Neutron radiography of Polymer Electrolyte Fuel Cells: From conventional towards energy selective neutron imaging

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presented by
Johannes Biesdorf

Dipl. Ing. in Mechanical Engineering
TU Kaiserlautern
born May 29th 1988
in Trier (D)

accepted on the recommendation of
Prof. Dr. T. J. Schmidt, examiner
Prof. Dr. A. Wokaun, co-examiner
Dr. P. Boillat, co-examiner

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Abstract

Polymer electrolyte fuel cells (PEFCs) are electrochemical energy converters, which provide electric power for stationary, automotive as well as portable applications. Especially for mobile usage, highest power densities are required to operate at high current densities ($> 1 \text{ Acm}^{-2}$). At these operating conditions, excessive product water accumulates inside the porous layers of the fuel cell, blocking the supply of reactant gases and leads to a significant drop in performance (so called mass transport losses). Besides that, liquid water accumulation risks to freeze under subfreezing conditions, which may lead to an irreversible failure of the fuel cell. In order to increase the power density or prevent the damage of a PEFC, the water transport is studied in this thesis with neutron radiography at subfreezing as well as at technical operating conditions. The work consists of three main contributions:

First, a new methodology to differentiate ice from water was developed. This technique relies on diverging neutron cross section of liquid and frozen water at low neutron energies ($> 4 \text{ Å}/5.1 \text{ meV}$). Based on the comparison of images recorded at two distinct neutron energies, water and ice can be differentiated inside fuel cells. This technique was applied with three energy selective imaging techniques: Neutron filter methodology, Velocity selector technique and time of flight method. In these studies, the best applicability regarding time, spatial and energy resolution for fuel cells was obtained with a motorized neutron filter. Based on this technique, the production of supercooled water at subfreezing temperatures was proven for the first time with a direct measurement methodology.

Second, a parametric study with different materials was performed in order to maximize the operating time under subfreezing conditions without failure of the cell. As the transition of supercooled to frozen water occurs spontaneously, a statistical analysis of 1200 cold starts was carried out on small scale PEFCs. It was found out that material variations have a minor influence compared to statistical effects induced by inhomogeneities of the material. Furthermore, the size of the active area has shown a significant influence. This effect could be explained based on a Monte Carlo simulation of the freezing event that highlights a more pronounced probability of facing a seed in larger fuel cells. Hence, for fuel cells of technical size, operating times longer than 5 minutes could not be achieved at subfreezing temperatures.
In the last part, the impact of hydrophobic coatings of commercial gas diffusion layers (GDL) on the water transport was studied based on four different combinations of PTFE-loadings on anode and cathode side. The experiments were performed on differential PEFCs which were analyzed with high resolution neutron radiography and two electrochemical methods: (1) pulsed gas analysis and (2) limiting current density measurements. By combining the neutron radiographs with the two electrochemical measurements, a novel insight on the influence of water on mass transport losses was obtained. It was found out that under high humidification conditions not more water accumulates inside GDLs without hydrophobic coating than inside coated GDLs. In fact liquid water distributes differently and builds up in the region under the flow channel, leading to significant mass transport losses. Despite a relatively small quantity of water, cells with high PTFE coating show higher mass transport losses, which can be explained by a different morphology of water accumulation.
Zusammenfassung

Polymerelektrolytbrennstoffzellen (PEFCs) sind elektrochemische Energiewandler, die elektrische Energie für stationäre, automobile, aber auch für portable Anwendungen liefern können. Speziell für mobile Anwendungen werden höchste Leistungsichten bei Stromdichten über 1 A cm\(^{-2}\) benötigt. Unter diesen Betriebsbedingungen kondensiert Produktwasser und sammelt sich in den porösen Schichten an. Bei hohen Wassersättigungen kann dies zu einer Blockierung der Reaktanden führen, was anschliessend eine Reduktion der Leistung bedingt (sog. Massentransportverluste). Zudem kann eine überschüssige Wasseransammlung bei Temperaturen unterhalb des Gefrierpunktes gefrieren und einen irreversiblen Schaden in der Zelle verursachen. Um den Wassertransport in der Zelle für hohe Leistungsichten zu optimieren und einen Schaden unterhalb des Gefrierpunktes zu verhindern, wird in der vorliegenden Doktorarbeit der Wassertransport mittels Neutronenradiographie unter technischen Betriebsbedingungen, wie auch bei Temperaturen unterhalb des Gefrierpunktes untersucht. Die Arbeit ist in drei Teile untergliedert:


Im zweiten Teil der Arbeit wurden Materialien hinsichtlich ihrer Eignung bei Betrieb unterhalb des Gefrierpunktes untersucht. Da der Phasenübergang von metastabilem unterkühltem Wasser spontan abläuft, wurde eine statistische Analyse von 1200 Kaltstarts mit Brennstoffzellen einer aktiven Fläche von 1 cm\(^{-2}\) durchgeführt. Hierbei konnte festgestellt werden, dass Materialvariationen lediglich einen kleinen Einfluss im Vergleich zu statistischen Effekten (z.

Im letzten Teil der Arbeit wird der Einfluss einer hydrophoben Beschichtung von kommerziellen GDLs auf den Wassertransport mit vier unterschiedlichen Kombinationen von PTFE-Beschichtungen auf der Kathoden- und Anodenseite untersucht. Diese Versuchsreihen wurden mit differentiellen Brennstoffzellen durchgeführt, welche sowohl mit hochauflösender Neutronenradiographie als auch mit zwei elektrochemischen Methoden wie der Gaspulsanalyse und der Grenzstromdichtemessung untersucht wurden. Mit der Kombination aus bildgebenden Verfahren und elektrochemischen Methoden konnte ein neuer Einblick hinsichtlich Massentransportverluste von Brennstoffzellen gewonnen werden. Es wurde festgestellt, dass GDLs ohne Beschichtung unter hoher Befeuchtung nicht mehr Wasser akkumulieren als beschichtet GDLs. Vielmehr verteilt sich das Wasser unterschiedlich und sammelt sich vor allem unterhalb des Gaskanals an, was zu hohen Massentransportverlusten führt. Zellen mit hoher hydrophober Beschichtung haben trotz geringerer Wassersättigung höhere Massentransportverluste, was mit einer unterschiedlichen Morphologie der Wasseransammlung erklärt werden kann.
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1

Introduction

1.1 Motivation

The world energy demand has grown over the past 100 years due to the population and wealth growth [1, 2]. This rising demand of energy is mainly satisfied by combustion of fossil fuels like natural gas, crude oil, or coal, releasing CO\textsubscript{2} as a reaction product to the atmosphere. Although nature is able to reconvert CO\textsubscript{2} to biomass and afterwards to fossil fuels again, this process takes several millions of years. Hence, with our current energy policy, more fossil fuels are converted into CO\textsubscript{2} than vice versa, leading to tremendous consequences on our climate like rising average temperatures.

One potential candidate for the replacement of fossil fuels is the utilization of renewable energies combined with hydrogen as an energy carrier. Hydrogen can be produced via e.g. water electrolysis [3] which can be fed by electricity gained from renewable energies like e.g. photovoltaic or wind energy. Via this conversion, electrical energy is transformed into chemical energy kept inside the hydrogen-hydrogen bond, which can be stored inside pressurized vessels of gaseous/liquid hydrogen or bounded in metal-hydrides. With regard to seasonal and daily fluctuations of renewable energies, these variations can be easily balanced with a hydrogen storage. The chemical energy of hydrogen can then be reconverted via fuel cells into electrical energy, which release H\textsubscript{2}O as single reaction product. With the combination of both techniques, high electron-to-electron round-trip efficiencies of up to 40% can be achieved [4]. By closing this hydrogen cycle [5] with the combination of water electrolysis and fuel cells, a fossil fuel based economy can be converted to a sustainable economy.

The first generation of polymer electrolyte fuel cells (PEFC) was successfully launched to the automotive market (e.g. Toyota Mirai). However, several improvements regarding costs, durability and cold start capability have to be addressed to ensure a reliable operation under all operating conditions [6] and to be competitive to fossil fuels. One of the key parameter, which directly impacts all these limitations, is the water management inside the PEFC. Although
various research was performed in previous studies (see literature review in subsection 2.1.2), a complete picture of the water transport phenomena at subfreezing ($T < 0^\circ \text{C}$) as well as at normal operation temperatures ($60 \leq T \leq 80^\circ \text{C}$) is still not existing. With the contributions of this PhD thesis, the picture about the water transport phenomena inside PEFCs is broadened, to accelerate the transition from a fossil fuel based economy to a hydrogen based economy.

