.2 Reliability of Local Resistance Measurement

Besides the accuracy of the current measurement (which is discussed in Section 2.5), the reliability of the obtained resistance distributions mainly depends on two factors: the rate of the current transient at the pulse edge (transition time) and the sampling rate of the voltage measurement for determination of the local currents. Thereby, the achievement of a sufficient temporal resolution is a smaller problem than the current rise time of the electronic load.
Although the transient measurement of a channel/rib current distribution poses high demands on the data acquisition system, the presented measurements are carried out with an adequately fast sampling rate for obtaining a satisfactory temporal resolution. The local potentials were recorded during the pulse using a set of multichannel data acquisition devices (National Instruments PCI 6250M), capable of achieving a sampling rate of 110 kS/s. The time $\Delta t$ between the current distributions $j_1^t$ and $j_2^t$ is therefore fixed to a minimum of 9 $\mu$s, which is more than 6 times shorter than the current rise time.

This current rise time, or transition time, is indeed a limiting parameter, since more voltage drop (cell voltage and wire potential) is influenced by relaxation stemming from other processes than ohmic conduction in the case of a long transition. As illustrated in Figure 2.30 a), current pulses with the length of 10 ms were applied during stationary operation for the local resistance measurements. The current is controlled and modulated using an electronic load (Höcherl & Hackl ZS 506-4), enabling a transition time at the current edge of ca. 60 $\mu$s at minimum.

![Figure 2.30](image_url)

**Figure 2.30**: a) Transient behaviour of voltage (gray) and current (black) during a pulse with the length of 10 ms; The current transient is not visible on the scale of milliseconds, while a distinct relaxation behaviour is observed for the cell voltage. b) Magnification of the current pulse edge; The current rise time (offset between $t_1$ and $t_2$) is determined as 63 ms, the instantaneous drop of cell voltage (representing the ohmic fraction) is determined at the end of the current transition ($t_2$).

In contrast to the ideal behaviour illustrated in Figure 1.12, the electronic load is not capable of producing a fast and ‘clean’ transition rather than approaching the new current $j_{cell}^{t_1} + \Delta j_{cell}$ slowly and asymptotic. The mentioned behaviour is shown in the magnification of the current pulse edge provided in Figure 2.30 b).

This ‘soft transition’ makes it problematic to determine the exact value of the instantaneous voltage drop $\Delta U_\Omega$, which represents the ohmic fraction of overvoltage. Therefore, the time $t_2$ is defined as the end of the current transition, i.e. when the current signal enters the range of values for $j_{cell}^{t_1} + \Delta j_{cell}$. This procedure is automized in MATLAB to find the correct values for $U_{cell}^{t_2}$ and $\phi_\Omega^{t_2}$. It becomes obvious, that a systematic error is induced by this principle regarding the extraction of resistance, which arises from the blurred current pulse edge. Assuming an infinitely short transition time with a slope of the value 1, smaller $\Delta U_\Omega$ are likely to be observed. As a consequence, the resistances calculated with Equations 2.7 and 2.9 using the instantaneous
voltage drop extracted from the 'soft' current transition are slightly too high.

The influence of the transition time can be observed in Figure 2.31, where the integral cell resistance $R_{cell}$, measured from the current pulse, is compared for different transition times. The electronic load used in the experiments features 3 transition modes: 'fast', 'medium' and 'slow'. The transition times for a current step with an amplitude of $\Delta j = 1.0 \, \text{A/cm}^2$ were determined as $63 \, \mu\text{s} \ ('\text{fast}')$, $171 \, \mu\text{s} \ ('\text{medium}')$ and $516 \, \mu\text{s} \ ('\text{slow}')$. It can be seen that the measured cell resistance is increasing asymptotically with the current rise time.

The obtained value of $89 \, \text{m}\Omega\text{cm}^2$ in the 'fast' mode is in the upper range of the literature values for Nafion 112 for operation with $\text{H}_2/\text{O}_2$ and saturated gases ($65 - 85 \, \text{m}\Omega\text{cm}^2$ [29, 160]). This indicates that the transition time is slightly too slow. Synchronous measurement of the cell resistance with an AC-milliohm-meter (Tsuruga Model 3566) returned a resistance value of $79 \, \text{m}\Omega\text{cm}^2$ for this experiment, which is 10% lower than the value from the single pulse measurement. Keeping that systematic error in mind, the transition time of the electronic load in the 'fast' mode is considered satisfactory for the experiments, although there would be some room for improvement.

![Figure 2.31](image1.png)

**Figure 2.31:** Integral cell resistance $R_{cell}$ as a function of the current step transition time, the rise time was altered by switching through the 3 modes of the electronic load: 'fast', 'medium' and 'slow'; Cell operated with $\text{H}_2/\text{O}_2$, $rh = 1.0$.

![Figure 2.32](image2.png)

**Figure 2.32:** Current transition time (solid line) and signal-to-noise ratio (dotted line) as a function of the step amplitude, a noise-free signal has to be traded against fast current transitions; Cell operated with $\text{H}_2/\text{O}_2$, $rh = 1.0$.

This improvement could be realized by adapting the parameters of the experiments. Careful investigations on the transition time show that the current rise time is a function of the step amplitude only when $\Delta j$ is smaller than $1.0 \, \text{A/cm}^2$ (see solid line in Figure 2.32). Thereby the current rise time can be decreased to $54 \, \mu\text{s}$ with $\Delta j = 0.6 \, \text{A/cm}^2$ and even to $45 \, \mu\text{s}$ with $\Delta j = 0.2 \, \text{A/cm}^2$.

The diagram furthermore shows the behavior of the noise coupled to the signal of the probe wires (dotted line). For the lowest transition time 38% of noise has been determined, which is not acceptable. The noise-to-signal ratio is desired to be smaller than the systematic error arising from the slow transition time, which was determined as 10% in the paragraph above. As a consequence, step amplitudes of $1.0 \, \text{A/cm}^2$ were chosen for all experiments to obtain a noise-to-signal ratio of ca. 8%, accepting a slightly lower current transition. Higher amplitudes achieve an even better noise ratio without enhancing the current rise time, but entail the danger of cell voltage reversion.
However, variation of the step amplitude can prove the validity of the step-pulse technique by reproducing the same resistance distribution from pulses with different $\Delta j$. Figure 2.33a) depicts the stationary and disturbed current distributions for a cell operated with $\text{H}_2/\text{O}_2$ and a relative humidity of 40%. The disturbed distributions $j_{t2}^i$ were obtained for step amplitudes of 0.5, 1.0 and 1.5 A/cm$^2$, respectively, with a conditioning time of 30 min at 1.0 A/cm$^2$ before the pulses. Figure 2.33b) shows that indeed nearly identical resistance distributions could be obtained, which only slightly differ due to fluctuations in the current distributions they are based on.

**Figure 2.33:** Validity of the pulse technique for obtaining local resistance: a) current distribution for three pulses with different amplitudes (0.5, 1.0 and 1.5 A/cm$^2$), b) the resistance distributions for these pulses; Cell operated with $\text{H}_2/\text{O}_2$, $r\text{h} = 0.4$.

Inspection of the resistance distributions in Figures 2.33b) and 2.29b) shows more or less pronounced peaks at the rib edges. These are found reproducible for most of the distributions and arise from minima in the difference of stationary ($j_{t1}^i$) and disturbed ($j_{t2}^i$) current distributions at these positions. Since the compressive stress in the GDL has a distinct maximum at the rib edges, peaks in current production and local resistance appear to be a compression effect and not artefacts of calculation.
2.7 Summary Chapter 2

This chapter described the development of the measurement method for measuring the local current and ionic resistance on the channel/rib scale. The computing procedures to obtain the current from measured potential data and to obtain the membrane resistance from transient measurements were discussed. Furthermore, the *ex-situ* characterization of the shunt resistors was described in detail and a comprehensive consideration of the errors has been provided. The most important facts are summarized below:

- The current distribution in PEFC on the scale of channels and ribs can be measured with a resolution of at least 0.2 mm by using the electron conductors in a plane perpendicular to the membrane (GDL and FFP) as shunt resistors, all other methods proposed so far fail due to high invasiveness or a lack of resolution.

- The method requires intricate *ex-situ* procedures regarding the characterization of these shunts.

- The distribution of compressive stress is non-uniform throughout the channel rib domain, it entails a highly anisotropic two-dimensional field of electric conductivity.

- The GDL causes nearly 50% of the voltage drop. Together with its contact resistance between GDL and FFP, it is the dominating resistor in terms of electric potential drop over the shunt.

- The current density is eventually obtained from the solution of LAPLACE’s equation in two dimensions. The $y$-component of the current at the CL-interface is considered the current distribution across channel and rib.

- The error of the current distribution is comparable between channel and rib covered areas, the trust range is ca. ±15%. Careful statistic data treatment (symmetrization, spline fitting, averaging over several independent cells) is required to eliminate artefacts attributed to inhomogeneities in the shunt properties.

- The difference of two current distributions extracted from the current transition during a pulse edge returns information on the local ohmic resistance with the same spatial resolution as the current measurement.

- The measurement of local resistance has room for improvement in terms of the transition time of the pulse edge. This is due to present technical conditions, i.e. the capabilities of the electronic load, which are connected to a systematic error of ca. 10% regarding integral cell resistance.

It has been shown on the basis of exemplary sets of data that neither the current nor the ionic resistance is distributed homogeneously across channel and rib. The comprehensive analysis of the local cell behaviour upon variation of operating conditions is provided in the following chapter.
Chapter 3

Influence of Operating Parameters

”Curiosity is always the starting point for solutions to a problem.”

Galileo Galilei, 1564-1642

In this chapter the dependence of local current density and membrane resistance on the channel/rib scale on the variation of parameters determining operating conditions is investigated. These conditions are in particular the membrane hydration, the system pressure, the cathodic reactant composition, and the cell compression. The studies aim to identify the process – or processes – which cause the relevant performance losses and are hence need to be considered in structural optimization efforts.

Figure 3.1 gives an overview on the parameters investigated with the specialized test cell in this chapter. Regarding the above-mentioned operating conditions, these parameters are the reactant dew points (T_{gas}), the compressed thickness of the gas diffusion layer (d_{GDL}), the reactant gas pressure (p_{gas}) and the concentration of the oxidant (p_{O_2}) as well as the type of inert gas. The figure shows over which pathways the local reaction rate is affected by a change of one parameter. It can be seen that the channel/rib current distribution is eventually determined by the interaction of only two transport processes: mass and charge transfer. The dependence of local generation on the relevant operating conditions may therefore be clarified by combined measurement of the current density and resistance distribution.

In terms of mass transport, changes of local current generation are induced by varying the oxidant concentration, the gas pressure and the inert gas, or by compressing the GDL porous structure. However, reactant humidification can also influence the diffusion of reactants. For example, water clogging upon high levels of humidification, or high current densities, is known as an important factor, but can not be accounted for quantitatively in experiments since the amount of liquid water in the GDL is difficult to adjust and to control.
Chapter 3. Influence of Operating Parameters

### Parameter to Adjust

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>absolute gas pressure ( p_{\text{gas}} )</td>
<td>( \Delta c_{\text{GDL}} )</td>
<td>1</td>
</tr>
<tr>
<td>oxidant partial pressure ( p_{\text{O}_2} ) and inert gas</td>
<td>( \sigma_{\text{Mem}} )</td>
<td>2</td>
</tr>
<tr>
<td>GDL compressed thickness ( d_{\text{GDL}} )</td>
<td>( \sigma_{\text{GDL}} )</td>
<td>3</td>
</tr>
<tr>
<td>reactant dew points ( T_{\text{gas}} )</td>
<td>( \varepsilon_{\text{GDL}} )</td>
<td>4</td>
</tr>
</tbody>
</table>

### Physical Process / Transport Resistance

- **Mass Transport**: 
  - Local reaction rate
  - Channel/rib current distribution
- **Charge Transport**: 
  - Ionic Conductivity
  - Charge Transport
- **Ohmic Resistance**: 
  - Effective Diffusivity
  - Mass Transport

### Resulting Phenomena

- **Local Reaction Rate**: channel/rib current distribution
- **Charge Transport**: ohmic resistance
- **Mass Transport**: effective diffusivity

---

**Figure 3.1:** Overview of chosen operating parameters and their affection paths on the channel/rib current distribution; The local reaction rate is influenced by interactions of mass and charge transport limitations.

Accordingly, mass transport processes are affected upon changing any of the above parameters, while charge transport is mainly influenced by variations of reactant humidity (membrane ionic resistance) and cell compression (GDL electric resistance). However, the distribution of membrane resistance can back couple to reactant mass transport processes by means of the resulting product water distribution, which again couples back with the GDL compression by swelling. In another example, the change of oxygen mobility by means of inert gas substitution also changes the quality of water removal and thus the membrane resistance. This shows that the dependencies are complex and require careful investigation.

Throughout the experiments, only one operating parameter is changed at a time, while standard conditions are applied for all others. These standard conditions apply for all oxidants and include the cell temperature, gas pressure, relative humidity, GDL compression, reactant flow rate and the geometric channel/rib dimensions. Their values are given below in Table 3.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel Width</td>
<td>( w_{\text{chan}} )</td>
<td>2.0 mm</td>
</tr>
<tr>
<td>Rib Width</td>
<td>( w_{\text{rib}} )</td>
<td>2.0 mm</td>
</tr>
<tr>
<td>Cell Temperature</td>
<td>( T_{\text{cell}} )</td>
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</tr>
<tr>
<td>Gas Pressure</td>
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<tr>
<td>Rel. Gas Humidity</td>
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<tr>
<td>GDL Compression</td>
<td>( 1-(d/d_0) )</td>
<td>35 %</td>
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<tr>
<td>Stoichiometries*</td>
<td>( \lambda_{\text{Anode}} )</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>( \lambda_{\text{Cathode}}(\text{Air}) )</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>( \lambda_{\text{Cathode}}(\text{O}_2) )</td>
<td>46</td>
</tr>
</tbody>
</table>

*) at constant flow of \( \dot{V}_{\text{gas}} = 200 \text{ ml/min} \ @ 1.0 \text{ A/cm}^2 \)

**Table 3.1:** Base case operating conditions for the experiments with the test cell.
In this chapter, a section is devoted to the investigation on each of the four parameters in Figure 3.1, plus one for the reactant flow rate \( \dot{v}_{\text{gas}} \). Due to the requirements of the sub-mm current measurement, the specialized test cell is designed for differential operation in order to avoid current gradients along the channel. Therefore, excessive reactant stoichiometries are applied using constant flows on both electrodes. However, convection effects are expected to influence the water management and changes of ionic resistance are possible. Hence, the variation of reactant flow rate aims to verify the state of differential operation in the test cell.

All experiments were conducted with the same electrochemical components and gas diffusion media (MEA), purchased from *Umicore*. They represent a recent state of the art in technical applications. The component specifications are given in Table 3.2, together with the dimension of the specialized test cell. Since channel and rib widths are subject to change in Chapter 4, they are considered as an operating parameter and are hence given in Table 3.1.

<table>
<thead>
<tr>
<th><strong>MEA Components</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer Membrane</td>
<td>NAFION® 112</td>
</tr>
<tr>
<td>Catalyst loading anode</td>
<td>0.2 mg Pt/cm(^2)</td>
</tr>
<tr>
<td>Catalyst loading cathode</td>
<td>0.4 mg Pt/cm(^2)</td>
</tr>
<tr>
<td>Gas diffusion layer</td>
<td>TORAY TGPH-060, 20 wt-% PTFE, with MPL</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Test Cell Specifications</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel length</td>
</tr>
<tr>
<td>Channel height</td>
</tr>
<tr>
<td>Active area</td>
</tr>
</tbody>
</table>

**Table 3.2:** Components used in the specialized test cell and their specifications.

The variance of relevant material properties has been comprehensively discussed in Chapter 2.5, where the necessity of averaging a result over several independent cells was pointed out when quantitative results are desired. This procedure was applied to most of the results shown in the following sections.

However, qualitative evaluations on the influence of a single parameter can already be made based on the data of one cell, since relative changes of current or resistance distributions do not underlie falsification due to material inhomogeneities. Therefore, no error bars are given in the plots of local current density and membrane resistance. The confidence interval determined in Chapter 2.5.3 holds however true regarding the absolute values.
3.1 Membrane Hydration

In the along-the-channel dimension of technical fuel cells, gradients of reactant humidity are unavoidable. It is established knowledge that dry conditions near the cell inlet lead to losses caused by an increased membrane resistance, while oversaturated gases near the outlet might result in electrode flooding and therewith in mass transport limitations. Thus, water management is of critical concern for optimizing cell structures. Generally, the membrane can be hydrated by humidification of the reactant gases (external humidification) or by the product water (internal humidification).

3.1.1 Hydration by Reactant Humidification

External humidification of reactant gases affects the cell performance independently of the integral current density. Figure 3.2 shows the behaviour of the integral membrane resistance $R_{\text{cell}}$ for a cell fed with $\text{H}_2/\text{air}$ and a cell fed with $\text{H}_2/\text{O}_2$ upon variation of reactant relative humidity between $r_{\text{h}} = 0$ and $r_{\text{h}} = 1.0$ (applied to both reactants). The results are obtained from measurements using the pulse technique introduced in Section 2.6, allowing for determination of integral and local ionic resistance. The asymptotic decrease of resistivity with increasing humidity is seen for both oxidants, which agrees with the theory (see Fig. 1.4).

![Figure 3.2: Integral cell resistance $R_{\text{cell}}$ as a function of reactant humidity; Results obtained for standard conditions at 0.4 A/cm$^2$ for a cell fed with $\text{H}_2/\text{air}$ (dotted line) and $\text{H}_2/\text{O}_2$ (solid line).](image)

Similar to the cell scale, local current generation on the sub-mm scale is also strongly influenced by reactant humidity. In the upper diagrams of Figure 3.3 the local currents, and in the lower diagrams the local resistance distributions are shown for the same conditions as discussed in Figure 3.2. In the graphs on the left side (a and c) results for operation with air at the cathode, and in the ones on the right side (b and d) results for operation with pure oxygen are shown. Independent of the oxidant, the quality of the current and resistance distributions is the same: under dry conditions current is predominantly produced under the ribs, while it shifts to the channel under operation with high humidities. The local resistance is changing almost only in the channel, from a minimum in the case of saturated gases to a distinct maximum for dry gases.
To understand this behaviour, a closer look to the cell’s water management is necessary. With dry gases ($rh = 0.0$ or $0.1$), no or very little water is available from the gas channel for membrane hydration. Ionic conductivity therefore relies exclusively on hydration by product water. However, the water available for the membrane hydration is in competition with evaporation to the channel. The saturation of the ionomer will therefore be higher at positions with long diffusion pathways towards the channel, being better protected from drying than areas where the water removal pathways are short. For this reason, the membrane resistance under the channel shows a peak, resulting in the majority of current being produced under the rib covered areas.

At high relative reactant humidities ($rh = 0.7$ or $1.0$), the reactant partial pressure is significantly decreased in the mixture with gaseous water. Now, the area under the channel – with short diffusion pathways through bigger pores – will benefit from lower mass transport restrictions as compared to rib covered areas. The compression of the diffusion layer under the ribs does additionally lead to a decline of transport efficiency with a depleted reactant. With the resulting high local current densities in the channel, the membrane hydration is highest in this location, leading to the lowest membrane resistance in the channel/rib domain. Thus, the product water distribution has also a significant impact on local generation with high degrees of humidification. Additionally, liquid water accumulations are assumed to contribute to the observed behaviour.
It is known from Neutron Radiography studies that condensation in the GDL occurs even for undersaturated conditions \([110]\), the presence of liquid holdup in the diffusion medium is therefore likely at \(rh = 0.7\) and \(1.0\). The shorter water removal pathways and the higher rate of convective flow in the region under a channel hereby contribute to improved reactant transport, since pore clogging is avoided. Consequently, higher currents are possible in the channel area.

Inspection of the Figures 3.3 a) and b) furthermore shows that – independently of humidification – less current is produced in the rib area when air is used as oxidant. This effect is attributed to increased oxygen mass transport limitations in the case of a diluted reactant. The considerably lower reaction rate at the rib positions with the use of air entails a decreased water production in these area, and in turn the fraction of water available for the ionomer hydration is decreased. This results in consistently higher local resistances for operation with \(H_2/air\) as compared to operation with \(H_2/O_2\), as it is seen from comparison of the Figures 3.3 c) and d) and the Figures 3.4 a) and b). This effect is responsible for the different integral resistances at low levels of humidification comparing operation with \(H_2/air\) and \(H_2/O_2\) in Figure 3.2.

This finding is in agreement with the hypothesis that the distribution of product water is a critical parameter for the membrane resistance throughout the entire range of external humidification. It again emphasizes that the sub-mm current distribution is a complex interplay of charge and mass transfer, since in this case mass transport limitations couple with charge transport processes.

Furthermore, the fact that the membrane resistance under the rib remains almost unchanged upon the strong variation of gas humidity between \(rh = 0.0\) and \(1.0\) indicates strong differences of membrane water management in rib covered areas as compared to the channel. This effect is also seen in Figures 3.3 c) and d), and is quantitatively deduced by comparing the local resistance averaged over channel and rib covered areas in Figure 3.4 for operation with \(H_2/air\) (a) and \(H_2/O_2\) (b) as a function of reactant humidity.

**Figure 3.4:** Local membrane resistance as function of reactant humidity at 0.4 A/cm\(^2\), data averaged over channel (dashed line) and rib covered areas (solid line); a) Operation with \(H_2/air\), b) operation with \(H_2/O_2\). Independent of the oxidant, the rib resistances change only for about 25\% of their values, the channel resistances change from ca. 100 up to 500\%.

It is seen that in both cases a change of integral resistance upon humidity variation stems predominantly from the channel area, which exhibits the same asymptotic behavior as illustrated in Figure 3.2. In contrast, the rib resistances drop with a significantly less steep slope upon
humidification, and even start to rise again towards the values for dry conditions at high $rh$. This behaviour might be attributed to the decreasing local current under the ribs. However, the change of rib resistance upon humidity variation is significantly smaller (ca. 150 mΩ cm$^2$ for operation with air and ca. 170 mΩ cm$^2$ for operation with oxygen) as compared to the change of resistance in the channel, which is decreased from ca. 460 (a) or 360 (b) to 50 mΩ cm$^2$, respectively.

Although this behaviour appears to be systematic, the reasons are speculative. One explanation could be that the application of compressive stress in rib covered areas might not only affect the porous GDL. It is possible that the water take-up capacity of the membrane is decreased in this location, since an unconstrained swelling is impeded when the cell’s clamping pressure is higher than the membrane swelling pressure. As a consequence, the rib resistance can not reach the low values observed in the channel for levels of high humidification. This hypothesis has been alluded in the literature referring to similar observations in PEFC operated with a pin type flow field layout [161].

A possible explanation for the unchanged rib resistance under dry conditions is based on the fact that local membrane hydration can only be assured by means of product water here. With the rib covered areas being the positions with highest current generation (combined with lower water removal rates), the degree of local membrane humidification accordingly remains high as compared to the situation in the channel.

### 3.1.2 Hydration by Product Water

The dependence of the rib resistance on product water is confirmed by the finding that the quantitative level of rib resistance is changing with the integral cell current rather than being a function of reactant humidity. Generally, the dependence on cell current is stronger with dry gases. In this context, Figure 3.5 shows the behaviour of integral cell resistance as a function of the cell’s load for operation with completely dry ($rh = 0.0$) and saturated ($rh = 1.0$) reactants.

![Figure 3.5: Comparison of integral cell resistance $R_{cell}$ for operation with dry gases ($rh = 0.0$, dotted line) and saturated gases ($rh = 1.0$, solid line) upon variation of the load current (0.1, 0.3 and 0.8 A/cm$^2$); Cell is operated under standard conditions with H$_2$/O$_2$. The integral membrane resistance is only load dependent for dry gases.](image-url)
The cell is operated with H$_2$/O$_2$ between 0.1 and 0.8 A/cm$^2$, representing the low and medium load range where severe mass transport limitations are unlikely to occur (excluding possible water clogging). It is seen that the cell barely changes its integral ionic resistance upon the increase of cell current when saturated gases are fed, the resistance remains practically constant at the typical value for this conditions (between 90 and 100 mΩcm$^2$). In contrast, a strong decline of resistance from more than 1 Ωcm$^2$ is observed in the case of operation with unhumidified reactants when the load – and therewith the production of water available for membrane hydration – is increased.

The different effect on the local current and resistance distributions comparing external and internal humidification is clarified in Figure 3.6, showing the local data for the measurement in Fig. 3.5. The current distributions $j_i$ at the different cell currents are shown for the cases of dry (a) and saturated reactants (b) in the upper two diagrams, the respective resistance data $R_i$ are plotted in the lower parts (c) and (d).

![Figure 3.6](image-url)

**Figure 3.6:** Local current- and membrane resistance distributions for a cell operated with H$_2$/O$_2$ at various current densities (0.1, 0.3 and 0.8 A/cm$^2$); Current distributions $j_i$ for a) $rh = 0.0$ and b) $rh = 1.0$; Resistance distributions $R_i$ for c) $rh = 0.0$ and d) $rh = 1.0$; The resistance is not only changing in the channel upon operation with dry gases.

Diagrams (a) and (b) show typical current distributions obtained for cells operated with the respective humidity: in the case of dry gases ($rh = 0.0$, diagram a) the maximum of the current is produced under the rib, while saturated gases ($rh = 1.0$, diagram b) promote the channel areas,
whereby in particular at higher load the rib currents are inhibited.

Inspection of diagram d) reveals that the respective local resistance can not be the reason for the changing channel/rib partition of current upon load increase, since the distributions are practically identical for all integral currents. This indicates that the membrane is saturated at every point of operation, and the observed stagnation of rib currents upon load increase is consequently attributed to transport limitations due to the presence of liquid water.

In contrast, the local current distributions for the dry condition (diagram a) show more or less a parallel offset along the current axis, when the load is increased. It is seen from diagram (c) that the respective local resistance is changing in both positions upon this load increase, predominantly in the channel (from 1.6 to 0.3 Ωcm$^2$) but also under the rib with current densities lower than 0.3 A/cm$^2$ (from 0.7 to 0.25 Ωcm$^2$). As a consequence, the change of integral resistance can not only be attributed to the channel area when the current production is to low under operation with dry gases.

![Figure 3.7](image)

Figure 3.7: Comparison of local current $j_{Rib}$ and resistance $R_{Rib}$, both averaged over the rib covered area; Operation with H$_2$/O$_2$ for various current densities, a) dry condition ($rh=0.0$) and b) saturated condition ($rh=1.0$). The resistance is decoupled from the current upon operation with dry gases.

Figure 3.7 elucidates this finding by comparing the current production and the resistance averaged over the rib covered area only. It is seen in diagram (a) for the dry condition that the rib resistance (solid line) changes its value in a wide range from 0.8 to 0.2 Ωcm$^2$ upon a load increase of 0.7 A/cm$^2$. This is even more as observed for the variation of reactant humidity from $rh=0.0$ to 1.0 at 0.4 A/cm$^2$ (see Fig. 3.3). This behaviour is attributed to the strong increase of rib current (dotted line) and the augmented local water production connected with this.

Diagram (b) shows the same plots for the saturated condition, disclosing the decoupled behaviour of current and resistance in rib covered areas. While the rib current at 0.1 A/cm$^2$ is comparable to the one of the dry condition, the resistance value shows that membrane hydration is relying on external humidification. The slight increase of rib resistance for higher cell currents is attributed to the anode drying effect, which is known for saturated membranes. It is caused by raised water mobility in the ionomer at high levels of hydration, leading to an increased osmotic drag towards the cathode in particular at high current densities.
### 3.2 Reactant Flow Rate

The channel/rib current distribution may be influenced by the flow rate by means of convective effects. Possible consequences of flow rate variation are the interference with reactant transport to the catalytic layer and the manipulation of water management in terms of water removal. Since the experiments on the sub-mm scale is supposed to be carried out under differential conditions, the variation of reactant flow rate aims to confirm that no changes of local and integral performance are found with operation at standard conditions as a consequence of the above-mentioned influence factors, and where non-differential operation begins.

![Graph](image)

**Figure 3.8:** Influence of reactant flow rate $\dot{V}_{gas}$ on a) the cell performance $p_{cell}$ and b) the cell resistance $R_{cell}$, operation with $H_2/air$ at 0.4 A/cm$^2$ and $rh=0.0$ (dotted line), 0.4 (dashed line) and 1.0 (solid line). The cell characteristics are only a function of flow speed for low flow rates and dry conditions.

Figure 3.8 illustrates the behaviour of integral cell performance (a) and resistance (b) for operation of $H_2/air$ with different reactant humidities ($rh=0.0, 0.4$ and $1.0$) as a function of flow rate (50 to 500 ml/min) for both gases. At a constant current density of 0.4 A/cm$^2$, these fluxes correspond to cathodic stoichiometries of $\lambda_{air}^{cath} = 6$ to 60. The diagrams elucidate that the integral characteristics of the cell only change for the dry case between 50 and 200 ml/min. Comparison of the integral resistance data for different reactant humidities indicates that the reason for the performance change is a drying effect starting to evolve for flow rates bigger than 100 ml/min.

The data sets of local current and resistance are plotted in Figures 3.9 a) and b) for the same cell, considering only the cases $rh=0.0$ and 1.0. Both groups of graphs can easily be distinguished by the shape of the current and resistance distribution as discussed in Chapter 3.1.

For all reactant flow rates the dry condition ($rh=0.0$) exhibits lower currents in the channel (diagram a), which accompanies a locally high membrane resistance (diagram b). It is seen in b) that the channel resistance decreases for low stoichiometries (50 and 100 ml/min), leading to a promotion of current generation in this position. Generally, the rib currents tend to lower values and the channel currents to higher values in the case of low flow rates between 50 and 200 ml/min ($\lambda_{air}^{cath} = 6$ to 24). However, the change of integral performance is attributed to increased membrane drying with high flow speed, as the behaviour of integral resistance in Fig. 3.8 b) shows. The local data confirms that this effects is attributed to the channel.
In the case of saturated gases, the current distribution is controlled by diffusion and very low currents close to zero are observed in the rib covered areas. This is attributed to the relatively low oxygen concentration (operation on $\text{H}_2/\text{air}$) in combination with a high reactant humidity. Changes of local current under the rib are not observed upon variation of the reactant flow rate, an interference due to altered mass transport with high flow speeds can hence be excluded. Also the local resistance in diagram b) shows virtually identical distributions for all flow rates, indicating that increased water removal with high flow speed is not a dominating effect with high levels of external humidification. In general, the very good agreement of local current and resistance distributions resembles the consistent integral behaviour of the cell upon the flow speed variation seen in Figure 3.8.

![Figure 3.9:](image-url)

Figure 3.9: a) Local current and b) local resistance distributions as a function of reactant flow rate $\dot{V}_{\text{gas}}$, operation with $\text{H}_2/\text{air}$ at 0.4 A/cm$^2$ and $\text{rh} = 0.0$ and 1.0. No improvement of rib currents is observed upon flow rate increase. The resistance in the channel is lower for low flow rates with the dry condition.

An influence of the different flow rates on local current distribution can therefore not be confirmed upon operation with high external humidification. However, interference of integral cell performance and local generation has to be expected for flow rates below 100 ml/min for operation with low degrees of external humidification, the corresponding cathodic stoichiometry is $\lambda_{\text{cath}} \approx 12$ at 0.4 A/cm$^2$. For flow rates above 200 ml/min no significant affection of drying or transport effects are observed with any degree of humidification. This finding justifies the use of this value as the standard flow rate for differential operation.
3.3 Reactant Gas Pressure

Reactant gas pressure \( p_{gas} \) is known to have a strong influence on PEFC performance [169]. Due to the higher activity of the reactant species, the kinetics of the half cell reactions are significantly improved upon pressure increase. It is however unclear how the local current generation reacts on changes of reactant pressure. Possible impact mechanisms are discussed below.

According to Figure 3.1, variation of the absolute gas pressure changes the binary diffusion coefficient \( D_{ij} \) of oxygen in a gas mixture. This is based on the Slattery-Bird relation (Eq. 1.27), where the factor \( 1/p_{chan} \) decreases the interdiffusivity of a component \( i \) in a gas mixture \( j \) upon raising the gas pressure in the channel \( p_{chan} = p_{gas} \). This seems logical regarding the increased number of molecule collisions in a gas with increased pressure. Consequently, the diffusion of oxygen is expected to be reduced upon pressure increase, in particular for prolonged diffusion pathways under the ribs.

Considering the simple formulation of oxygen transport by Fick’s law (Eq. 1.21), also the driving force for diffusion, \( \Delta c_{chan,cl} \), is influenced by variation of the gas pressure. Although the mole fraction in the channel remains unchanged – since all components in the gas mixture change their partial pressure and concentration – the reactant concentration at the catalytic layer \( c_{cl} \) is subject to be influenced by the effect of oxygen mobility as discussed in the previous paragraph, which results in a change of the driving force for diffusion.

Since the concentration at the CL is unknown as it is a function of the load current, increasing the absolute gas pressure can have a promoting (due to the bigger driving force) or alleviating (due to the lower \( D_{ij} \)) effect on local current generation. Which scenario eventually holds true is assumed to depend on the reactant oxygen fraction \( p_{O_2} \) and oxygen consumption rate \( j_{cell} \).

Therefore, experiments with variation of reactant gas pressure from 1.0 to 2.0 bar\(_{abs}\) (both gases) for different cathodic oxygen fractions at various current densities are carried out. To enhance the effect of mass transport limitations, a relatively high cell compression (45% of initial GDL thickness) was chosen.

Figure 3.10 shows the expected positive influence on performance for a cell operated with a) 5% \( O_2 \) in the cathodic gas, b) air and c) pure oxygen as the oxidant. All three gas compositions show an increasing performance gain towards higher load currents with reactants at 2.0 bar\(_{abs}\) as compared to atmospheric pressure (1.0 bar\(_{abs}\)).

The quality of local current generation is displayed in Figure 3.11 for all three oxidants, whereby only the average current drawn from channel and rib covered areas is compared for the load range of the performance curves. The figures reveal that – independently of reactant concentration and consumption – basically no change of the channel/rib partition can be observed upon pressure increase, despite the relatively large effect on cell performance. The small deviations of channel- and rib currents at the different pressure levels are inside the error bars, which also holds true for the local distributions as function of the \( x \)-positions (no plots provided).

These results indicate a decoupled relation between local current generation and cell performance. Upon doubling the reactant gas pressure, the cell shows virtually identical channel/rib current partitions with a particular oxidant composition at a specific current density. Obviously, the changes of the binary diffusion coefficient by a factor of two do not dominate the channel/rib partitioning of current for any oxidant composition or load current.
3.3. Reactant Gas Pressure

Figure 3.10: Influence of gas pressure variation (1.0 and 2.0 bar\textsubscript{abs}) on cell performance; a) Operation with H\textsubscript{2}/5\% O\textsubscript{2} in N\textsubscript{2}, b) Operation with H\textsubscript{2}/21\% O\textsubscript{2} in N\textsubscript{2} (air), c) Operation with H\textsubscript{2}/O\textsubscript{2}; \(rh = 0.4\), GDL compression = 45\% of initial thickness. Gas pressure significantly influences the cell performance for a wide range of oxidant O\textsubscript{2} fractions.

A possible reason for this could be the partly counterbalancing effect of the increased driving force \(\Delta c_{\text{chan,cl}}\), leaving a significantly smaller factor than two for affecting oxygen transport. The observed increase of cell performance is thus mainly attributed to the improvement of catalytic activity. However, Subsection 3.5.2 will show that a disproportionately stronger manipulation of oxygen mobility (factor of 8) is very well affecting the channel/rib current distribution.

Figure 3.11: Influence of gas pressure variation (1.0 and 2.0 bar\textsubscript{abs}) on channel/rib current partition, current averaged over the channel- or rib width, respectively; a) H\textsubscript{2}/5\% O\textsubscript{2}, b) H\textsubscript{2}/air and c) H\textsubscript{2}/O\textsubscript{2}; \(rh = 0.4\), GDL compression = 45\% of initial thickness. In contrast to Fig. 3.10, gas pressure does not influence the partition of channel and rib currents.
3.4 Cell Compaction

Cell compression is influencing mainly the GDL structural properties, since this component has the lowest Young’s modulus of all materials and will therefore experience highest deformation upon application of compressive stress. Nevertheless, it can be deduced from Chapter 3.1 that the ionomer is also influenced by compacting pressure, in particular when its tensile strength decreases under high levels of hydration. In this section, however, the effect of compressive stress is only discussed for the porous gas diffusion medium.

Compression influences the porosity and tortuosity [162, 163, 102] as well as the electrical properties of the GDL (see Chapter 2.3.2). On the one hand, compressive strain increases the electrical conductivity of the GDL predominantly under the rib areas (where the stress and deformation is highest) and co-actively decreases the contact resistance to the rib. On the other hand, the effective diffusivity of the porous medium is impaired upon compression by reducing porosity and increasing tortuosity.

Furthermore, the influence of GDL compression on water management has been studied by Basylak et al. [164]. The authors correlate the cracking of carbon fibres and the changing morphology of the PTFE impregnation to an increase of water mobility. Essentially, the changing proportion of hydrophilic and hydrophobic surface area is found to improve the water removal and to decrease the quantity of liquid holdup in the porous structure.

Effect on GDL Effective Diffusivity. The decrease of free pore volume is affecting the cell performance predominantly in the mass transport regime. It is incorporated in the form factor $\varepsilon/\tau$ of the effective diffusivity in Fick’s first law as formulated in Equation 1.21. Inspection of this equation clarifies, that decreasing porosity and increasing tortuosity lower the rate of reactant transport through the compressed region.

The Figures 3.12 and 3.13 show the change of cell performance and the dependence of the channel/rib current distributions on compressive stress for a cell operated with H$_2$/air and H$_2$/O$_2$, respectively. Here, the GDL compression is increased stepwise by 5% starting at the initial standard value of 35%.

The polarization curves in a) illustrate the different behaviour comparing the two oxidants air and pure oxygen: while the performance decreases upon compression in a wide load range with air as oxidant, differences are only observed at high currents with the use of pure oxygen.

In general, the cell exhibits a lower limiting current density for higher compaction pressures – independently of the oxidant. Since the decrease of performance is stronger at high reactant consumption, it is obvious that mass transport limitations are increased as a consequence of the reduction of effective pore volume. It seems consistent with the theory of diffusion through porous media that this effect has a lower impact when pure oxygen is fed to the cathode. This result emphasizes that transport limitations in the GDL are more significant at low oxygen partial pressures.