1.2 Working principle of Polymer Electrolyte Fuel Cell

In this section, the working principle of the PEFC will be presented based on Figure 1.1, representing the anode on the left and the cathode on the right side.

A fuel cell is a galvanic cell which converts chemical into electrical energy by an electrochemical reaction of hydrogen and oxygen (see Figure 1.1). The produced ionic charge is transported through an electrolyte in between the two half-cells, whereas the remaining electrons are forced to pass through an external electric circuit, where electric power can be extracted. Although many properties are identical compared to a battery, the main difference is the continuous supply of the reactant gases to the cell [3].

![Figure 1.1: Schematics of the working principle of a PEFC. Adapted from [7].](image)

Different types of fuel cells can be classified according to the electrolyte, reactant gases, operating temperature [8]; all experiments presented in this thesis are performed on the PEFC. The proton conductivity of PEFCs relies on a polymer membrane, which consists of a hydrophobic backbone structure (typically PTFE/Teflon-like) substituted with side chains terminated by a
1.2 Working principle of Polymer Electrolyte Fuel Cell

sulfonic acid group ensuring the proton conductivity (more details are given in subsection 1.4.1). The main advantage of this cell technology is a high proton conductivity at low temperatures (< 100°C); major drawback is a rather complex water management required by the membrane [8].

The anode is defined as the electrode where the hydrogen oxidation, the cathode where the oxygen reduction takes place. On the anode side, \( H_2 \) is oxidized into \( H^+ \) and \( e^- \) according to the hydrogen oxidation reaction (HOR):

\[
H_2 \rightleftharpoons 2H^+ + 2e^- \quad (1.1)
\]

As the polymer electrolyte is proton conductive and electrically insulating, the \( H^+ \) can be transported across the membrane to the cathode, whereas the \( e^- \) have to pass via an external circuit, creating an electrical current. On the cathode side \( O_2 \) is reduced into water according to the oxygen reduction reaction (ORR):

\[
\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O \quad (1.2)
\]

The sum of the two half-cell reactions results in the following overall reaction of a fuel cell:

\[
H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O \quad (1.3)
\]

Based on the reaction enthalpy \( \Delta H_r^0 \) of the reaction under standard conditions (depicted as \( ^0 \)) [3], a thermo-electric cell voltage \( U_{th}^0 \) can be calculated as follows:

\[
U_{th}^0 = -\frac{\Delta H_r^0}{zF}, \quad (1.4)
\]

where \( z \) depicts the number of electrons transferred, \( F \) is the Faraday constant. Under standard conditions, a voltage of 1.48 V is obtained for the PEFC. However, according to the second law of thermodynamics, entropy losses have to be taken into account. Hence, a reversible voltage \( U_{rev}^0 \) is introduced, which is calculated based on the Gibbs energy \( \Delta G_r^0 \) according to the following equation:

\[
U_{rev}^0 = -\frac{\Delta G_r^0}{zF}, \quad (1.5)
\]

Under standard conditions, a voltage of 1.23 V is obtained. As PEFCs are commonly operated at deviating temperatures and pressures, the temperature dependence of the Gibbs energy \( \Delta G_r \) has to be taken into account as follows [9]:

\[
\Delta G_r(T) = \Delta H_r(T) - T\Delta S_r(T), \quad (1.6)
\]

where \( \Delta S_r \) denotes the entropy of the reaction. Based on Equation 1.6, a temperature dependent \( U_{rev}(T) \) can be calculated:

\[
U_{rev}(T) = -\frac{\Delta G_r(T)}{zF}, \quad (1.7)
\]
A pressure dependency can be included into Equation 1.7 based on the Nernst-Equation, which can be derived from the chemical potential [10]. For the PEFC the equation results as follows:

\[ U_{\text{rev}}(T,p) = U_{\text{rev}}(T) + \frac{RT}{2F} \ln \left( \frac{p_{\text{H}_2} \cdot p_{\text{O}_2}^{0.5}}{p_{\text{H}_2O} \cdot p_{\text{O}_2}^{*}} \right), \]