Considering operation with H$_2$/air in Figure 3.12, it can clearly be seen that both, cell performance (a) and the quality of the current distribution (b and c), are changing noticeably even with this relatively small variation of compression. At a load of 0.4 A/cm$^2$ the rib current is restrained below 0.1 A/cm$^2$ at the highest compression, while more than twice as much current...
3.4. Cell Compaction

Figure 3.12: Comparison of current distributions for operation with H₂/air, standard conditions with GDL compression 35, 40 and 45% of initial thickness; a) Polarization curves, b) channel/rib current distributions at 0.4 A/cm² and c) at 0.8 A/cm²; Mass transport limitations upon cell compression occur throughout the whole load range.

is generated at this position when the GDL is least compressed (see diagram b). At the same time the channel currents are increasing accordingly when generation under the rib is hindered. Conclusively, the shape of a current distribution is more homogeneous for smaller compacting forces.

The same pattern can be observed in diagram c), where the local current distributions for an integral current of 0.8 A/cm² are plotted. Compared to diagram b), the individual levels of rib currents are unchanged upon doubling the integral current, indicating that these regions are limited by mass transport. The local limiting current under the rib therewith depends directly on porosity decrease.

Figure 3.13: Comparison of current distributions for operation with H₂/O₂, standard conditions with GDL compression 35, 40 and 45% of initial thickness; a) Polarization curves, b) channel/rib current distributions at 0.4 A/cm² and c) at 2.0 A/cm²; Mass transport limitations upon cell compression occur only at high oxidant consumption.
The picture of this mass transport limitation is further clarified when the results from operation with H₂/O₂ are analyzed. (Figure 3.13). It can be seen in diagram b) that virtually identical current distributions are observed in the case of low consumption at 0.4 A/cm². As seen with the behaviour of the polarization curves in diagram a), significant mass transport limitations are only relevant for currents higher than 1.5 A/cm². For the high load regime (diagram c) at 2.0 A/cm², the local current distributions show a similar behaviour as observed in the case of air at much lower current densities, e.g. at 0.8 A/cm².

As a consequence it can be deduced that at low current densities and operation with pure oxygen transport is not a limiting process, the oxidant appears to be uniformly distributed across channel and rib even with high levels of GDL compression. The transport limitations will however become dominating for high current densities and operation with air, i.e. when the consumption rates are high and/or the oxygen concentration is low due to reduced oxygen fraction or increased water production.

**Effect on GDL Electric Properties.** The influence of compressive stress on GDL electric conductivity and the contact resistance between FFP and GDL has been analyzed in Chapter 2.3.2. A possible impact on the cell performance and local generation is given through the decrease of electric resistance in the GDL and at interfaces upon compaction of the fuel cell, as it is also confirmed in numerous publications [165, 166, 167, 168].

However, with the graphitic cell components used, the fraction of the ohmic drop stemming from the electronic conductors is only in the order of a few percent of the total overvoltages. This can be confirmed by the magnitude of the measured values of $\phi_i$, representing the voltage drop of the electric components of one electrode: $\bar{\phi}$ makes up approximately 5% of $U_{cell}$, and it changes its resistance only for ca. 20% upon a 10 percent increase of compression.

The changes in conductivity therefore result in a negligible positive influence on electric losses, which is not seen in the channel/rib partitioning of the current and in the integral cell performance from inspection of the Figures 3.12 and 3.13. A perceptible influence on the channel/rib current distribution was found in modelling studies by Meng and Wang for GDL in-plane conductivities of 300 S/m [12], which is more than two order of magnitude below the values of the materials used here.

In conclusion, the dominating effect upon cell compression for a wide range of conditions is the decrease of the effective GDL diffusivity. The above results show that integral losses stem from local GDL gas transport limitations on the channel/rib scale, as long as the GDL electric resistance holds only a small share on cell polarization. This finding furthermore shows that random deviations of the electrical GDL properties are minor sources of error as compared to random variations of GDL thickness and density, since the latter will noticeably influence local generation by changing the gas transport properties on the sub-mm scale. An influence of water management upon compression could not be observed, the measurement of local membrane resistance (no figure provided) did not yield any changes.
3.5 Cathodic Gas Composition

A quite perspicuous way to examine mass transport limitations in the sub-mm domain is the variation of the oxidant composition (oxygen fraction and inert gas), while keeping all other parameters constant. The transport pathway from the gas channel through the macroporous GDL structure is characterized by diffusion in the multi component gas mixture (water vapour and inert gas), diffusion through macro- and micro porous media (GDL, MPL and CL) and solid state diffusion through the polymer film surrounding the catalyst particles.

Numerous publications deal with the question, which of these processes contributes most significantly to the cathodic concentration losses in PEFC. On the one hand, the influence of microporous layers and thin polymer films on mass transport limitations is confirmed in models [170] and experiments [57, 171]. The authors find a distinct influence of pore size (microporous or macroporous) and the share of convective flow in the GDL on the limiting current. It is concluded that bulk diffusion in the macroporous GDL is not always the dominating limitation, in particular in the high current regime, with low flow rates and thick substrate layers.

On the other hand, EIS examinations of mass transport overvoltages show that manipulation of the bulk diffusion process has the strongest influence on cell performance [172]. This result has been predicted by modelling and validation experiments, accounting for the properties of the macroporous diffusion layer only [173, 174]. However, the authors also confirm the significance of oxygen diffusion through the microporous agglomerates of the CL near the limiting current density. In an older publication, this diffusion in the active layer is found to determine the slope of the linear region of the polarization curve [175, 176]. The authors furthermore relate the departure from linearity in the mass transport region to the decrease of oxygen diffusivity in the mixture with increasing water vapour partial pressure.

Consequently, pore diffusion according to Knudsen (see Eq. 1.28) and the thin film diffusion through the polymer (see Eq. 1.29) contribute to the overall mass transport limitations not only in the mass transport regime of a polarization curve. However, these processes are obviously not influencing the transport processes denoting the channel/rib distribution of reactant and therewith local current density, since the microporous domains of MPL and CL oppose the same diffusion pathway under the channel as under the rib. Only the bulk diffusion in the macroporous carbon paper of the GDL is therefore of interest for the consideration of mass transport losses contributing to local current generation.

In this GDL domain, the diffusivity is dominated by the interdiffusion of oxygen in the multi component gas mixture. As pointed out in Chapter 1.1.5, collisions between molecules are the constitutive limitation prior to collisions with the pore walls. However, the geometric conditions may not be neglected since the tortuous void structure in the porous medium prolonges the diffusion pathway. Effective transport is thus a function of the binary diffusion coefficients and the GDL structural properties.

The transport of oxygen through the macroporous GDL bulk can – in a simplified way – be described by Fick’s first law in the formulation given below. It has to be mentioned at that point that Fick’s law is a simplification in the case of an air fed fuel cell, because it is not properly dealing with the ternary gas mixture of oxygen, water vapour and inert gas. It provides however a clear illustration for the influence of the main parameters. For exact treatment, application
of the Stefan-Maxwell equations is required. Reactant transport through the macroporous GDL can hence be described as follows:

\[
\dot{n}_{O_2} = \frac{\varepsilon}{\tau} \cdot D_{ij} \cdot \frac{\Delta c_{O_2}}{\Delta x},
\]

whereby the ratio of the porosity \( \varepsilon \) and the tortuosity \( \tau \) defines the geometrical form factor of the porous diffusion medium, \( D_{ij} \) the diffusion coefficient of oxygen in a binary gas mixture, \( \Delta c_{O_2} \) the oxygen concentration gradient between the gas channel \( c_{chan} \) and a given location at the catalyst layer \( c_{cl} \), and \( \Delta x \) the diffusion pathway length. While the form factor is solely influenced by GDL structure and compression, the binary diffusion coefficient \( D_{ij} \) is a function of the oxygen partial pressure and the nature of the inert gas (or generally the component \( j \)). Besides this coefficient, the initial oxygen concentration in the gas channel \( c_{O_2} \) is another influence factor on oxygen transport.

According to Eq. 3.1, with the form factor (cell compression) and diffusion pathway length (channel/rib dimensions) being fixed, changes of the channel/rib current distribution at a given position stem from changes of either oxygen partial pressure and/or oxygen mobility. Therefore, the oxygen fraction and the nature of the inert gas (nitrogen or helium) were varied in order to shed more light into the complex mass transport limitations in the GDL.

### 3.5.1 Variation of Oxygen Partial Pressure

Both absolute cell performance and current density distribution are a strong function of the cathodic oxygen fraction. Figure 3.14a) shows the decrease of cell performance for operation with decreasing oxidant partial pressures (pure oxygen, 21, 10 and 5 Vol.% oxygen in nitrogen, here referred to as Nitrox). The information on the partition of generated current, averaged over channel- and rib covered areas, is given in Figure 3.14 b). This plot elucidates the dependence of local current generation on the integral current density \( j_{cell} \), and therewith on reactant consumption. Moreover, the channel/rib inhomogeneities at the same load (or consumption) differ with the oxidant fraction. The lower the concentration of oxygen in the channel, the earlier the local currents deviate from the bisector denoting homogeneous current distribution between channel and rib covered areas.

For higher oxygen fractions (e.g. Nitrox 21 and pure oxygen), a fairly homogeneous distribution of channel- and rib currents can be observed up to about one third of the limiting current before departure from linearity. This point marks the beginning of considerable mass transport limitations in the GDL bulk, which are not clearly visible in the U-I curves. Consequently, operation with very low oxygen concentrations (Nitrox 5 or 10) leads to higher current in the channel area throughout the entire load range.

In the case of pure oxygen, the development of an inhomogeneity between channel and rib in the high load range might be explained with the increasing fraction of product water, which lowers the effective \( O_2 \) diffusion in the binary gas mixture. Additionally, the distribution of membrane resistance promotes higher currents in the channel at these conditions, as shown in Section 3.1 in terms of local membrane hydration by product water. This effect is also assumed to contribute to the behaviour observed with lower oxygen fractions, which again emphasizes the complex
interrelation of charge and mass transport contribution to the sub-mm current distribution.

Figure 3.14: Oxygen dependency of a) Polarization curves and b) The channel/rib current partition (mean current over area); cell operated on \( r_h = 0.4 \), \( p_{\text{gas}} = 1.5 \text{ bar}_{\text{abs}} \), GDL compression 35\% of initial thickness, oxidants: pure \( \text{O}_2 \), 21, 10 and 5 Vol.\% \( \text{O}_2 \) in \( \text{N}_2 \); data averaged over 2 independent cells.

Hence, it can be concluded that cell operation with an oxidant containing a low oxygen fraction entails mass transport limitations in the GDL even at low cell currents. These limitations are apparently more pronounced in areas with prolonged diffusion pathways, since the rib currents stagnate at a certain load with all diluted oxidants. While the cell area under the gas channel compensates this stagnation with increased current generation, even a decrease of current production under the rib is observed.

Figure 3.16 indicates that this behaviour corresponds to the local limiting current density, since the stagnation level is increasing with the oxygen concentration. The diagram depicts the trends of the stagnation level of the rib currents as function of the oxygen fraction in the cathodic gas (left bar plot), and the integral cell current at which this local limiting current has been reached for 5, 10 and 21\% of oxygen (right bar plot). The relative limiting rib current density is increasing with the oxygen fraction from 30\% (Nitrox 5) to 60\% (Nitrox 21) of the load current. For oxygen fractions above 21\% no local limiting current is observed.

Additional information is provided in Figure 3.15, where the corresponding local current distributions \( j_i \) are shown. In the case of galvanostatic operation mode (Fig. 3.15a) the graphs represent the local generation at very different cell voltages. The current distribution for pure oxygen at the total current of 0.4 A/cm\(^2\) is rather homogeneous. In contrast, a current density of
Chapter 3. Influence of Operating Parameters

Figure 3.16: Local limiting current density in rib covered area; The rib currents stagnate at a particular current level (local limiting current density) as a function of the oxygen fraction (left side). The cell’s load current at the point of stagnation shows a stronger increasing trend with the oxygen fraction (right side).

0.4 A/cm² is close to the limiting current for Nitrox 5, showing a high peak in the channel area and rib currents close to zero. Current generation in the rib covered areas is completely suppressed when the cell is operated at the same load with fully saturated gases ($rh = 1.0$) instead of $rh = 0.4$ (as shown for the case of $H_2/air$ in Figure 3.3 a), indicating the influence of condensed water on the diffusivity in the GDL.

Conclusively, the rib currents appear to be strongly dependent on the oxygen partial pressure. The channel currents consequently need to compensate and are therefore developing local peaks up to 400 percent of the integral cell current $j_{cell}$.

Under potentiostatic operating conditions (see Fig. 3.15 b), every part of the cell produces the maximum possible current to contribute to the integral performance, and the sum of overvoltages is the same for all oxidant concentrations. Comparison of the local current distributions in potentiostatic mode therefore yields information on local limitations without the need of the compensation effect of local current enforcement. The results in diagram b) show that both, channel and rib covered areas, benefit from the increase of oxygen partial pressure, although the effect is more pronounced in the rib covered areas. This indicates that the increased diffusion pathway under the ribs – which is prolonged by a factor of 5 to 10 – is not the only parameter to limit the cell performance upon low concentrations of oxygen.

Integral cell performance is predominantly depending on the chemical activity of the oxidant (denoting the catalytic performance), which is defined by the oxygen concentration or partial pressure in the reactant gas mixture. As a consequence, lowering the oxygen concentration at a constant potential will result in a decline of current generated from all areas, even if all transport limitations from porous media could be switched off.

Interpretation of the above results is thus still difficult, since changing the oxygen fraction affects two parameters at a time: the initial oxygen concentration in the channel $c_{O_2}^{chan}$ and the binary diffusion coefficient $D_{ij}$. For more detailed insight, the change of a single parameter influencing oxygen transport in the porous structure is required, variation of the inert gas as done in the following subsection in one possibility.
3.5.2 Inert Gas Variations

To distinguish the cathodic transport losses attributed to bulk diffusion from dependencies on reactant activity, substituting the inert gas nitrogen with helium (these gas mixtures are referred to as Helox) is known to be a worthwhile method. Mass transport limitations depending on oxygen mobility can be examined, since the binary diffusion coefficient is altered without a concomitant change of partial pressure. Furthermore, mass transport limitations in the MPL and CL can be distinguished from those in the macroporous GDL bulk. Since collisions with pore walls or the solubility of oxygen in the polymer are the dominant limitations in the case of the microporous and active layer, substitution of the inert gas will not cause substantial changes here [177].

Unfortunately, this gas substitution does not only affect the mobility of oxygen but also the one of water vapour in the ternary mixture. When diluting oxygen in helium instead of nitrogen, the binary diffusion coefficient of oxygen increases by a factor of ca. 8 according to the Slattery-Bird relation (see Table 1.1). In the ternary mixture including water vapour, oxygen and helium, the mobility of water synchronously increases by a factor of about 3. Compared to the case of nitrogen as inert gas, the enhanced water mobility can induce variations of the membrane hydration and complicate the conclusions drawn from the experimental results on oxygen mobility [178]. Hence, identifying diffusion limitations by means of inert gas variations can therefore only be interpreted correctly when the influence on water mobility is considered. This is accounted for with the simultaneous measurement of local membrane resistance.

![Figure 3.17](image_url)

**Figure 3.17:** a) Integral performance and b) integral resistance for a cell operated on 5 and 21% O\textsubscript{2} in N\textsubscript{2} and He, respectively; Operation with standard conditions. The integral resistances are consistently higher for cells operated with Helox, while the performance curves are intersecting upon operation with H\textsubscript{2}/air.

Figure 3.17 shows polarization curves and integral cell resistances for operation with Helox and Nitrox containing 21 and 5% oxygen, respectively. Performance, integral current and integral resistance are compared at 0.2 and 0.8 A/cm\textsuperscript{2}. While the performance with Helox 5 is superior to Nitrox 5 over the entire load range (case (I)), Helox 21 shows lower performance in the low load range as compared to Nitrox 21 (case (II)). As illustrated in Figure 3.17 b), the integral cell resistances are consistently higher with Helox, due to the improved water diffusion to the channel in the lighter inert gas. The decrease of cell resistance for both inert gases with higher current density (0.8 A/cm\textsuperscript{2}, case (III)) is associated to the increased production of water.
Figure 3.18: Local current distributions for a) case (I): comparison of Nitrox 5 and Helox 5 at 0.2 A/cm², b) case (II): comparison of Nitrox 21 and Helox 21 at 0.2 A/cm², c) case (III): comparison of Nitrox 21 and Helox 21 at 0.8 A/cm². Higher currents in rib covered areas are consistently observed upon operation with Helox.

Figure 3.19: Local resistance distributions for a) case (I): comparison of Nitrox 5 and Helox 5 at 0.2 A/cm², b) case (II): comparison of Nitrox 21 and Helox 21 at 0.2 A/cm², c) case (III): comparison of Nitrox 21 and Helox 21 at 0.8 A/cm². Higher channel resistances are consistently observed upon operation with Helox.

In the Figures 3.18 and 3.19 the local current- and resistance distributions for the cases (I) to (III) are shown. It is seen for case (I) (Nitrox 5 compared to Helox 5 at 0.2 A/cm²) that the rib currents are about 25 % higher in the case of Helox. The increase of cell resistance seen in the integral data stems mainly from the channel area, the higher current density in rib covered areas compensates for the increased water loss with Helox. Eventually, the cell performance with Helox benefits from the improvement of mass transport, which dominates the negative effect on the membrane resistance.

In contrast, a better performance is observed with Nitrox 21 at the same current density (case (II)). Figure 3.18b) elucidates that the local current distributions are comparable for both inert gases, since the oxygen concentration is high enough – and the consumption at 0.2 A/cm² low
enough – to avoid significant transport losses under the rib. Consequently, the increase of membrane resistance in operation with Helox is dominating the cell performance. Its distributions (lower graphs) show equal shapes for Helox and Nitrox, but feature a noticeable offset to higher resistances in the case of helium as the inert gas.

Case (III) finally illustrates the situation at 0.8 A/cm² with the Nitrox/Helox 21 oxidants. In contrast to case (II), the high consumption of oxygen now induces significant mass transport limitations in the rib covered areas, and the resistance distribution is now controlled by local hydration from product water, as described in Section 3.1. The higher rib currents in the case of Helox coincide with lower local membrane resistance, while a high channel current in the case of Nitrox apparently improves the membrane hydration at this position. The average resistances are comparable for Nitrox and Helox, indicating that again the improvement of mass transport dominates the overvoltages, leading to a better cell performance in the case of Helox.

Figure 3.20: Influence of inert gas on channel/rib current distribution, average currents from channel and rib area as function of oxygen fraction in He and N₂: a) Cell voltage 700 mV, b) 600 mV, c) 500 mV, d) 400 mV, e) 300 mV; Standard conditions, data averaged over 3 independent cells. The rib currents remain in the same range throughout the potential variation, they show also the highest changes regarding the variation of inert gas.
For a more comprehensive picture of the inert gas effect, Figure 3.20 compares the currents averaged over channel and rib for the entire range of oxygen fractions in nitrogen and helium for potentiostatic operation between 700 and 300 mV. The most noticeable feature is that current generation in the rib areas is at a similar level for all voltages, indicating the existence of a local limiting current which can not be overcome at these positions. When decreasing the cell potential, the additional current is generated predominantly in the channel area.

For oxygen fractions lower than 50 %, the relative difference of the local currents between Nitrox and Helox is considerably bigger under the rib areas than under the channel. Except for the low load case of 0.7 V shown in diagram a), the rib currents are consistently higher upon operation with Helox. This data clearly illustrates the loss due to gas diffusion in the porous structure of the GDL, although the low gains in the channel area indicate again that oxygen mobility is not the only parameter here.

The above findings are elucidated in Figure 3.21 a), where the relative performance gain of rib currents with helium is plotted for all cell voltages. The gain with using Helox instead of Nitrox is thereby observed to be biggest at the lowest oxygen fractions (between 80 and 190 % with 5 % O₂), but not at the lowest potentials. It is seen from Figure 3.21 b) that – independent of the oxygen concentration – the highest improvement with helium is achieved at a cell voltage of 0.5 V, while the helium gain is comparably small for low or high potentials.

An explanation for this effect in the case of low load currents (0.6 and 0.7 V) is assumed to be found in the lower reactant consumption rates at these potentials as compared to 0.5 V. Therefore, smaller mass transport limitations are experienced, which could be improved with Helox. The negative effect of helium on the membrane hydration is less probable to serve as an explanation, since it applies predominantly to the channel area.

The reason for the observed decrease of helium gain for potentials higher than 0.5 V is however speculation. A possible explanation could be that (in agreement with the literature in [170] and [171]) limitations due to pore- or thin film diffusion in the microporous layers become dominant at high load conditions, which can not be improved by increasing the oxygen mobility in the gas mixture.
Additionally, water clogging in the rib areas becomes more likely at low potentials, resulting in the loss of whole pores. An attenuation of the helium performance gain can then be related to the significance of mass transport limitations, which can not be compensated with increasing the oxygen mobility. In the channel area, however, an interesting effect of Helox on water management is observed for high oxygen fractions in Figures 3.20(c), (d) and (e). For oxygen fractions of around 80% and high channel currents near or above 2.0 A/cm², Helox shows a considerable higher performance compared to Nitrox and pure oxygen. This is presumably due to improvements of water evacuation. As a consequence, the integral performance of a cell is highest when 10 to 20% of oxygen is replaced by helium.

Concludingly, the transport losses in the GDL are considerably augmented with decreasing oxygen partial pressure. While with pure oxygen a relatively homogeneous current distribution is observed, the rib currents are considerably lower compared to the channel with low oxygen partial pressures. It is learned that mass transport overvoltages exist over the entire load range in particular for diluted oxidants and not only in the mass transport regime of a polarization curve. The comparison of operation with different inert gases shows that the helium gain – and therefore the transport loss in nitrogen – is substantial in rib covered areas. However, the investigation of the single factors contributing to the total mass transport overvoltage remains difficult, even with data of current distribution and local ionic resistance available at the same time.
3.6 Summary Chapter 3

In this chapter, the influence of relevant operating parameters on the channel/rib current distribution was examined. The membrane hydration, the reactant flow rate, the gas pressure, the cell compression and the oxidant composition was varied and the influence on local current and ionic resistance investigated. The following points can be concluded from the results:

- The distribution of water and oxidant are the substantial influence factors on local current distribution. Thereby strong bipartite interrelations exist between local membrane resistance and local current production.

- 'Resistance controlled' (maximum of current produced in the rib covered areas) and 'mass transport controlled' (maximum of current in the channel) current distributions can not simply be distinguished by their shapes. For a wide range of conditions, ionic resistance is also the significant regime for a distribution with the maximum of current being produced in the channel.

- Upon variation of humidity, the membrane resistance changes predominantly in the channel. The resistance under the rib is more depending on hydration by product water, and therewith on the cell current. Therefore, the distribution of reactant on the channel/rib scale couples back to the membrane resistance.

- Mass transport limitations occur throughout a wide load range, also in the quasi-linear regime of a polarization curve. They are observed under the ribs while they are not visible in the integral polarization behaviour.

- The manipulation of oxygen mobility shows that interdiffusion through the macroporous GDL bulk causes substantial inhomogeneities on the sub-mm scale. However, it is not the only factor causing non-uniform partitioning of channel and rib currents.

- The effect of compression is amplifying the mass transport limitations in the rib areas. Already small changes of compression (10%) can modify rib currents by a factor of 2.

- Variation of the reactant flow rate confirms that the chosen standard conditions represent a state of differential operation.

- Modifying the reactant pressure has a very strong influence on cell performance, but induces only marginal changes in the channel/rib current partition.

Essentially one can say that the reactant humidification and the local oxygen concentration at the catalytic layer are the most prominent influence factors for local current generation. In general, changing the humidity affects the membrane resistance in the channel area, and mass transport limitations hamper the current generation predominantly under the rib. These findings are exploited for the structural optimization on the channel/rib scale in the following chapter.
Chapter 4

Variation of Flow Field Design

"La technologie évolue toujours du primitif au compliqué avant de devenir finalement simple.”

(Technology always evolves from the primitive to the complicated to the simple.)

Antoine de Saint Exupery, 1939

This chapter discusses the impact of cell design on the local current generation and the integral performance by means of altering the geometrical flow field structure. As pointed out in Chapter 1.2.4, flow field design in PEFC is characterized by the layout of the flow channel across the active area (single cell scale) and the dimensions of channels and ribs at the sub-millimeter level. The variation of channel and rib width, respectively, yields information on the influence of reactant diffusion pathways and water management on the local current generation and integral cell performance. The deeper understanding of the processes on the sub-mm scale gained from these studies are eventually the base for the optimization of the flow field layout at the single cell level.

This optimization procedure in fuel cells of technical size emanates from the fact that local conditions differ along the flow channel, which results in inhomogeneous current distributions such as illustrated in Figure 1.16. Aiming for loss reduction, a homogenization of the along-the-channel current gradients could be possible by means of manipulating charge and mass transport processes on the channel/rib scale. Hence, different channel dimensions for positions near the gas inlet and positions near the gas outlet are proposed. This so called ‘adaptive’ flow field layout aims to provide the best possible conditions for every position in the cell. The design optimization process thereby has to account for the conclusions drawn from Chapter 3.
4.1 Variations of the Channel-Rib Ratio

The dimensions of flow field channels and ribs are a crucial impact factor for cell performance, which is founded on their influence on mass and charge transport processes on the sub-mm scale. As can be figured from the conclusions of the last chapter, variation of the channel width will influence the electrode’s water management and therewith the local and integral membrane resistance. Altering the width of the rib will on the other hand influence mass transport limitations at positions remote from the channel.

Consequently, the experiments described in the following subsections aim to clarify the impact of channel/rib dimensioning on the integral and local cell performance, as well as on the channel/rib current partitioning. For this purpose a set of 12 flow field plates was manufactured (see Figure 4.1), covering technical relevant channel and rib widths from 0.5 to 3.0 mm, respectively. In the following, a particular design is denoted as the combination of channel width (C) and rib width (R). The standard geometry of 2.0/2.0 mm is thus referred to as C2R2, and a flow field with 1.0 mm channel and 0.5 mm rib is denoted as C1R05.

<table>
<thead>
<tr>
<th>rib width (R)</th>
<th>channel width (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.0 mm</td>
</tr>
<tr>
<td>3.0 mm</td>
<td></td>
</tr>
<tr>
<td>2.0 mm</td>
<td></td>
</tr>
<tr>
<td>1.0 mm</td>
<td></td>
</tr>
<tr>
<td>0.5 mm</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.1: Variation of the channel/rib dimensions for values between 0.5 and 3.0 mm, respectively. The combinations are denoted after the channel width (C) and rib width (R) in millimeter (without comma). The array of dashes above the channel structure marks the position of the 30 probe wires. The respective rib ratios are the numbers given inside the sketches of the flow field plates.

As a characteristic parameter the ratio of rib in a repetitive unit (referred to as ‘rib ratio’ \( r_{rib} \)) is defined for evaluation of the different designs, ranging from 0.2 to 0.8 for the 12 flow fields in the above Figure. The rib ratio is defined as:

\[
r_{rib} = \frac{w_{rib}}{w_{rib} + w_{chan}} = 1 - r_{chan}, \tag{4.1}
\]

wherein \( w_{chan} \) and \( w_{rib} \) denote the respective widths and \( r_{chan} \) represents the analogue of \( r_{rib} \), the ‘channel ratio’. Thus, the flow fields can be classified by their geometrical rib coverage rather than by absolute values. For example, the geometries C1R1 and C2R2 have both a rib ratio of 0.5, whereby a possible impact of the absolute channel and rib widths on cell performance is not accounted for with this classification.
4.1. Variations of the Channel-Rib Ratio

4.1.1 Influence of Rib Ratio on Cell Performance

Although the flow field layout at the single cell level is a wide field of interest in the PEFC modelling community [179, 89, 147], only few experimental studies are known from the literature concerning the impact of channel dimensions and channel spacing on cell performance.

On the one hand, Yoon et al. observed an increase of cell performance upon reducing the channel spacing at constant channel width [105]. This improvement of performance for lower rib ratios holds in particular true in the high load range, while the polarization curves were found practically identical at low and medium cell currents.

On the other hand, Scholta et al. provide a more comprehensive analysis [106], essentially showing the opposite behaviour. The authors alter the channel and rib width, respectively, and find an optimum between 0.7 and 1.0 mm for both measures. These values can be considered the technical interesting range, since for wider dimensions the prolonged diffusion- and electron pathways become significant limitations while intricate machining procedures, high pressure drop and possible water clogging complicate cell operation with smaller dimensions. Inside the optimum range, however, a positive correlation between rib coverage and performance is found. The HFR measurement of integral cell resistance shows that improved membrane water management is the reason for the observed behaviour with a higher rib ratio.

The findings of Scholta – and partly those of Yoon – could be confirmed in experiments carried out with the different flow field geometries as introduced in Figure 4.1. The performance of each flow field geometry under standard conditions is compared in Figure 4.2 at a potentiostatic cell voltage of 0.6 V for operation with pure O₂, air (21 % O₂ in N₂) and depleted air (5 % O₂ in N₂).

The most perspicuous feature to recognize is the varying correlation of performance and rib ratio with different oxidants. While a positive trend is observed upon increasing the rib ratio with pure oxygen, the improvement is alleviated with the use of air and completely suppressed with 5 % oxygen in nitrogen. This also elucidates the essence of the findings in the literature: without dominant mass transport limitations the performance is increasing with the rib ratio. A
clear decrease of performance with the rib coverage – as expected accounting for mass transport limitations – can however not be observed with any oxidant composition at 600 mV.

Figure 4.2 furthermore depicts that geometries with the same rib ratio – e.g. C2R2 and C1R1 (0.50), or C1R2 and C05R1 (0.66) – do not show the same performance. This could be due to the influence of diffusion pathway as a function of absolute channel/rib dimensions, or effects of compressive stress distribution. The performance is generally biggest for high rib ratios with small absolute dimensions. Conclusively, the behaviour of cell performance as a function of the rib ratio is depending on the absolute values of channel and rib width as well as on the operating conditions.

To illustrate the dependence of cell performance on the load current $j_{cell}$, Figure 4.3 provides the polarization curves for the 5 chosen geometries, which are highlighted in Figure 4.2. Starting from the standard geometry C2R2 with a rib ratio of 0.50, the channel width is reduced to 1.0 mm (C1R2, $r_{rib} = 0.66$) and to 0.5 mm (C05R2, $r_{rib} = 0.80$) while keeping the rib width constant. In the opposite direction, the channel width is kept constant and the rib is narrowed to 1.0 mm (C2R1, $r_{rib} = 0.33$) and 0.5 mm (C2R05, $r_{rib} = 0.20$). The cell behaviour is compared for the 3 oxidant compositions pure O$_2$ (a), 21% O$_2$ (b) and 5% O$_2$ (c) in N$_2$, respectively.

Inspection of the graphs brings to light that also the findings of YOON et al. hold true. Obviously, the correlation of cell performance and rib ratio is a strong function of oxygen concentration and consumption, as the improvement of performance with wide ribs is less and less pronounced with low oxidant O$_2$ fractions and high currents. Essentially, the correlation reverses at high load currents and now the cells with low rib ratios show better performance and higher limiting current densities.

This effect is clearly due to mass transport limitations under the rib covered areas, since it is more pronounced in cells operated with low oxygen fractions (see Figures 4.3b) and c). Hereby the intersection of the graphs is shifted to higher potentials and lower currents, the latter being a measure for reactant consumption. This behaviour of cell performance as a function of oxygen consumption (load and oxygen fraction) is further elucidated in Figure 4.4, where the performance curves for the single geometries are plotted versus the cell voltage in potentiostatic mode.

In the cases of pure oxygen or air as the oxidant (Figures 4.4a) and b) it can be seen that the maximum power point (MPP) of the curves is shifting towards high potentials, which is an effect of increasing mass transport limitations under the ribs. While this holds true only for rib ratios higher than 0.5 in the case of H$_2$/O$_2$ (diagram a), all geometries show this trend in the case of H$_2$/air (diagram b). In general, the cell voltage on the x-axis, at which the performance with a particular geometry passes through the MPP, can be seen as the point from where on the total overvoltage of the cell is dominated by mass transport. A good example for the negative correlation of cell performance and rib ratio is given in diagram c) (5% O$_2$ in N$_2$). Here, the cell performance for the cell with $r_{rib} = 0.8$ is dominated by mass transport limitations throughout a wide load range. This statement is based on the observation that an improvement of performance with the use of low rib ratios is already seen already at ca. 670 mV.

These important results prove that the influence of rib ratio on performance is quantitatively changing with the reactant consumption ($j_{cell}$) and the concentration in the gas channel ($c_{O_2}$). In the technical reasonable span of channel and rib widths ranging from 0.5 to 2.0 mm, respectively, a positive correlation of rib ratio and cell performance is observed above 600 mV for cathodic
4.1. Variations of the Channel-Rib Ratio

Figure 4.3: Polarization curves for different rib ratios (0.2 to 0.8), the corresponding geometries are highlighted in Figure 4.2, standard conditions in operation with a) $\text{H}_2/\text{O}_2$, b) $\text{H}_2/\text{air}$ (21% $\text{O}_2$ in $\text{N}_2$), c) $\text{H}_2$/depleted air (5% $\text{O}_2$ in $\text{N}_2$). Better performance is achieved by higher rib ratios for low and moderate load currents and high oxygen partial pressures, lower rib ratios on the other hand facilitate higher limiting current densities.

Figure 4.4: Performance curves for different rib ratios (0.2 to 0.8) as a function of the potentiostatic cell voltage (800 to 400 mV), standard conditions in operation with a) $\text{H}_2/\text{O}_2$, b) $\text{H}_2/\text{air}$ (21% $\text{O}_2$ in $\text{N}_2$), c) $\text{H}_2$/depleted air (5% $\text{O}_2$ in $\text{N}_2$). The maximum of the performance curves is shifted to lower potentials for cells with low rib ratios: less mass transport limitations are accounted for geometries with wide channels and/or narrow ribs.

oxygen fractions higher than 5%. This behaviour is believed to be due to water management and/or compression effects, continuative examinations regarding this topic are to be presented in the next subsections. For lower cell voltages or oxygen fractions, the performance is found to be highest with wide channels. This emphasizes the role of mass transport limitations in the rib covered areas, which are the dominating losses in this case.
4.1.2 Influence of Rib Ratio on Local Current Generation

To confirm the influence of mass transport limitations on cell performance upon rib ratio variation, the local current distribution is measured for the 5 chosen geometries from Figures 4.3 and 4.4 with the standard operating conditions, the results are thus valid for a humidity of \( rh = 0.4 \). Thereby it is of interest to compare the situation at 600 mV (where high rib ratios show best performance) to the situation at 400 mV where low rib ratios accompany a higher performance.

![Diagram](image)

**Figure 4.5:** Local current distributions for different flow field geometries (rib ratios 0.2 to 0.8), the corresponding geometries are highlighted in Figure 4.2. The diagrams on the left side (a), (c) and (e) display the situation at 600 mV, the diagrams on the right side (b), (d) and (f) the situation at 400 mV. Upper row (a) and (b): operation with \( \text{H}_2/\text{O}_2 \); middle row (c) and (d): \( \text{H}_2/\text{air} \) (21% \( \text{O}_2 \) in \( \text{N}_2 \)); lower row (e) and (f): \( \text{H}_2/\text{depleted air} \) (5% \( \text{O}_2 \) in \( \text{N}_2 \)). Standard conditions (see Table 3.1); The greyscale bars mark the position of the rib.
Figure 4.5 displays the local current distributions obtained for potentiostatic operation with H$_2$/O$_2$ for 600 (a) and 400 mV (b), as well as for operation with H$_2$/air (in (c) and (d)) and H$_2$/depleted air (in (e) and (f)). Comparison of the different flow field geometries reveals that – independent of cell voltage and oxidant composition – the current distribution is distinctly more homogeneous for cells with high rib ratios.

This behaviour is best seen in diagram (a) for the case of 600 mV with pure oxygen: according to the order of best cell performance, the cell with a channel width of 0.5 mm and 2.0 mm ribs ($r_{rib} = 0.8$) exhibits the most homogeneous distribution and the highest current production at this voltage, despite the high rate of rib coverage. In contrast, the cell with the smallest rib coverage ($r_{rib} = 0.2$) shows the worst performance and the highest inhomogeneity of local current distribution, with the rib currents being significantly lower compared to the channel. In the case of pure oxygen, mass transport limitations under the ribs are unlikely to be dominant at 600 mV, the reason for this behaviour is therefore assumed to be a charge transport limitation.

When the cell current is increased (case 400 mV), a different behaviour of the flow field geometries can be observed in diagram (b). While in the cells with high rib ratios (0.5 to 0.8) both channel and rib currents are raised, predominantly the channel current contributes to the load increase in cells with low rib ratios (0.2 and 0.33). This anti-intuitive behaviour again indicates that a process other than mass transport is dominating the channel/rib current distribution here.

When lowering the oxygen fraction to 21, and eventually 5% of O$_2$ in N$_2$ (diagrams (c), (d), (e) and (f)), the level of the rib currents is decreasing faster than the level of current generated under the channel, which goes along with the observations in Chapter 3.5.1. However, distinct peaks in the channel area are observed for cells with low rib coverage. High rib ratios, in contrast, obviously facilitate a more uniform current distribution even in cases with high consumption and low oxygen concentration (diagram (f)), where the performance with this geometries is worst compared to all others.

Concludingly, cells with high rib ratios behave more like a single rib covered area, the current generation in the channel does not significantly differ from the rest of the active area. In contrast, current generation in cells with low rib ratios is dominated by the channel area, the rib currents are distinctly lowered even in the case with no dominant mass transport limitations.

This shows that the diffusion pathway is not the limiting parameter on cell performance for the standard operating conditions, which represent a technical interesting range. Figure 4.6 clarifies this finding by comparing the averaged current generation from channel and rib covered areas for the cases illustrated in Figure 4.5. Diagram (a) thereby shows the situation at 600 mV, which resembles the integral behaviour shown in Figure 4.2. It is seen that – independent of the oxygen concentration – the channel/rib current partition becomes more and more uniform towards higher rib ratios, whereas in particular the rib currents are rising with increasing rib width and decreasing channel width.

Figure 4.6 b) shows that this unexpected effect holds even true for higher load currents in most cases. Given that the decrease of integral performance with higher rib ratios in the case 400 mV and 21 or 5% oxygen is attributed to reactant starvation in the rib areas, there must be an even more dominant limitation hampering the local current generation under the flow field shoulder in the case of small ribs. This statement relies on the observation that (except for $r_{rib} = 0.8$) the rib currents are rising when the rib width is increased, also with low oxygen fractions. In
contrast, the current generation in the channel shows a decreasing trend with higher rib ratios, which is eventually the main reason for the decline of cell performance. However, also in these cases high rib ratios foster a more uniform current distribution without any qualitative evidence of starvation exclusively in the rib covered area.