where \( p_{\text{H}_2} \) and \( p_{\text{O}_2} \) denote the partial pressures of hydrogen and oxygen, and \( p_{\text{H}_2O} \) the partial pressure of water at the catalyst. The exponent (\( * \)) expresses the individual pressure at standard conditions. Inside the catalyst layer, \( p_{\text{H}_2O} \) can be assumed to equal to the saturation pressure of water. Hence, under typical operating conditions (Air operation under \( T = 70^\circ \text{C} \) and \( p = 2 \text{ bar}_{\text{abs}} \)), a reversible voltage \( U_{\text{rev}} \) of around 1.19 V is obtained.

### 1.3 Loss mechanisms

In this section, the occurring loss mechanisms during operation are being presented. The individual cell components mentioned - in particular the catalyst layer (CL), the gas diffusion layer (GDL) and the flow field (FF) - will be introduced later on in section 1.4.

Equation 1.8 describes the theoretical equilibrium potential of a PEFC given by thermodynamics without any exchange of charge. However, experimentally this condition cannot be reached. Any deviation of the cell voltage \( U_{\text{Cell}} \) from the Nernst potential is defined as overpotential \( \eta \), being equivalent to a performance loss:

\[ \eta = U_{\text{rev}}(T,p) - U_{\text{Cell}} \]

![Figure 1.2: UI-curve of a PEFC operated under Air at 70°C and 2 bar_{abs}, showing the different loss contributions.](image)
1.3 Loss mechanisms

A valuable tool to characterize these overpotentials is a so-called polarization curve (also UI-curve), which plots the cell voltage as a function of the cell current normalized to its geometrical active area. Figure 1.2 shows an example of a UI-curve of a PEFC operated under air at 70°C and 2 bar abs. As can be seen, the Nernst-Potential is not reached, which can be explained by fuel crossover and unavoidable parasitic reactions on the cathode side [11]. Furthermore, as the membrane is not a perfect isolator, some minor electric currents in the range of a few milliamperes may cross the membrane decreasing the cell voltage [11]. The intercept of the y-axis will be defined as open-circuit voltage (OCV).

The cell potential is determined by three major performance loss mechanisms: (1) charge transfer overpotentials $\eta_{\text{HOR}}$ and $\eta_{\text{ORR}}$, (2) ohmic $\eta_{\text{IR}}$ as well as (3) mass transport overpotentials $\eta_{\text{bulk,MTL}}$ and $\eta_{\text{non-bulk,MTL}}$. The effective cell potential can be best described as follows:

$$U_{\text{cell}} = U_{\text{rev}}(T,p) - \eta_{\text{CT}} - \eta_{\text{Ohm}} - \eta_{\text{MTL}}$$  \hspace{1cm} (1.10)

In the following sections, the individual loss contributions are presented in more detail.

1.3.1 Charge transfer overpotential

The charge transfer overpotential is linked to an energy barrier which separates the oxidized from the reduced species of an electrochemical reaction. This energy barrier results from the differences of the Gibbs Energy of the surface chemisorption on the catalyst layer (CL) and the charge transfer reaction itself [10]. This energy barrier limits the kinetics of the electrochemical reaction and can be described according to the Butler-Volmer equation. For the HOR on the anode side of a fuel cell, the net current $i_{\text{anode}}$ can be described as follows:

$$i_{\text{anode}} = i^+ + i^- = i_{0,\text{HOR}}^+ \cdot e^{\eta_{\text{CT,HOR}}^+ \frac{a_{\text{HOR}}}{{RT}}} + i_{0,\text{HOR}}^- \cdot e^{-\eta_{\text{CT,HOR}}^- \frac{a_{\text{HOR}}}{{RT}}}$$  \hspace{1cm} (1.11)

where $i_{\text{anode}}$ depicts the net current on the hydrogen electrode which is the sum of its current in anodic $i^+$ and cathodic $i^-$ direction, $\alpha_{\text{HOR}}^+$ and $\alpha_{\text{HOR}}^-$ are the transfer coefficients for the anodic and cathodic reaction, respectively. $i_{0,\text{HOR}}^+$ and $i_{0,\text{HOR}}^-$ represent the exchange current density of the anodic and cathodic reaction. The ORR of a fuel cell can be described analogical:

$$i_{\text{cathode}} = i^+ + i^- = i_{0,\text{ORR}}^+ \cdot e^{\eta_{\text{CT,ORR}}^+ \frac{a_{\text{ORR}}}{{RT}}} + i_{0,\text{ORR}}^- \cdot e^{-\eta_{\text{CT,ORR}}^- \frac{a_{\text{ORR}}}{{RT}}}$$  \hspace{1cm} (1.12)