A possible reason for this could be the compression behaviour of the GDL: the structural mechanics calculations are able to show for small channels – as in the case of C05R2 with a rib ratio of 0.8 – that the GDL is also strongly compressed in the middle of the channel (no illustration provided). Compared to e.g. the standard geometry C2R2, the distribution of compressive stress is thus much more uniform across channel and rib and the tortuosity is in average higher, also in the channel area.

However, lowered electric drop in the GDL with wide ribs (plus lower contact resistance) can not explain the improvement of performance. Recalling the statements of SCHOLTA et al. in [106], the rate of rib coverage furthermore impacts the ionic resistance by means of its impact on water management. Therefore, the superior performance of cells with high rib ratios for a wide range of conditions could be a consequence of better water management, while the decline of performance in cases with low oxygen partial pressures and high reactant consumption might be due to the in average lower porosity and higher tortuosity in the diffusion medium.

An improvement of the membrane water management with wide ribs can easily be verified with the measurement of local membrane resistance for different flow field geometries. Since a more distinct effect is expected for dry conditions, these experiments were carried out at a reduced reactant humidity of \( rh = 0.1 \). Based on the standard geometry C2R2, Figure 4.7 compares the local current and resistance distributions at potentiostatic operation (600 mV) with \( \text{H}_2/\text{air} \) for the flow field variations with reduced rib width at a constant channel of 2.0 mm (C2R1 with \( r_{\text{rib}} = 0.33 \) and C2R05 with \( r_{\text{rib}} = 0.20 \), diagrams (a) and (c)), to the flow fields with reduced channel width at a constant rib of 2.0 mm (C1R2 with \( r_{\text{rib}} = 0.66 \) and C05R2 with \( r_{\text{rib}} = 0.80 \), diagrams (b) and (d)).
4.1. Variations of the Channel-Rib Ratio

In general, the same pattern of the current distributions (Figures 4.7 a) and b)) is observed for the lowered humidity as compared to the standard conditions ($rh = 0.4$) in Figure 4.5: low rib ratios entail comparably low rib currents and the maximum of current generation is shifted to the channel, while high rib ratios facilitate a more or less uniform current distribution at the same operating conditions. Furthermore, the cell performance is again higher in cells with wide ribs for these conditions, as the given values of integral current density indicate.

Inspection of the resistance distributions in Figures 4.7 c) and d) clarifies that indeed membrane resistance is the substantial parameter denoting the cell performance. The local resistance in cells with low rib ratios (diagram c) shows high peaks under the small ribs, ranging up to more than $1.0\,\Omega\,cm^2$ (C2R1) and $2.3\,\Omega\,cm^2$ (C2R05). Furthermore, also the channel resistances are found to be at a rather high level. In contrast, the resistance distributions of the cells with higher rib ratios (diagram d) are in general uniform an their integral values are significantly lower.

Although it is now possible to explain the low rib currents found in cells with small ribs with the high local membrane resistance, the reason for this behaviour remains unclear yet. Heat transport and temperature effects on the channel/rib scale as discussed in [113] could offer a possible explanation, examinations here are however not possible with the current measurement setup. The low resistance in cells with small channels and wide ribs can on the other hand straightforwardly be explained with slower water removal to the channel, evading the drying of the membrane.

Figure 4.7: Comparison of cells with reduced rib widths and reduced channel widths, based on the standard geometry C2R2; a) Current distributions for C2R1 and C2R05, b) Current distributions for C1R2 and C05R2; c) Resistance distributions for C1R2 and C05R2, d) Resistance distributions for C1R2 and C05R2. Operation with H$_2$/air at 600 mV, standard conditions with $rh = 0.1$ for both reactants. Considerably lower resistances are found in the case of high rib ratios.
4.2 Adapted Flow Field Layouts

The findings from the last section show that relevant operating conditions such as reactant humidity and oxygen partial pressure influence the cell behaviour comparing different flow field geometries. This leads to the idea that the flow field design – meaning channel/rib dimensions on the sub-mm scale and the channel layout at the single cell level – might be adapted to the operating conditions of the cell.

One possibility is to tailor a specific channel structure to the operating conditions, at which the fuel cell will be operated most of the time. This requires predominantly stationary application with rare dynamic changes of the operating point, since changing the geometry during operation is impossible at this time. However, operating parameters are changing not only with time, they vary also along the channel of a single cell as discussed in Chapter 1.3.2. Thus, another option is to adapt the channel/rib dimensions to the respective conditions between in- and outlet of a technical fuel cell, i.e. the flow field structure changes its dimensions along the gas channel.

Although this concept seems quite simple, no descriptions of experiments and only very few theoretical considerations are found in the literature up to date, whereas these publications deal only with variation of the channel height. For example, LIU et al. propose a tapered channel with a constant decrease of channel height towards the outlet [180], while WENG et al. alter the channel depth in steps or ‘contractions’ [181]. Eventually, KUO et al. introduce protuberances in the channel wall opposite of the diffusion medium, inducing perturbations in the reactant gas flow [182, 183].

All of these approaches aim to change only the convective behaviour of the gas flow in the channel by means of local alterations of the flow speed. The cell performance might thereby improve through better gas transport in the porous medium and increased liquid removal rates. The influence of rib width on gas transport and the impact of channel width on the membrane water management is not accounted for in any of these publications. The following subsections however show that it is worthwhile to adapt the channel and rib width along the flow path, whereby the channel height is kept constant.

4.2.1 Relating Sub-mm Current Generation to Along-The-Channel Gradients

As explained in Chapter 1.3.2, gradients of operating parameters in the along-the-channel direction (z-direction) are characterized by the depletion of oxygen and the enrichment of water towards the outlet. It has been alluded that losses in the inlet region stem from the deficient saturation of the electrolyte, whereby this situation is aggravated by excessive flow rates. In contrast, the dominant losses in the outlet region of the cell are mass transport limitations. The depleted cathodic reactant becomes enriched with product water near the outlet and thus only carries a fraction of the initial oxygen concentration. Additionally, flooding of the transport medium or even channel clogging is possible with a high level of humidification or load current.

For measuring the local current and resistance distributions across channel and rib, which accompany these different situations, relevant ‘inlet-’ and ‘outlet conditions’ have to be defined for operation of the specialized test cell. This way it is possible to scrutinize and confirm the origin of losses near the cell inlet and outlet. In this case, the specialized test cell literally serves as a
differential cut-out of several channel/rib units from the active area in a cell of technical size, allowing for the reproduction of along-the-channel gradients with sub-millimeter resolution. The conditions at the inlet are hereby characterized by a low reactant humidity and the use of non-depleted air as oxidant. This resembles an air fed fuel cell with low inlet humidity, as it is a realistic combination for operating mobile PEFC systems. The assumption of a cathodic stoichiometry of $\lambda_{\text{cath}} = 1.3$ leads to the depletion of oxygen concentration to ca. 10% in the middle of the channel and 5% at the cell outlet, whereby the relative humidities are increased to 0.4 and 1.0 for both gases at the respective positions ($T_{\text{cell}} = 70°C$, standard condition).

The values for inlet, middle and outlet conditions are recapitulated in Table 4.1, they are – in particular the assumption of saturated outlet gas – sufficiently realistic estimations concerning the operation of technical PEFCs.

<table>
<thead>
<tr>
<th>Position</th>
<th>Oxygen Fraction [Vol.%]</th>
<th>Rel. Humidity [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet</td>
<td>21</td>
<td>0.1</td>
</tr>
<tr>
<td>Middle</td>
<td>10</td>
<td>0.4</td>
</tr>
<tr>
<td>Outlet</td>
<td>5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Table 4.1:* Assumed conditions for the inlet, middle and outlet position of a channel in a technical size PEFC. All other operating parameters are maintained at standard values (see Table 3.1).

The diagrams in Figure 4.8 illustrate the channel/rib resolved behaviour of cells with different flow field structures when they are operated under inlet, middle or outlet conditions. For this figure only the sequence with reduced channel size is considered for the sake of lucidity, including the geometries C2R2, C1R2 and C05R2 with rib ratios of 0.50, 0.66 and 0.80. The local current (upper diagrams) and resistance distributions (lower diagrams) for the inlet condition are plotted on the left side in diagrams (a) and (d), the middle condition is considered in diagrams (b) and (e) and the outlet condition is accounted for in the right two diagrams (c) and (f).

It is seen that the cell with the highest rib ratio (0.8) shows superior performance under inlet conditions (a), which is obviously a consequence of the low ionic resistance with this geometry (d). Independently of the position across channel and rib, the membrane resistance is rising with the factor of three upon increasing the channel width from 0.5 to 2.0 mm, which is the crucial factor determining the current generation of the cell.

At the condition in the middle of the channel the oxygen fraction is reduced from 21 to 10%. The consequence is the shifting of the current production to the channel areas in the case of all three geometries investigated. The increased membrane hydration by product water in the channel area is visible by the development of local minima in the resistance distributions (e). Thereby the resistances in the channel are noticeably decreased for all geometries, while the respective rib resistances change only slightly. Still, the order of rib ratio is going along with the order of best cell performance, which is coupled to the level of membrane resistance.

With respect to the outlet condition, it is known from the considerations in the previous section that designs with high rib ratios can not compete any more with geometries having a wider channel, when an oxidant with an $O_2$ fraction of around 5% is fed. As it is seen in diagram (c), this observation holds true also for saturated reactants. Although the resistance of the
cell with the rib ratio of 0.8 is still the lowest and homogeneous across channel and rib, the current production is hampered by severe mass transport limitations now. As a consequence, its channel/rib current distribution is now comparable to the one with the rib ratio of 0.5. It is seen that the geometry C1R2 with $r_{rib} = 0.66$ shows a slightly superior performance in this case, whereby mainly the wider channel compared to C05R2 is responsible for the improvement (c). The lower rib currents – despite identical rib widths – can be explained with the higher membrane resistance under the ribs, which is seen in diagram (f). This negative effect of resistance is also the reason why the geometry with the widest channel, C2R2, shows worse performance as compared to C1R2.

**Figure 4.8:** Comparison of local current and resistance distributions for conditions between inlet and outlet of technical sized PEFC, potentiostatic operation at 600 mV. Current distributions for cells with reduced channel width (C2R2: $r_{rib} = 0.50$, C1R2: $r_{rib} = 0.66$, C05R2: $r_{rib} = 0.80$) for a) inlet conditions ($rh = 0.1$, $c_{O_2} = 21\%$), b) middle conditions ($rh = 0.4$, $c_{O_2} = 10\%$) and c) outlet conditions ($rh = 1.0$, $c_{O_2} = 5\%$). Resistance distributions for the same cells are given in d) for inlet conditions, e) middle conditions and f) outlet conditions; all other parameters are standard values (see Table 3.1).

Concludingly, the channel/rib partition of current underlies quantitatively and qualitatively significant changes between the inlet and the outlet regions of a PEFC. While the membrane resistance in geometries with small channels remains virtually unchanged and homogeneous throughout a humidity variation from $rh = 0.1$ to 1.0, the resistance distribution of designs with wide channels develops minima in the channel, which decrease the integral resistance level. This is a consequence of increased external humidification and the shifted distribution of product water upon a simultaneous reduction of the oxygen partial pressure. Thus, one can say that in general designs with low rib ratios are now not limited by resistance in the channel any more, but entail lower mass transport overvoltages. Consequently, they show superior performance compared to high rates of rib coverage at low oxygen fractions and saturated conditions.
This systematic behaviour of the integral values for current and resistance is summarized in Figure 4.9 a) and b), respectively. Diagram (b) elucidates that the positive effect of wide ribs on cell resistance can be observed in the inlet as well as in the outlet region of a technical fuel cell. However, the resistance is not always the dominating factor, as the trends in diagram (a) show. In the case of the outlet condition, the lower resistance in cells with small channels cannot compensate for the performance loss due to the low oxygen fraction, the cell performance is hence not rising with increasing rib ratio.

The Figure furthermore shows in (a) that high oxygen concentrations accompany higher cell performance, even though the cell resistance (b) is also raised. Considering i.e. the case of C2R2 \((r_{rib} = 0.5)\) at inlet condition, the performance is superior to the one at middle or outlet conditions by a factor of 1.5, despite the high cell resistance. However, the performance can further be improved by more than a factor of two when the channel width is reduced to 0.5 mm, which is a consequence of decreasing the high level of resistance.

The measurements therewith provide valuable information about the impact of a limitation: it can be read from the results that the performance gain from decreasing the membrane resistance (achieved by flow field design) is bigger than the performance gain from increasing the oxygen partial pressure (5 to 21 %) with the operating conditions used here. The dominating limitation is thus identified as the membrane resistance, which can be significantly improved by reducing the channel width. The only case not following this pattern is the outlet condition with very low oxygen concentrations, where a wider channel is favourable. This leads to the conclusion that it is more worthwhile to adapt the channel/rib dimensions to the respective conditions along the flow channel instead of making efforts to control the depletion of reactant and the enrichment of water along the channel.
4.2.2 Development of an Adapted Design

The intended adaption needs to be based on the knowledge gained from the previous chapters. Being aware that the membrane resistance in the channel dominates the cell resistance – which is again dominating the cell performance in most cases – and being aware that membrane drying can be avoided by reducing the channel width, first concepts of an optimal channel geometry can be developed. It has also been shown that the positive effect of wide ribs and small channels is compensated by mass transport limitations in the case of low oxygen fractions and saturated gases (which applies in the cell outlet region), disclosing the necessity for wider channels there. However, there are boundaries with respect to the reduction of channel width and increasing the rib width. As Figure 4.10 illustrates, the relevant limitations are the flow field’s pressure drop for very small channels (a), and the concentration at the catalytic layer in positions remote from the channel in cells with very wide ribs (b).

Figure 4.10 a) shows the behaviour of pressure drop between the channel in- and outlet $\Delta p$ as a function of the channel width $w_{chan}$. The data is obtained from a calculation involving air in laminar flow of 1.0 l/min in a straight channel of the length $l_{chan} = 400$ mm. The algorithm follows the treatment applied for HAGEN-POISSEUILLE flows [184], whereby the properties of air were implemented at $70^\circ$C and 2.0 bar$_{abs}$. It is seen that the pressure drop is a strong exponential function upon the decrease of the channel width. The channel cross section is accounted for by conducting the calculation with different channel heights $h_{chan}$ from 0.3 to 2.0 mm.

In fuel cells for technical applications a pressure drop higher than 500 mbar between in- and outlet is typically not viable in practice, values above 300 mbar are considered problematic. Consequently, a channel width of 0.5 mm is reasonable as long as the channel is higher than 0.2 mm. In general, minimum channel widths down to 0.3 mm are feasible with typical channel heights between 0.5 and 1.0 mm. Below this value, the pressure drop is outside the common parameter range for operation of PEFC and can induce disturbance of cell performance. On the other hand, a too wide channel (in the order of a centimeter) can accompany limitations due to prolonged electron pathways. Furthermore, to prevent delamination, a good bonding of the

![Graph showing pressure drop and oxygen fraction](image-url)

**Figure 4.10:** Limitations encountered with the use of too wide ribs and too small channels; a) Flow field pressure drop ($\Delta p$) as function of the channel width $w_{chan}$ for different channel heights $h_{chan}$; channel widths below 0.3 mm should be avoided. b) Oxygen fraction at the catalytic layer under the middle of the rib as function of the rib width $w_{rib}$ for different current densities $j_{cell}$; for the sake of eluding reactant starvation in the rib areas, rib widths above 3.0 mm should be avoided.
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electrode to the membrane is necessary then.

The dominating limitation when increasing the rib width is the reactant transport pathway under the rib. Figure 4.10 b) therefore provides information on the oxygen fraction at the catalytic layer after experiencing different diffusion pathways. Accounting for anisotropic diffusion in the transport medium (through plane tortuosity $\tau_{tp} = 1.6$, in plane $\tau_{ip} = 3.0$, [162]), the oxygen concentration at the active layer for a given initial concentration (e.g. air) is a function of the consumption ($j_{cell}$) and the in-plane/through-plane diffusion pathway length ($w_{rib}$ and $d_{GDL}$). Thereby the active layer concentration $c_{cl}$ in the middle of the rib approaches the value of zero if the rib is too wide or the current too high.

A simple calculation following Fick’s law with anisotropic diffusivity in the porous medium allows for estimating the oxygen fraction at the catalytic layer for specific cell currents, whereby the maximum rib width $w_{rib}^{max}$ for zero oxygen concentration can be identified. Although this approach provides only a rough estimation of the situation in the diffusion medium – i.e water vapour is neglected – it can be deduced from Figure 4.10 b) that a rib width of around 5.0 mm is still applicable under operation with air at low current densities (ca. 0.4 A/cm$^2$). When the consumption is increased to around 2.0 A/cm$^2$, however, a maximum rib width of only 1.0 mm is feasible without severe oxygen starvation.

The same systematic holds true when the initial oxygen fraction in the channel is lowered below 21 Vol.%, which is the case near the cell outlet (no graphs provided). Thus, the rib width in an air fed fuel cell operated at typical current densities should not exceed 3.0 mm near the inlet, the maximum outlet value is depending on the oxygen fraction and thus on the cathodic stoichiometry. A rib width close to zero would naturally facilitate higher oxygen fractions at the active layer, even for high currents and low initial O$_2$ fractions. However, stability issues, promoted membrane drying and suboptimal current drain would be the consequences.

To confirm the systematics of geometrical effects inside a reasonable range of channel and rib widths, the relevant flow field variations are once more compared as a function of the operating conditions at inlet, middle of channel and outlet referring to the values of reactant humidity (both gases) and oxygen fraction as given in Table 4.1. Thereby the two variations with reduced channel width (C05R2 and C1R2) and the two flow fields with reduced rib width (C2R1 and C2R05) are considered. The standard geometry C2R2 is not shown since it is technical less relevant: the absolute dimensions are outside the optimum range, so that this geometry does not seem a worthwhile design for any position along the channel.

The Figures 4.11 and 4.12 show the trends of cell performance and cell resistance for the considered flow field geometries when the oxygen fraction is decreased (upper x-axis) and the humidification is concomitantly increased (lower x-axis). It is seen that in general the geometry C05R2 with a rib ratio of 0.8 would be favoured for all conditions from a resistance point of view. However, Figure 4.11 b) shows that with increased current (500 mV is a relative high load in technical fuel cells) the mass transport effect discussed in the previous subsection is responsible for reversing the situation for the case of outlet conditions. Here, the geometry C2R05 with a rib ratio of 0.2 is best performing. A transition between the two flow field variations involving other rib ratios than 0.8 and 0.2 can not be confirmed, since with only three data points it is difficult to accurately evaluate the trend.
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Figure 4.11: Integral cell performance for different flow field geometries (C05R2: \( r_{rib} = 0.80 \), C1R2: \( r_{rib} = 0.66 \), C2R1: \( r_{rib} = 0.33 \), C2R05: \( r_{rib} = 0.20 \)) as function of inlet/outlet conditions (reactant humidity and oxygen fraction) during potentiostatic operation at a) 600 mV and b) 500 mV. The best performing flow field is changing from lowest to highest rib ratio upon lowering the \( O_2 \) fraction and increasing the load.

As a consequence of the above results, an adapted flow field layout should feature wide channels and small ribs with a rib ratio around 0.8 over most of the channel length, while an expansion to a rib ratio of around 0.2 near the outlet of the channel is proposed\(^1\). The transition between the inlet and outlet channel dimension is thereby best to be done near the cell outlet.

Since the flow field on the single cell scale (comprising a number of parallel channels) needs to maintain a rectangular shape, the absolute width of a repetitive channel/rib unit needs to be independent of the rib ratio, which is the case for the variations C05R2 and C2R05 (\( r_{rib} = 0.8 \) and 0.2, both 2.5 mm) or for C1R2 and C2R1 (\( r_{rib} = 0.66 \) and 0.33, both 3.0 mm). Because of superior integral performance, the couple C05R2/C2R05 was chosen for the inlet/outlet dimensions. The transition between the two geometries thereby follows an exponential function, which was chosen based on its shape featuring more than 90% of the expansion in the last third of the channel length. Figure 4.13 provides this function together with an illustration of the adapted shape in one repetitive channel/rib unit for a channel length of \( z = 400 \) mm.

\(^1\)Significantly higher or lower rib ratios might result in the dominance of limitations, which do not stem from processes of the sub-mm scale denoting the particular shape of an adapted flow field design, see Fig. 4.10.
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Figure 4.13: Realization of an adapted flow field layout based on the knowledge gained from the sub-mm resolved current measurements; The channel/rib dimensions (x-coordinate) are changing from C05R2 at the inlet to C2R05 at the outlet (z-coordinate), the shape of the expansion follows an exponential function given in the illustration.

The overall dimensions of the flow field plate, including the channel length and the number of channels, are based on the design of the linear diagnosis cell used in the laboratory of PSI for local current measurement in the along-the-channel direction (segmented cell approach). The details concerning these measurements, and the results from the experiments with the adapted layout, are presented in the following subsection.

4.2.3 Experimental Evaluation of Single-Cell Flow Field Layouts

The technique of local current measurements on the single cell scale by means of segmented current drain has been introduced in Chapter 1.3.1, the details of the measurement setup with a linear cell design at PSI are comprehensively discussed in [13]. However, the setup used in the experiments discussed here is somewhat more simple, since there is no need for localized gas sampling, local temperature control and operation of a fuel cell stack. An illustration of the linear measurement cell is provided in Figure 4.14 a), a drawing of the standard flow field plate used in this setup is provided below in part b).

Characteristics of the Linear Test Cell. The cell consists of the membrane electrode assembly (MEA) sandwiched between semi-segmented flow field plates. Semi-segmented means that grooves with the depth of 1.0 mm are machined in the back side of the plates perpendicular to the channel direction, following the gaps of the 10-fold segmented current collector. This way, leakage currents between the segments of the current drain are reduced.

The MEA comprises the ionomer membrane Nafion® 212 with a dry thickness of 52 µm and an equivalent weight of 1100 g/mol. The electrodes used are catalyzed carbon cloth (Etek Elat V 2.1, thickness 350 µm) with a catalyst loading of 0.6 mg Pt/cm² identical for anode and cathode. For sealing of the cell elastomer gaskets (Viton, DuPont) are employed at the cathode, the lining groove surrounding the active area can be seen in Figure 4.14 b). A PTFE subgasket with a thickness of 220 µm was furthermore introduced around the active area to adjust the proper compression of the diffusion layer.

The active area itself has a size of $200 \text{ cm}^2$, whereby its width and length are the area which is covered by the parallel flow channels (400 by 50 mm). The flow field plates (BMA 5, SGL Carbon) are made from a carbon composite material based on PVDF (polyvinylidene difluoride).
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Figure 4.14: a) Schematic of the linear cell for the segmented measurement of the along-the-channel current distribution; The 10 segments connected to HALL sensors can be recognized on the cathode side. b) Drawing of the standard flow field plate for the linear cell, 28 channels with channel widths of 0.8 and rib widths of 1.0 mm are arranged in parallel over a length of 400 mm, the active area thus calculates to 200 cm$^2$.

With respect to the width of the flow field structure, the standard geometry for this cell allows for 28 channels with the dimensions of $w_{rib} = 1.0$ mm and $w_{chan} = 0.8$ mm. Gas supply is ensured by gas ports outside the active area via distributing manifolds.

The current drain of the 10 segments is realized on the cathode side by gilded copper plates, each connected to a HALL sensor. The segments on the anode side are hot-wired with a strong copper bar and do not participate in the measurement. Both sets of current collectors – the segmented ones at the cathode and the hot-wired ones at the anode – are electrically insulated against the aluminium end plates, which clamp the cell together by means of bolt connections around the active area’s perimeter. To ensure uniform cell compaction, they are tightened using a torque wrench and aligned by guiding rods.

**Experimental.** The test bench environment does not significantly differ from the periphery used with the specialized test cell for the sub-mm resolved measurements. The cell temperature was controlled by electric heaters, whereby no infrastructure for cooling was needed for the operation of a single cell. Reactant gases were supplied by mass flow controllers (Brooks 5866), their humidity was controlled by passing them through bubbling type humidifiers. Heated pipes were used to avoid condensation between the humidifiers and the cell, the dew point was measured at the inlet with humidity sensors (Vaisala HMP 243).

The current was modulated by means of an electronic load (Höcherl & Hackl ZS 3606), the signals of the HALL sensors plus the ones of cell voltage and current were digitalized via a data acquisition board (National Instruments PCI-E 6033). In addition, the integral cell resistance was measured...
by means of the HFR principle using a digital AC-milliohm-meter (Tsuruga Model 3566), which has a trust range of ca. 10 mΩ cm$^2$. The reactant flow rates, the gas pressure and the temperatures of the water reservoirs in the humidifiers were all controlled over an interface with the software LabView.

For the experiments with the different flow field layouts, operating conditions close to the standard values as quoted in Table 3.1 are applied. The most significant deviations are the channel/rib dimensions of the standard flow field, with $w_{\text{rib}} = 1.0 \text{ mm}$ and $w_{\text{chan}} = 0.8 \text{ mm}$ yielding a rib ratio of 0.56 instead of 0.50, and the operating pressure of 2.0 instead of 1.5 bar$_{\text{abs}}$. Furthermore, the cell was operated in constant stoichiometry mode rather than constant flow mode, since the systematic variation of reactant stoichiometry (both gases) is an experimental issue. The compression was fixed by means of the above-mentioned PTFE sub gaskets to ca. 37% of initial electrode thickness, which is close to the 35% in the test cell for the sub-mm resolved measurements. All cells were operated with H$_2$/air at 70°C with a dew point of 50°C ($r_h = 0.4$) for both reactant gases.

The current generation in the single segments as a function of the channel length is measured for various current densities (Figure 4.15) and reactant stoichiometries (Figure 4.16) with co-instantaneous recording of the integral cell resistance, respectively. The data plotted in the Figures shows the typical behaviour of current distributions at the single cell level upon variation of cell current and stoichiometry.

The polarization curve in Figure 4.15 a) depicts the cell performance of the linear cell with standard geometry, the departure from linearity above 0.4 A/cm$^2$ indicates the upcoming mass transport limitation under operation with H$_2$/air. The slight decrease of cell resistance from 147 to 107 mΩ cm$^2$ upon load increase is thereby attributed to the increasing share of product water contribution to membrane hydration.

Figures 4.15 b) and 4.16 b) provide the local current distributions measured during the polarization curve and stoichiometry variation in the along-the-channel direction, respectively. Every data point refers to the position of the middle of one of the ten current drain segments between cell inlet at $z = 0$ and cell outlet at $z = 400 \text{ mm}$. In analogy to the sub-mm scale measurements, the integral of a curve has to match the load current during the measurement.

To comply with the results shown in Subsection 4.2.1 concerning the performance at different positions along the channel, the operating humidity for the reactant gases should have been $r_h = 0.1$. However, a humidity of $r_h = 0.4$ was chosen since a significantly better cell performance can be achieved this way. Thus, the trend of performance from inlet to middle to outlet depicted in Figure 4.9 can not be reproduced exactly. It is in any way difficult to relate the conditions assumed for three positions along a channel to measured data with a resolution of 10 points in the same domain.

In the case of the load variation (Fig. 4.15 b), two characteristics are important to note. First, the shape of the current distribution shows the typical attributes as discussed in Section 1.3.2: the current generation exhibits its maximum at around one third of the channel length, whereas at the inlet losses are due to the undersaturated ionomer and cell regions towards the outlet suffer from reactant starvation. This observation holds roughly true for all integral current densities investigated. Second, the behaviour of the distribution upon load increase from 0.1 to 0.7 A/cm$^2$ shows the expected shape alterations according to the local loss mechanisms: the area with lower
current generation at the inlet is decreased at higher rates of water production (in particular from 0.5 to 0.7 A/cm²), which is also visible in the decrease of integral cell resistance in Fig. 4.15 a). At the same time, the current in the second half of the cell (towards the outlet) does not increase linearly with the cell’s load as a consequence of the depleted reactant. Since current generation in the outlet region seems to be limited towards stagnation at high rates of consumption, the inlet region has to compensate by increased current production, which entails higher overvoltages. The inhomogeneity of a current distribution in the along-the-channel direction is thus directly coupled to cell performance.

The nature of the loss mechanisms – ionic charge transport in the inlet region and mass transport in the outlet region – can be confirmed more significantly with the variation of reactant stoichiometry (Fig. 4.16 b). Very low stoichiometries at a fixed current of 0.4 A/cm² accompany also very low oxygen fractions at the cell outlet – in the case of λ = 1.1 only 2.4 Vol-% – resulting in outlet currents near zero. At the same time the low flow rates facilitate a better membrane hydration in the inlet region, since less product water is removed with the gas flow. Consequently, the integral cell resistance is lowest at low stoichiometries (compare Fig. 4.16 a) and current production is
shifted towards the cell inlet. Stepwise increase of the stoichiometric factor to $\lambda = 2.4$ indeed solves the problem of low outlet currents: an almost homogeneous distribution is observed in the last two thirds of the channel. However, the increased stoichiometric ratio entails high flow rates and -speeds, which leads to increased water removal in the undersaturated inlet region. The local currents here exhibit significant minima as a consequence of high ionic resistance. Thus, the cell performance stagnates and does not increase with the outlet currents, although the local mass transport limitations in the outlet region are overcome with stoichiometries above $\lambda = 1.8$.

The position of the maximum current along the channel is therefore an indicator for the regime of limitations, since it shifts upon variation of mass and charge transport relevant operating conditions. It can be seen from Figures 4.15 and 4.16 that the maximum current generation is situated closer to the inlet for higher currents (high reactant consumption and water production rate) and low stoichiometries (reactant starvation and low water removal rates). In accordance to the argumentation in the above paragraphs, these two regimes of operation have one thing in common: a lower integral cell resistance. The $z$-position of the maximum current generation can therefore be related to the cell resistance, or parameters influencing the cell resistance.

![Figure 4.17](image-url)  
Figure 4.17: Relation between integral cell resistance $R_{\text{cell}}$ and the $z$-position of the maximum of current generation of the along-the-channel distributions; The resistance data is extracted from the test runs shown in Figure 4.15 a) (polarization curve, white marker) and Figure 4.16 a) (stoichiometry characteristics, gray marker), the $z$-position of the maximum current is obtained from a spline fit of the respective along-the-channel distribution (error ca. 20 mm). An increasing trend is observed for the distance from the inlet with increasing cell resistance.

Figure 4.17 plots this $z$-position of maximum current production as a function of the resistance $R_{\text{cell}}$ obtained from data of the load current variation (white markers) and the stoichiometric variation (gray markers). The pattern of this relation shows a clear trend for both sets of data, whereas operation with low integral ionic resistance shifts the position of maximum current towards the cell inlet. The error bars thereby arise from the accuracy of determining the maximum of the current distribution along the channel, which depends on the quality of the spline fit through the data points. The error is thus in the order of 20 mm, which is half the width of a segment (10 segments x 40.0 mm).

This finding clearly shows that local losses can be influenced by means of manipulating operating
conditions such as those influencing the membrane resistance. However, for the data shown in Figures 4.15 to 4.17 a reduction of one limitation could only be achieved at co-active amplification of the other one. The behaviour of integral cell performance thereby followed the increase or decrease of the dominant limitation, respectively. An improvement of cell performance might however be achieved by countering mass transport issues in the outlet region and charge transport limitations in the inlet region at the same time, which becomes possible by the employment of the adaptive flow field structure introduced in Subsection 4.2.2.

For the experimental evaluation of the adapted design the comparison to non-adapted flow field layouts is mandatory. Only this way it can be proven that not only the overall channel/rib dimensions, but also their adaptive change along the channel flow path leads to an improvement of cell performance. For that reason two more flow field layouts with no change along the channel direction have been tested in addition to the standard geometry. They feature a constant

Figure 4.18: Sketches of the flow field layouts used in the experiments, a repetitive, symmetric channel unit is shown, anode and cathode are identical. Top: Constant narrow channel flow field (NC) with ‘inlet’ design, $r_{rib} = 0.8$; Second: Constant wide channel flow field (WC) with ‘outlet’ design, $r_{rib} = 0.2$; Third: Original adapted design with expansion at cell outlet (AO), $r_{rib}$ decreases from 0.8 to 0.2; Last: 180° turned adapted design with expansion at cell inlet (AI), $r_{rib}$ increases from 0.2 to 0.8.

Figure 4.19: Measured behaviour of pressure drop during a polarization curve for the five different flow field layouts from Figure 4.18 for a) Cathode side and b) Anode side. Operation with constant stoichiometry ($\lambda = 1.4$, both gases), a flow rate can be assigned to every integral current density. A minimum flow has to be ensured at low load: 0.31/min H$_2$ at anode and 0.51/min air at cathode. In general, the order of lowest average channel width is correlated with the order of highest pressure drop.
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dimensioning of the channel geometry with the geometry of the cell inlet, and the geometry of the cell outlet of the adapted design, respectively. Furthermore, another experiment is carried out with the adapted design having the expansion located at the gas inlet instead at the outlet. If this variation results in worse performance compared to the original orientation, the processes on the single cell and sub-mm scale on integral cell performance has been understood correctly.

Figure 4.18 provides sketches of the four different flow field variations. On top, the non-adapted version with a narrow channel (NC) is shown, as it is the dimensional design for the inlet region of the adapted layout with a rib ratio of 0.8 \((w_{rib} = 2.0 \text{ mm}, w_{chan} = 0.5 \text{ mm})\). Consequently, it is followed by another variation of a non-adapted flow field with a wide channel (WC), featuring the channel/rib widths of the outlet region of the adapted version \((w_{rib} = 0.5 \text{ mm}, w_{chan} = 2.0 \text{ mm})\); its rib ratio is 0.2. Eventually, the adapted layout with the expansion at the outlet (AO) – as shown in detail in Figure 4.13 – is shown as the third variation. The rib ratio is changing from 0.8 at the inlet to 0.2 towards the outlet. The last of the sketches shows its counterpart, the 180 degree rotated version with the expansion in the inlet region (AI). Its rib ratio increases from 0.2 at the inlet to 0.8 towards the outlet. The channel dimensions (average width and height) and the rib ratios of the different designs are summarized in Table 4.2.

It is important to note that the performance with these layouts can not be compared straight forwardly without considering the different pressure drop throughout the flow field. A geometry with a small channel cross section is connected with a higher pressure drop, which – in certain boundaries – can increase cell performance by means of higher inlet pressures. This improvement is however not a consequence of effects from the sub-mm scale, regarding for example an adapted channel design. Thus, the pressure drop of the flow field plates with the above layouts were evaluated in order to confirm comparability. The pressure drop is thereby influenced by the (average) channel width and the channel height.

Figure 4.19 provides the results of this evaluation, is depicts the characteristics of pressure drop during a polarization curve with constant stoichiometry \((\lambda = 1.4 \text{ for both gases})\) for the cathode side in a) and for the anode side in b). In operation with constant stoichiometry every current density during the polarization curve (lower \(x\)-axis) can be assigned to a respective flow rate, which is given at the upper \(x\)-axis.

However, at low current densities the reactant fluxes are too small to maintain the system pressure of 2.0 bar abs, which necessitates the definition of a minimum flow rate. This minimum flow rate is 0.31/min for the case of hydrogen at the anode, and 0.51/min for the case of air at the cathode side. During operation with this minimum flow rate at several low current densities, the pressure drop remains mostly constant. Even a slight decrease is found with the current density in some cases, which is a consequence of the growing reactant consumption upon load increase. Outside this region, the values for \(\Delta p\) are roughly in the range of the estimation in Figure 4.10 a), deviations are originating from discrepancies in the operating conditions applied in reality and assumed for the calculation.

The average anodic and cathodic channel cross sections can be deduced from the geometric specifications given in Table 4.2. Inspection of Figure 4.19 reveals that indeed the order of channel cross section is roughly consistent with the order of pressure drop. Figure 4.19 a) compares the pressure drop of air in the cathode flow fields, all are equipped with a channel height of 0.55 mm. The geometry with the smallest channel (NC, 0.5 mm) thus shows the highest \(\Delta p\), followed by the
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<table>
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<th>Layout</th>
<th>avg. channel width $\bar{w}_{\text{chan}}$</th>
<th>number of channels</th>
<th>rib ratio $r_{\text{rib}}$</th>
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<td>20</td>
<td>0.80</td>
</tr>
<tr>
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<tr>
<td>AO</td>
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<td>0.80 $\rightarrow$ 0.20</td>
</tr>
<tr>
<td>AI</td>
<td>0.73 mm</td>
<td>20</td>
<td>0.20 $\rightarrow$ 0.80</td>
</tr>
</tbody>
</table>

Table 4.2: Geometrical specifications of the flow field layouts, the 'Std' flow field is added for comparison. The channel heights are 0.50 mm (anode side) and 0.55 mm (cathode side) for the geometries NC, WC, AO and AI.

two adapted geometries (AO and AI, both 0.73 mm), which generate virtually identical values. The lowest pressure gradient, about half of those of AO and AI and by a factor of 2.5 below NC, are found for the layout with relatively wide channel (WC: 2.0 mm).

As a consequence of the much lighter gas, pressure drop is a smaller issue on the anode side fed with hydrogen. As shown in Figure 4.19 b), the values for all other geometries – with a channel height of 0.5 mm each – are found to be rather distorted, only a weak trend to increased pressure drop at higher load is recognized. Thereby the low channel widths (NC, AO and AI: 0.5 and 0.73 mm) entail slightly higher pressure drops compared to the geometry with the wide channel (WC: 2.0 mm).

Essentially, the cell behaviour with respect to performance and local generation can be considered comparable, accounting for the low qualitative and quantitative differences in pressure drop. Reactant diffusion processes and water management are not expected to be significantly altered, since the pressure drop is in the same order of magnitude.

Results for Load Current Variation. The recording of local current distributions in the along-the-channel direction during a polarization curve aims to evaluate the behaviour of the different flow field layouts upon increased reactant consumption and concomitant increase of membrane hydration by product water. The polarization curves were obtained at operation with constant stoichiometry ($\lambda_{\text{An.},\text{Cath.}} = 1.4$), and a relative reactant humidity of $rh = 0.4$ for both gases at an operating temperature of 70° C, referring to the standard conditions. The flow rates at each load point are given in Figure 4.19.