As the kinetics of the HOR are several orders of magnitudes higher compared to the ORR [11], the overall reaction is mainly determined by the sluggish kinetics of the ORR. Hence, the total current density $i$ of a PEFC can be defined as follows:

$$i = i_{\text{cathode}} = i^+ + i^- = i_{0,\text{ORR}}^+ \cdot e^{\eta_{\text{CT,ORR}}^+ \frac{a_{\text{ORR}}}{{RT}}} + i_{0,\text{ORR}}^- \cdot e^{-\eta_{\text{CT,ORR}}^- \frac{a_{\text{ORR}}}{{RT}}}$$  \hspace{1cm} (1.13)
1. INTRODUCTION

Under usual fuel cell operating conditions with \( i^- > 10 \cdot i^+ \), the anodic contribution \( i^+ \) of the ORR can be neglected. Hence, Equation 1.13 can be reformulated to the so called Tafel equation [12]:

\[
\eta_{CT} = \frac{RT}{a_{O_{2}R} z F} \ln \left( \frac{i}{i_{0,ORR}} \right)
\] (1.14)

1.3.2 Ohmic losses

The ohmic losses arise due to three different contributions: (1) ionic resistance of the ionomer \( r_{ion} \) inside the membrane and the CL, (2) electrical resistance of the different layers \( r_{elec} \), and (3) electrical contact resistances between the different layers \( r_{contact} \). The three terms can be summarized into a resistivity \( r \) and linked to an overpotential \( \eta_{Ohm} \) as follows:

\[
\eta_{Ohm} = (r_{ion} + r_{elec} + r_{contact}) \cdot i = ri.
\] (1.15)

In commonly used materials, around 50% of \( \eta_{Ohm} \) results from the ionic resistance. As was already stated in a previous section, the conductivity of the polymer membrane is highly dependent on the operating condition; the higher the hydration state and temperature, the higher the conductivity. According to ref [13], the conductivity of a membrane \( \sigma(T_{cell}, \lambda) \) at a temperature \( T_{cell} \) and the hydration state \( \lambda \) can be best described as follows:

\[
\sigma_{mem}(T_{cell}, \lambda_{hydra}) = \exp \left( \frac{T_{1}}{T_{2}} \cdot \left( \frac{1}{T_{3}} + \frac{1}{T_{cell}} \right) \right) (a \lambda_{hydra} - b).
\] (1.16)

The hydration state \( \lambda_{hydra} \) describes the ratio between water molecules and the number of \( SO_3^- H^+ \) sites. \( T_1, T_2, T_3, a \) and \( b \) are constants which can be found in the glossary. The membrane thickness should be minimized as it scales proportionally with the resistivity [3]. However, the thinner a membrane is, the more hydrogen and oxygen molecules can diffuse across the membrane (so called crossover), which reduces the open-circuit voltage and the efficiency of a cell. A typical thickness of state of the art materials is around 20 \( \mu m \).

The second half can be attributed to limited electrical conductivity of the different layers and electrical contact resistances between the different layers. \( r_{elec} \) is dependent on the electrical conductivity of the fuel cell materials like flow fields, current collector and the GDL. \( r_{contact} \) results from the at least four interfaces of flexible materials. Especially the interfaces of the porous GDL and flow field are assumed to account for a significant portion. The contribution of the contact resistance can be reduced by higher compression rates (see subsection 2.5.5).