The polarization curves for the flow field geometries NC, WC, AO and AI (a), together with the respective integral cell resistances (b), are given in Figure 4.20. Inspection of diagram b) reveals that once more the rib ratio – or also the average channel width – can be related to the integral cell resistance. The geometry NC with the smallest channel (0.5 mm) and the highest rib ratio (0.8) does best in protecting the membrane from drying. Thus, the lowest integral resistance – in particular at high currents with increased water production – is observed. The two adapted geometries (AO and AI) show perceptibly higher resistances, which can be related to the share of rib ratio which is smaller than 0.8. The version with the expansion at the cell inlet (AI) thereby shows only slightly, but consistently higher values for $R_{\text{cell}}$. This shows that the positioning of the expansion in the inlet region, which is prone to membrane drying, worsens the water management in the ionomer. In this case the outlet region is better protected from increased water removal, which is not necessarily needed due to the higher water vapour partial pressure at the end of the flow path. Finally, the flow field with the widest channel (WC) accompanies the
4.2. Adapted Flow Field Layouts

Figure 4.20: Integral behaviour of the different flow field layouts (NC, WC, AO, AI) during variation of the load current $j_{\text{cell}}$: a) Polarization curves, b) Cell Resistance. Operation with $\text{H}_2/\text{air}$ at constant stoichiometry ($\lambda = 1.4$ for both gases), all other conditions as specified in the 'Experimental' section. An increasing trend between channel width and cell resistance is found, whereby the rib width determines the cell performance in the high load range.

The highest resistance values of all, a significant increase by a factor between 2 and 3 is observed when increasing the average channel width from 0.5 mm (NC) or 0.73 mm (AO and AI) to 2.0 mm.

The systematic of the relation between channel width (or rib ratio) and ionic resistance coincides with the observations made with the small differential cell for measurement of the sub-mm current distribution in Section 4.1.2. Consequently, the cell performance of the different geometries could be expected to obey the order of the ionic resistance. The Figures 4.20 a) and 4.21 a) however show that this does not hold true in case of the adapted designs.

While the performance of the flow field layouts with constant channel geometries (NC and WC) strongly reflects the behaviour of the membrane resistance, the values measured with the adapted designs lie not in between them (as the resistance values do). For low and moderate load currents, they both show identical performance to the narrow channel design. At higher load, however, the behaviour of cell performance essentially decouples from the behaviour of cell resistance.

Figure 4.21: Overall cell performance of the different flow field layouts (NC, WC, AO, AI) during variation of the load current $j_{\text{cell}}$: a) Performance curves, b) Performance $p_{\text{cell}}$ at the maximum power point (MPP, left part) and the respective load current at MPP (right part). Operation with $\text{H}_2/\text{air}$ at constant stoichiometry ($\lambda = 1.4$ for both gases), all other conditions as specified in the 'Experimental' section. The AO geometry exhibits the best performance at the highest load current density.
the influence of the adapted design on mass transport limitations is clearly visible.

According to the considerations in the previous sections, mass transport limitations stem mainly from the rib covered areas and are strongest near the cell outlet with depleted reactants. Hence, the geometry with the smallest rib entails least mass transport overvoltages. This effect can be well observed when comparing the adapted design with the channel expansion at the outlet (AO) to the one with a constant narrow channel (NC), and to the one with the expansion at the inlet (AI).

As seen in Figure 4.21 a), the best performance is achieved with the AO-layout, accommodating the combination of low ionic resistance in the dry inlet region and good reactant accessibility in the mass transport critical outlet region. The AI-layout in contrast shows for high currents almost identical behaviour compared to the NC-design, which is attributed to the same small channel dimension in the outlet region responsible for a higher mass transport overvoltage.

Although the design with the constant wide channel (WC) is associated with the least mass transport limitations, its performance is worst compared to all other flow fields. Obviously, the high ionic resistance overcompensates the positive effect of improved reactant accessibility to the active sites.

Figure 4.21 b) highlights these results by quantitative comparison of the maximum power point (MPP) and the load current, at which this maximum performance has been reached. It is seen that the AO-layout is not only the variation with the highest MPP, the maximum power point is also found at the highest load current. This again indicates lower mass transport losses with the use of this flow field layout, it apparently operates best at high current densities. Excluding the WC-layout and considering only the cells with comparable membrane resistance, the position of the MPP seems to be a function of the outlet channel width. Hence, the values of NC and AI are almost identical as a consequence of similar geometrical conditions in this mass transport relevant region.

The above findings can be confirmed by interpretation of the along-the-channel current distributions given in Figure 4.22. It is seen for a low current density of 0.1 A/cm$^2$ (diagram a) that almost identical distributions are obtained for the different geometries of NC, AO and AI, which coincides with their identical cell performance. Solely the layout with the constant wide channel (WC) shows lower performance connected with its high cell resistance, which is also seen in reduced current generation in the inlet region. As the only flow field layout, its maximum current production at this load is in the second half of the channel length at ca. $z = 300$ mm, and is superior to the other geometries in this position. This observation indicates that the proposed mechanism holds true: a wide channel entails lower mass transport overvoltages, but also worse water management. The negative effect of high cell resistance dominates the cell performance, whereby the relevant limitation stems from the inlet region.

The discussed behaviour is observed in a more distinct way when increasing the current to 0.3 A/cm$^2$ (diagram b), where all cells are in the quasi-linear region of the polarization curve. Still the WC-layout exhibits its maximum current production in the rearmost part of the flow field (around $z = 200$ to 250 mm), whereby the shifting of this maximum towards the inlet region is visible when comparing to diagram (a). Again, the lowering of cell resistance upon the load increase (compare Fig. 4.20 b) is responsible for the diminishing of the area with low local current production in the inlet region, as shown in Figure 4.17.
4.2. Adapted Flow Field Layouts

Figure 4.22: Local current distributions along the channel for the flow field geometries NC, WC, AO and AI, data obtained during variation of load current at a) $j_{\text{cell}} = 0.1 \text{ A/cm}^2$, b) $j_{\text{cell}} = 0.3 \text{ A/cm}^2$ and c) $j_{\text{cell}} = 0.5 \text{ A/cm}^2$. Operation with H\textsubscript{2}/air at constant stoichiometry ($\lambda = 1.4$ for both gases), all other conditions as specified in the 'Experimental' section. The most homogeneous distribution is achieved with the AO-design at high current densities.

Regarding the other flow field layouts, small differences between NC, AO and AI begin to emerge at $0.3 \text{ A/cm}^2$. The layouts NC and AO still exhibit identical cell performance at this point, associated with virtually identical current profiles along the channel. The AI-cell with the 2.0 mm channel expansion at the inlet, however, is obviously not capable of maintaining the inlet current at the same level as compared to the flow fields with the inlet channel width of 0.5 mm. This is a consequence of increased local membrane resistance at this position. The result is a lowered local current production in the inlet region and a compensating peak at $z = 150 \text{ mm}$. This increased degree of inhomogeneity entails higher total overvoltages, which utters in a slight decrease of cell performance at $0.3 \text{ A/cm}^2$ compared to NC and AO (see Fig. 4.20 a).

Diagram (c) finally provides the current profiles for the load point $0.5 \text{ A/cm}^2$. Here, all cells are in the mass transport regime of the polarization curve and exhibit different cell voltages. These differences can be explained by the behaviour of the local current distributions, where the significance of mass transport limitations can be related to the local current density in the outlet region. It is seen that the order of current generation at positions between $z = 300$ and $400 \text{ mm}$ related to the order of the outlet channel width: The highest currents are generated with the WC-design, followed by the AO-layout with the outlet expansion to 2.0 mm. Least
current is generated in the two cells with an outlet channel width of 0.5 mm (NC and AI). The resistive limitations in the inlet region are still dominant for the cells with the wide channel at this position: the lowest inlet currents are observed for the WC-layout followed by the AI-geometry. NC and AO exhibit the same inlet channel width of 0.5 mm, whereby the NC-design shows higher currents since it has to compensate the lower production near the outlet compared to AO.

Essentially, the adapted flow field layout with the expansion at the outlet (AO) shows – as intended – best performance as a consequence of the most uniform current distribution. It is therefore superior to the version with a high rib ratio and constant channel geometry (NC), whose dimensions are similar over 75% of the channel length to those of the adapted design. Alone the reduction of mass transport limitations in the outlet region is thus responsible for the improvement of performance from NC to AO. The 180° rotated version (AI) performs even worse compared to the constant flow field with narrow channel (NC), as a consequence of the expansion being in the wrong region. Comparable mass transport limitations in the outlet, but higher membrane resistance in the inlet leads to the performance decline in this case. Another example for the crucial effect of geometry-induced membrane water management is the – despite the low mass transport limitations – very poor performance of the WC-geometry, which is attributed to the high ionic resistance in the inlet region of this flow field.

**Results for Stoichiometry Variation.** As a consequence of the above findings, the use of adapted flow field layouts with an expansion at the cell outlet becomes an interesting principle in particular for points of operation with are associated with high mass transport limitations. However, fuel cells are typically not operated in the mass transport regime at high loads (i.e. the departure from linearity in polarization curves), but operation with little excessive reactant feed on the cathode is nevertheless advantageous for achieving a higher system efficiency. In these cases of reduced air stoichiometry, the mass transport regime shifts to lower current densities. Cell performance can then be improved through structural optimization by means of adapted flow field layouts. For this reason, the local current generation along the channel with the different channel designs is in the following examined for the variation of the reactant stoichiometry.

Initially, Figure 4.23 depicts the behaviour of the integral characteristics of the four flow field designs upon variation of the stoichiometry for both reactant gases between $\lambda = 1.1$ and 2.4. Diagram (a) elucidates for a load of $j_{cell} = 0.4 \text{A/cm}^2$ that – independent of the channel layout – low stoichiometries are connected to significantly lower cell voltages. Increasing the excessive feed, however, does not result in an unimpeded improvement of cell performance rather than showing asymptotic behaviour, which marks the end of severe mass transport limitations. A similar behaviour is observed for the integral cell resistances in Figure 4.23 b).

To understand these observations, it needs to be mentioned that the variation of reactant stoichiometry does not only influence the mass transport overvoltages. Due to the increased flow rates for high values of $\lambda$ the water removal rate is increasing, which leads to higher membrane resistances in particular with undersaturated conditions. Therefore, an increase of the cell resistance is observed for all geometric variations, with this increase being more significant in the cell with the widest channel (WC). Consequently, the lowest performance is again accompanied with this channel design.
4.2. Adapted Flow Field Layouts

Figure 4.23: Integral behaviour of the different flow field layouts (NC, WC, AO, AI) during variation of the anodic and cathodic reactant stoichiometry $\lambda$; a) Cell voltage, b) Cell Resistance. Operation with H$_2$/air at constant load ($j_{\text{cell}} = 0.4$ A/cm$^2$), all other conditions as specified in the 'Experimental' section. The cell performance is increasing asymptotically with the stoichiometry, a quasi-stagnation is reached for $\lambda > 1.5$. The cell resistance is growing with the stoichiometric flow rate, which is a result of increased water removal.

The other cells are performing in the order of their mass transport related flow field characteristics or their integral membrane resistance, depending on the stoichiometric factor. For high values of $\lambda$ (above 1.4) mass transport limitations are unlikely to disturb cell performance, hence the order of cell performance relates to the order of cell resistances. With little excessive feed, however, mass transport is the dominating limitation – predominantly in the outlet region of the cell, where low oxygen partial pressure prevails. Thus, a clear connection between outlet channel width and cell voltage can be observed comparing NC, AI and AO at $\lambda = 1.1$.

Although the AI and NC flow fields are designed with the same outlet width of 0.5 mm, the adapted geometry with expansion at the inlet exhibits a higher performance despite its higher cell resistance. This indicates that mass transport limitations might also be present in the inlet region at this low stoichiometry, and are minimized by reducing the rib ratio in this region. The same behaviour is also observed comparing the performance curves of AI and NC in Figure 4.20 a) in the high load range. A yet more pronounced improvement can be expected by operating the cell with the adapted geometry having the expansion at the outlet, since this is the position with the crucial mass transport limitations. Indeed, the AO-design achieves a boost of cell voltage by ca. 250 mV at $\lambda = 1.1$ compared to NC.

Again, the above findings can be further scrutinized by the inspection of the respective current profiles along the channel, which are given in Figure 4.24. The most distinct differences comparing the flow field variations are seen in diagram (a) at the lowest stoichiometry ($\lambda = 1.1$). One interesting feature of this plot is the fact that all layouts exhibit similar current generation around 0.1 A/cm$^2$ near the outlet, which is only ca. 25% of the load current. Even the advantage of cells with wide channels is only marginal here. This indicates that the very low oxygen fractions at this location ($\approx 1\%$) entail concentration losses, which are strongly dominating the diffusion losses on the channel and rib scale.

Upstream of the outlet, however, the oxygen partial pressure appears to be high enough to cause a diversification with respect to the current profiles of the different flow field layouts. Between $z = 200$ and 300 mm the local current generation again relates to the order of the rib ratios in this
Figure 4.24: Local current distributions along the channel for the flow field geometries NC, WC, AO and AI, data obtained during variation of reactant stoichiometry at a) $\lambda = 1.10$, b) $\lambda = 1.25$ and c) $\lambda = 1.80$. Operation with $\text{H}_2/\text{air}$ at constant load ($j_{\text{cell}} = 0.4 \text{ A/cm}^2$), all other conditions as specified in the 'Experimental' section. The homogenization of the current profile with the adapted layout AO yields the best performance gain for low stoichiometries.

region: the wide channel (WC) shows best performance with $w_{\text{chan}} = 2.0 \text{ mm}$, followed by the AO-design with the channel width expanding from ca. 0.7 to 1.0 mm at this positions. The flow fields with low channel widths in the outlet region (NC and AI, both ca. 0.5 mm) are observed to produce current at a lower, but comparable level.

Concerning the inlet region, the local current generation is again controlled by resistance in case of the wide inlet geometries (AI and WC, both ca. 2.0 mm). For these flow fields a rather strong decline of current generated in the first, or even the first two segments (between $z = 0$ to 40 and 0 to 100 mm) is observed. There are two reasons why the inlet current is higher for the AI design compared to WC: first, the adapted design features a significant reduction of channel width inside the first 100 mm channel length (membrane drying is less pronounced), and second, the AI-design has to compensate the lower currents in the outlet region (which are a consequence of the low channel width there).

A similar effect can be observed comparing the NC with the AO design, whereby both show less reduced local currents in the inlet as a consequence of the high rib ratio in this water management critical region. The higher currents observed with NC in the first two segments are thus again a
compensation effect for the lower outlet generation. As mentioned before, this forcing of current entails higher total overvoltages, which are the reason for the superior cell performance of AO at low stoichiometries.

Finally, the consideration of the Figures 4.24b) and c) shows that the positive effects of the adapted layout AO are diminishing with higher reactant feed. At $\lambda = 1.25$, the current profile of AO is only slightly more homogeneous, and eventually identical with NC at $\lambda = 1.80$. The highest performance gain with the use of the adapted design AO is consequently achieved at low stoichiometries. In contrast, the systematic patterns regarding the current profiles of WC and AI show the expected dependence with increasing stoichiometric ratio: the current generation in the inlet region decreases drastically with the reactant flow rate, while the outlet currents are promoted in the cell with the wide channel.
4.3 Summary Chapter 4

This chapter investigated the role of the flow field geometry in terms of the local current generation on the sub-mm scale and at the single cell level. The relation between local generation and integral cell behaviour was scrutinized and conclusions were drawn concerning an optimal design for the flow field geometry in technical fuel cells. Eventually, the knowledge gained was used for the development of an adapted channel geometry, which changes channel and rib width along the flow path. The results of these studies are summarized below:

- Both, oxygen diffusion and water management, have a crucial influence on the channel/rib current generation and therewith integral cell performance.

- There is an optimum range of channel and rib dimensions, inside which the performance increases with the ratio of rib covered cell area. Outside this optimum range, parameters such as pressure drop, diffusion pathway or electric resistance become dominant limitations.

- Wide ribs and small channels can facilitate a more homogeneous channel/rib current distribution and a better cell performance. The reason for this is the improved water management since wide ribs prevent membrane drying accompanying low cell resistances.

- Operating conditions associated with strong mass transport limitations (low oxygen concentration, high currents) fall out of this pattern, here wider channels are preferred for maximum performance.

- The limitations on the sub-mm scale can be related to current gradients measured at the single cell level between in- and outlet of a cell. The inlet region is thereby prone to membrane drying (which is a channel issue), while the outlet suffers from low reactant concentrations (which hampers the current generation predominantly under the rib).

- The proposal of adapted channel geometries featuring small channels and wide ribs near the inlet, and wide channels and small ribs at the outlet was thus deduced as an optimal design.

- The fabrication and experimental evaluation of such a design reveals that indeed an improvement of cell performance can be achieved as compared to the non-adapted designs equipped with constant channel dimensions.

- It has been shown that the performance gain with the adapted design is biggest with little excess feed, which is a desired operating condition for technical PEFC systems since parasitic power losses are reduced.

Concludingly, the positive results with the flow field adaption proves that the processes on the sub-mm scale have been understood correctly. The method for sub-mm current measurement has proven a worthwhile tool for diagnostics on PEFC, aiming for the structural optimization of the cell design. Possible extensions of the measurement principle and ideas for further optimization of the adapted flow field designs are discussed in Chapter 5.
Chapter 5

Synopsis and Future Work

The findings and achievements of this work are finally summarized and evaluated on the background of their significance for the research and development community. Furthermore, ideas are collected of how to enhance the principle of sub-mm current distribution measurement and how to improve the reliability of the method. Based on the results of this study, eventually proposals for further optimization of cell structures are made. Thereby the situations on the sub-mm as well as the along-the-channel scale is reflected.

5.1 Conclusions

In general two achievements have been made in this thesis, which have not been part of the common knowledge or know-how concerning PEFC research and technology: First, the development and successful application of a measurement method to assess the current density distribution on a scale smaller than the flow field’s channels and ribs; and second, the also successful employment of adaptive flow field layouts at the single cell level.

Sub-mm Scale. It has been shown that it is possible to obtain current density distributions across channel and rib with a spatial resolution of at least 200 µm. This became feasible by measuring the potential drop over the cell components in the current drain with a set of filigree probe wires inserted at the interface between the catalytic layer and the GDL. The diffusion medium and the flow field plate therewith serve as internal shunt resistors. However, comprehensive ex-situ studies needed to be conducted with respect to the electrical and mechanical behaviour of these shunts when the cell is in a compressed state.

It has been elucidated that in particular the diffusion medium is not a precision resistor, and is thus a major source of error. However, reliability of the principle can be assured by averaging the same experiment over several independent cells or applying spline fits to elude disturbances by deviations of the material properties. Eventually, it could be shown that statistic fluctuations of electric properties do only alter the obtained current distribution up to 5%, while deviations in local material density lead to much higher uncertainties. As a consequence, the accurate adjustment of cell compression is a crucial issue concerning reliability and reproducibility of the results. A specialized test cell with small active area designed for differential operation was
developed for the experimental examinations on local current distributions. Another key achievement is the enhancement of this measurement method into the temporal domain. The time-resolved measurement of sub-mm current distributions during an electric perturbation (i.e. a pulse) allows for extracting the local ohmic resistance with the same spatial resolution across channel and rib. The total ohmic drop can be corrected for the electrical fraction by means of the voltage signals measured with the probe wires. Hence, the obtained data closely describes the ionic resistance of the membrane. Reliability of the resistance measurement is thereby strongly dependent on the capability of achieving a short current transient at the pulse edge. Although reliable resistance distributions are obtained from a qualitative view, it has been deduced from the evaluation of the set-up characteristics that there is still room for improvement regarding the instrumentation (i.e. the electronic load device) for reducing the quantitative error.

The measurement results obtained with the specialized test cell reveal that inhomogeneous current and resistance distributions occur under most of operating conditions. In some cases, the distribution of current is determining the distribution of membrane resistance by means of the product water distribution (i.e. dry conditions), in other cases the local membrane resistance defines the degree of current generation at a particular position (i.e. operation with high oxygen fractions). Both mass and charge transfer are closely interrelated and interfere with each other. However, it could be shown that charge transport losses (high ionic resistance) stem predominantly from the channel areas and mass transport losses (low oxygen concentration at the catalytic layer) are more pronounced under the ribs.

Regarding the variation of reactant humidity, high peaks of membrane resistance are developing in the channel area upon dry operation, while a minimum resistance is found in the same region when moist or saturated gases are fed. The resistance under the ribs is only slightly changing upon the variation of external humidity from zero to saturation, although the local current changes significantly. Reason for this is assumed to be the water management of the rib areas, preventing the water from being removed with the gas flow at dry conditions, and not taking up high amounts of water from the channel during saturated operation as a consequence of limited current density due to oxygen transport limitations in the porous GDL structure.

The variation of the oxidant composition revealed that the reduction of GDL pore size as a consequence of cell clamping pressure in combination with the long diffusion pathways under the rib are the dominating source of mass transport losses on the sub-mm scale. Experiments with variation of oxygen mobility (substitution of inert gas) have shown that in particular at low oxygen concentrations in the channel, the starvation in rib covered areas becomes substantial. However, the breakdown of mass transport limitations is still difficult, since the inert gas approach using Helox also influences the local membrane resistance.

Finally, the variation of the flow field geometry has shown that wide ribs and small channels accompany a higher cell performance inside a rather large range of operating conditions. This effect could be attributed to significantly lower membrane resistances, which are a consequence of improved water management with the use of wide ribs. Only at very low oxygen fractions (around 5%) the situation is reversing, and geometries with small ribs and wide channels are favoured. However, these conditions exist in fuel cells of technical size near the outlet, they cause part of the integral losses of the cell and are responsible for substantial gradients in the along-the-channel direction.
Single Cell Scale. It could be shown with the sub-mm measurements that different geometries show best performance for conditions typical at inlet and outlet in a technical sized PEFC. Consequently, an adapted flow field layout is deduced for reducing the inhomogeneity of current generation along a channel. Accounting for the knowledge that the inlet region suffers from inappropriate membrane hydration and the outlet region is prone to reactant starvation, a design featuring small channels and wide ribs for the inlet and small ribs combined with wide channels at the outlet has been developed. The cell used for the evaluation of this flow field layout is a test cell with segmented current drain and linear channels, which has been established as the standard diagnostic tool for measurement of along-the-channel current distribution.

The experiments revealed that indeed the adapted layout accompanies higher performance compared to non-adaptive designs with constant channel and rib widths along the channel (with dimensions such as comprised in the adaptive geometry). In general, all geometries exhibit a decline of current generation near the inlet (attributed to insufficient membrane hydration under unsaturated conditions) and near the outlet (due to the depleted oxidant). In the case of non-adapted geometries, the prevention of one limitation (e.g. by altering the reactant flow rate) leads to an aggravation of the other one.

Regarding mass transport limitations, one has to distinguish losses due to upstream depletion from losses due to diffusion on the sub-mm scale (the latter is strictly speaking also a kind of 'cross stream' depletion). While the depletion of reactant along the flow path (decrease of channel concentration, increase of water vapour partial pressure) is unavoidable also by layout optimization, the losses stemming from diffusion in the GDL can be alleviated by the tailored channel design. As a consequence, improved current generation is found near the outlet with the adapted geometry. At the same time the inlet region is prone to membrane drying, which can again be eluded by tailoring the local channel design. The results have shown that the current generation in this region is strongly connected to the inlet channel width: the wider the channel, the more significant the losses due to high membrane resistance. The respective dominant loss mechanism – drying near the inlet or starvation near the outlet, depending on the operating conditions – entails the enforcement of current in the non-dominant region, which leads to higher total overvoltages.

Essentially, the use of adapted flow field layouts achieves a small reduction of the total over-voltage, which is attributed to the noticeable uniformization of the along-the-channel current distribution. This improvement of cell performance is highest in particular for little excessive reactant flows and dry conditions. The maximum performance gain is therewith accomplished at operating conditions, which are desirable for mobile PEFC systems to reduce parasitic power and peripheric expenditure. Nevertheless, a detailed optimization of the overall channel geometries has to follow the proof of principle given here.
5.2 Outlook

This section aims to collect ideas and to give impulses for future work concerning the sub-mm current measurement and the related optimization efforts at the single cell level, a subsection is devoted to each of these items.

5.2.1 Advancement of the Sub-mm Current Measurement

**Anode or Cathode Side Measurement.** A number of improvements can be made to increase the accuracy and significance of the results gained from the sub-mm current measurements with the specialized test cell, most of them dealing with minor constructive details not worth mentioning here. One question, however, has to be emphasized: is the insertion of the probe wires better to be done on the anode or on the cathode side?

Up to date, the probe wires are inserted at the interface of CL and GDL on the anode side of the cell. This procedure is a consequence of the start-up phase of the measurements. At that time, carbon fibres were used as potential probes, which showed a rather strong interaction with the electrode processes. To reduce the perturbations, the anode side with less electrode polarization was chosen for the measurement.

However, in particular mass transport processes emanate from the cathode side; part of the substantial loss mechanisms in PEFC are hence not measured at the place of their origin. For example, operation of an air fed cell at a sufficiently high current density causes zero current in the middle of the rib covered area. According to the membrane’s in-plane conductivity, the current distribution measured at the anode will yield values different from zero for this position. Calculations have shown that the anodic and cathodic current density are not substantially different, which is a consequence of the thin membrane with its rather low conductivity. An even more accurate picture of cathodic mass transport limitations could nevertheless be drawn from measurements on the cathode side, also because these experiments are straightforward possible without any constructive changes.

In the following a few ideas for new experiments are addressed:

**Combined Measurements Sub-mm Current – Imaging Methods.** The distribution of liquid water in the porous diffusion medium is expected to have a substantial influence on the sub-mm current distribution. The channel/rib positioning of liquid water holdup at specific operating conditions as well as the water removal rates with different flow field geometries can be determined by applying imaging methods such as Neutron Radiography (NR) or micrometer resolved X-Ray Computer-Tomography (µ-CT). Up to now, however, only separate measurements on the respective channel/rib current distribution can be related to the radiograms and tomograms.

Thereby liquid water in the porous GDL structure is assumed to be the main reason for the behaviour of the sub-mm current distribution in several cases, e.g. the very low channel resistances and low rib currents upon operation with saturated gases. The current peak in the middle of the channel is thereby narrowing upon increase of the reactant humidity. This observation goes along with results from NR examinations by Boillat and coworkers [185]: liquid water accumulations
are found in the rib covered areas, and expand towards the channel over the rib edges for high humidity conditions.

However, complete reconstruction of the test cell would be required under the aspect of neutron transmittability. Materials such as polymer gaskets have to be avoided because of their high absorbance, the favoured material for the end plates would be the corrosion prone aluminium. Nevertheless, combining the measurement methods seems worthwhile for examining the mechanisms of pore clogging and their impact on the local current generation.

Similar qualitative results can be expected from the combination of the local current density and concomitant x-ray tomography measurements with micrometer resolution ($\mu$-CT). In terms of quantitative analysis, results shown in [88] prove that the 3D liquid water distribution and the solid structure of the GDL can be imaged simultaneously with a resolution of about 1 $\mu$m. Furthermore, it has most recently been shown that it is possible to obtain radiograms of active cells under operation, or subsequently to operation. The available data can be incorporated in an ‘in-situ model’ concerning the transport processes, since accurate knowledge on the porous structure is available.

Less effort for cell reconstruction is necessary here, the biggest problem for operation in an x-ray tomography setup is however the assurance of constant operating conditions without interfering with the measurement.

**Channel/rib Resolved Degradation Measurements.** Another point of interest is the connection between local current distribution and component degradation. It is known that specific degradation mechanisms (i.e. the loss of sulfonic groups) are connected to stress caused by the flux of ions and water through the ionomer. Furthermore, moist environment facilitates the sintering of catalyst, leading to a loss of active area. Both mechanisms are promoted or inhibited with the level of current.

Hence, the degradation of the polymer electrolyte and the catalytic layer might be very different comparing areas covered by a rib to areas in the channel. First evidence of these gradients are described by GUBLER et al. [186, 187], a relation to local current generation could however not be confirmed up to date. Having the tool for sub-mm current measurement available, long-term measurements under different stationary conditions (with qualitatively different current distributions), respectively, and subsequent degradation analysis of the membrane (FTIR) and the active area (CV) would be profitable experiments. The procedure would be possible to realize without major reconstruction efforts.

**Influence of Convective Effects on Sub-mm Current Distribution.** As the last point a sub-mm experiment concerning channel layout is proposed. As mentioned in Chapter 1.2.4, channel structures in technical PEFC typically feature bends or serpentines in order to increase the convective flow under the rib. In doing so, the channel/rib current distribution is expected to be substantially affected, in particular close to bends.

Cooperations with industrial partners have shown that there is a specific interest to understand the impact of these convection effects on the channel/rib current distribution and eventually on cell performance. While a correlation to experimental data has not been made, the problem was
accounted for in modelling [188]. It was found that the convective flow between neighbouring channels induces significant shifting of the oxygen partial pressure distribution towards the rib edge of the flow field shoulder separating the high pressure channel from the low pressure channel. This leads to strongly asymmetric current distributions across channel and rib, with the highest limiting currents at this very rib edge.

To validate this findings, it is possible without major reconstruction of the specialized test cell to modify the straight channel design of the small flow field plates in a way to experimentally assess the current distribution at a desired position after a 90° or 180° turn. For this, the flow field plate needs to be divided in an GDL covered area with parallel channels and an inactive area containing the serpentines or bends. This would go along with a further reduction of the electrochemically active area, which is unproblematic with differential operation. Figure 5.1 illustrates this idea of flow field plates made from two different materials for the case of serpentine channel layouts (a) and the case of channel bends with a specified angle $\alpha$ (b).

![Flow field plate configurations for the measurement of the channel/rib current distribution](image)

**Figure 5.1:** Flow field plate configurations for the measurement of the channel/rib current distribution after a) a serpentine and b) a bend with a specific angle $\alpha$. The plates are divided into an inactive part made from non-conductive material (light regions), containing the channel bends, and an active part made from the original graphitic material (dark regions), containing only parallel channels. The measurement is performed inside the active part, a slot in a subgasket defines the position of measurement.

The Figure illustrates that the actual area of measurement (dark regions) would be restricted to the part with parallel alignment of the channels, which is solely covered by a GDL. The light regions are made from a non-conductive material and have to be insulated with a sub-gasket to prevent perturbation of the wire signals. As a consequence of non-differential operation along the channel, this sub-gasket features only a small slot for allowing contact of the probe wires with the cell components. The width and position of this slot thereby denotes the position of measurement in a specified distance from the serpentine or bend, respectively. This setup allows
5.2. Outlook

for experimental evaluation of the influence of cross-channel convection on the channel/rib current distribution without the need of an intricate change of the wire alignment.

Another idea would be to divide the test cell’s inlet and outlet gas vacuities into two parts, respectively, which are sealed against each other. This way neighbouring channels of the flow field plate could be fed with reactant gas of slightly different pressure, and convection in the GDL is forced under the rib from one channel into another as a consequence of the pressure gradient. Differential operation of the test cell could be maintained as best as possible with this setup.

5.2.2 Optimization of Cell Structures

In this subsection approaches for optimizing cell performance by means of homogenization of the current gradients on the sub-mm and on the single cell scale are discussed. A more uniform current distribution is expected to cause lower total overvoltage, and furthermore to contribute to increased cell lifetime by alleviating stress factors.

Cell Optimization on the Sub-mm Scale. The results of Chapter 3 and 4 emphasize that transport processes in the porous diffusion medium – and their impact on charge transport – are responsible for the quality of local current distribution. Thereby, reactant and product diffusion pathways, and the state of compression of the porous layer, have been highlighted as important issues. To elude limitations stemming from decreased permeability under the ribs, the use of non-compressible materials such as metal foams is proposed for homogenizing the current generation on the sub-mm scale.

![Figure 5.2](image_url)

**Figure 5.2:** Non-compressible foam material as porous transport medium. The rectangular channel design with only one porous wall can be improved by machining round (a) or triangular (b) channels into the foam-type GDL. Electron and diffusion pathways are improved, the channel ratio can be increased and the thickness of the FFP-GDL compound is reduced. Possible materials are stainless steel or carbon composites.

This idea has been accounted for in modelling studies [179, 189], which aimed to develop and evaluate channel-less flow distributors based on conductive foam fleeces sandwiching the electrolyte. However, without a channel structure deteriorating water management would be a consequence of low flow speeds besides high pressure drop. Another idea would thus be to integrate the chan-
nels partly or even completely in the foam-type GDL (thickness ca. 0.5 mm), whereby round (a) or triangular channel shapes (b), rather than rectangular ones, shorten the diffusion pathways to the active layer as illustrated in Figure 5.2. Guided gas flow can be maintained this way, but having porous ribs available could significantly reduce mass transport limitations. The thickness of the non-porous, rib-less flow field plate can thereby be significantly reduced to below one millimeter. At the same time the non-compressible and highly conductive foam provides optimal electron drain without long in-plane transport pathways. The contact to the active layer can be additionally improved by tailoring the pore size distribution in the y-direction; smaller pores are expected to accompany lower electric resistance.

However, there appear to be two problems with this idea. First, the water management with metal foams is unclear. Although hydrophobic coatings can prevent pore clogging with liquid accumulations, the short diffusion pathways could lead to an increase of the water removal rate and entail high cell resistances such as observed in cells with wide channels (see Chapter 4). Careful design studies need therefore to be conducted to optimize water management. Second, finding corrosion-stable metal foams is a material issue. The use of noble metals is implicitly not an option as a consequence of the amount of material needed. Stainless steel could provide an alternative, although also in this case passivation at the non-hydrophobic coated interfaces to the active layer and the FFP could hamper electric conduction with time. A possible solution could be the development of carbon foams such as used as the graphitic matrix in composite bipolar plates. In this case the mechanical stability is however another issue.

**Cell Optimization on the Single Cell Scale.** Regarding the layout of flow channels across the active area of a technical size fuel cell, refinement of the adapted geometry concept and optimization of constructional details, i.e. absolute channel dimensions, has to be done. Increasing the number of channels in the cell while maintaining the rib ratio – therefore smaller channel and rib dimensions are proposed – could further improve cell performance, since the absolute diffusion pathways are shorter and the distribution of compressive is more homogeneous. It is thereby of importance to account for particular operating parameters, since the pressure drop in a channel – as elucidated in Chapter 4.2.2 – is a limiting factor here.

For example, operation with $\text{H}_2/\text{O}_2$ has not been considered in Chapter 4, although the performance gain might be of significantly different quality compared to $\text{H}_2/\text{air}$. Since mass transport limitations near the outlet are less pronounced with the feeding of pure oxygen, expanding the channel in this region could even have a negative influence on performance as a consequence of the decreased flow speed, which reduces the removal rate of liquid accumulations. The concomitant decrease of channel height could however solve this problem. In general, the use of pure oxygen is expected to require smaller expansions in the outlet region, since only the depletion effect of upstream consumption and water enrichment lowers the reactant concentration.

Another field of future development is to account separately for the origin of limitations with respect to anode and cathode side. On the one hand it is a well known context that water drag and cathodic water production results in anode drying. Since both electrodes have always been humidified with identical amounts of water, this effect was not accounted for. On the other hand, it was emphasized in the summary of Chapter 1 that anodic mass transport processes are small and therefore negligible, which remains a realistic assumption. Consequently, losses due to
high membrane resistance stem from the anode side, while the overwhelming majority of mass transport limitations are a problem originating from the cathode. This leads to the proposal to use different flow field dimensions and layouts for both electrodes, different as done in Chapter 4. Accounting for the low mass transport overvoltage stemming from the anode side, an expansion is not necessary here. In fact, a rather high rib ratio between 0.8 and 0.9 with constant width from inlet and outlet seems a worthwhile design, avoiding membrane drying by hampering water removal. The decreased channel cross section is also less problematic with the light hydrogen gas, regarding the pressure drop. Retaining the adapted layout for the cathode, and changing the anode design to constant channel dimensions with a high rib ratio, is expected to be a promising concept for operation of technical PEFC. Experiments on the cell behavior concerning the local current generation on the sub-mm and single cell scale with different anode and cathode geometries can be conducted easily with both test cells; major reconstructive efforts would not be necessary.

Last but not least, the impact of local current homogenization with the adapted design concept on cell lifetime could not be examined throughout this work. However, it can be expected that – as mentioned in Subsection 5.2.1 – some degradation mechanisms are alleviated when the current distribution is more uniform. Subsequently to channel/rib resolved degradation analysis the durability of technical sized fuel cells featuring adapted flow field layouts can be investigated by long term experiments. The lapse of charge and mass transport limitations in the in- and outlet regions can additionally be scrutinized by applying locally resolved impedance spectroscopy (LEIS).
<table>
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**Sub- and Superscripts**

- electron
- proton
- standard state
- activation
- anode side, anodic
- critical
- capillary
- cathode side, cathodic
- of integral cell
- channel related
- catalytic layer
- concentration
- contact interface
- convective
- contact resistance
- catalyst surface
- charge transfer
- osmotic drag
- diffusive
- effective
- electric
- hydraulic
List of Symbols

\begin{itemize}
\item \(i\) species \(i\) or position index
\item \(\text{ion}\) ionic
\item \(\text{int}\) integral
\item \(j\) species \(j\)
\item \(\text{lim}\) limiting
\item \(\text{liq}\) liquid
\item \(K\) Knudsen
\item \(\text{net}\) netto
\item \(\Omega\) ohmic
\item \(r\) reaction
\item \(\text{rev}\) reversible
\item \(\text{rib}\) rib related
\item \(s\) surface
\item \(\text{sample}\) referring to the sample
\item \(tf\) thin film
\item \(\text{th}\) thermal
\item \(\text{tot}\) total
\item \(x, y, z\) in \(x, y, z\)-direction / plane
\end{itemize}

\begin{center}
\begin{tabular}{lll}
\hline
\textbf{Constants} & & \\
\hline
\(R\) & Universal Gas Constant & 8.314 J/K\cdot mol \\
\(F\) & Faraday constant & 96'485.3 C/mol \\
\hline
\end{tabular}
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\begin{tabular}{ll}
\hline
\textbf{Abbreviations} & \\
\hline
PEFC & Polymer Electrolyte Fuel Cell \\
OCV & Open Circuit Potential \\
MPP & Maximum Power Point \\
MEA & Membrane Electrode Assembly \\
CCM & Catalyst Coated Membrane \\
CL & Catalytic Layer \\
GDL & Gas Diffusion Layer \\
MPL & Microporous Layer \\
FFP & Flow Field Plate \\
CC & Current Collector \\
CFD & Computational Fluid Dynamics \\
FEM & Finite Element Method \\
EIS & Electrochemical Impedance Spectroscopy \\
LEIS & Localized EIS \\
NR & Neutron Radiography \\
\(\mu\)-CT & Micrometer-resolved X-Ray Tomography \\
\hline
\end{tabular}
\end{center}
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