From Equation 1.15 it is expected that \( \eta_{Ohm} \) scales linearly with the current density. However, especially under dry conditions, deviating results are obtained experimentally, which can be explained by a higher back-diffusion rate of product water.
1.3 Loss mechanisms

1.3.3 Mass transport losses

While operating a cell under air instead of pure oxygen, additional mass transport losses (MTL) are arising at high current densities due to diffusion limitations of oxygen in nitrogen. This effect is mainly caused by two mechanisms: First, inside technical fuel cells with low stoichiometries ($\lambda_{stoic} < 2$) oxygen is consumed along the channel, leading to reduced partial pressures of oxygen towards the outlet of the cell. Second, the supply of reactants is limited by the diffusion across the GDL from flow field to CL as well as in lateral direction to overcome the pattern of the flow field. In a first approximation, the diffusion inside the GDL of a thickness $\delta$ can be described by one dimensional Fick’s diffusion. If we assume a reference concentration of oxygen $c_{O_2,ref}$ inside the flow channels of the flow fields and a Diffusion coefficient $D$, the diffusion induced by the consumption of oxygen $c_{O_2}$ can be described as follows:

$$i = zFD \left( \frac{c_{O_2,ref} - c_{O_2}}{\delta} \right). \quad (1.17)$$

Consequently, the maximal current - also called limiting current $i_{lim}$ - can be calculated at a full depletion of the oxygen concentration on the catalyst surface ($c_{O_2} = 0$) and results as follows:

$$i_{lim} = zFD\frac{c_{O_2,ref}}{\delta} \quad (1.18)$$

The effect of reduced concentration of reactant gases at the electrode reduces both the Nernst potential $U_{rev}(T,p)$ (see Equation 1.8) as well as the exchange current density $i_{0,ORR}$. These effects can be summarized in the following equation:

$$\eta_{MTL} = \left( 1 + \frac{1}{\alpha_c} \right) \frac{RT}{zF} \ln \left( \frac{c_{O_2,ref}}{c_{O_2}} \right) \quad (1.19)$$

It has to be remembered that Equation 1.19 is derived based on the one-dimensional law of Fick diffusion. In a fuel cell, a full description of the mass transport becomes more complicated, as the diffusion is three dimensional inside an anisotropic porous medium (see section 2.2).

Diffusion processes

Inside the PEFC, three main diffusion processes can be distinguished: Bulk diffusion, Knudsen diffusion and thin film diffusion.

**(1) Bulk diffusion:** The bulk diffusion occurs inside pores with sizes significantly larger than the mean free path of the gas molecules, which is predominantly the case inside the GDL. For diffusion processes of structures with condensed liquid water, an effective diffusivity $D_{eff}$ has to be calculated [14]:

$$D_{eff} = \frac{\epsilon(s)}{\tau(s)} D_{bin}, \quad (1.20)$$

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Figure 1.3: Schematics of different types of diffusion processes inside porous media: (a) Knudsen diffusion, (b) Film diffusion, and (c) Bulk diffusion.

where $D_{bin}$ depicts the binary diffusion coefficient of oxygen in nitrogen. The tortuosity $\tau(s)$ and the porosity $\epsilon(s)$ are functions of the water saturation level $s$ inside the GDL.

(2) Knudsen diffusion: In case the pore diameter $d$ is in the range of the mean free path of the gas molecules ($<35\text{ nm}$ in case of O$_2$ at 2 bar [15]), Knudsen diffusion has to be taken into account. Knudsen diffusion coefficient $D_{Kn}$ can be described as follows: [16]

$$D_{Kn} = \frac{2}{3} \sqrt\frac{8RT}{\pi m} \frac{d}{2},$$

with $m$ being the molar mass of the gas mixture. As the gas molecules interact more frequently with the pore wall than with gas molecules, Knudsen diffusion is only dependent on the partial pressure and independent on the inert gas (e.g. not affected by exchanging the carrier gas N$_2$ by Helium).

(3) Film diffusion: The third diffusion mechanism is thin film diffusion which occurs inside the CL, where oxygen has to diffuse through films of ionomer or water in order to reach the triple-phase-boundary. Similar to the Knudsen diffusion, thin film diffusion is only dependent on the partial pressure of the gas and not on the carrier gas.

1.4 Cell components

In this section, the different cell components of a fuel cell will be presented.

1.4.1 Membrane

The polymer electrolyte membrane has to fulfil three different requirements: Proton conduction, electrical insulation, and separation of reactant gases [17]. The commonly used electrolyte for PEFCs is a perfluorsulphonic acid (PFSA), which is a co-polymer composed of two components
1.4 Cell components

(see Figure 1.4). First, the membrane consists of a hydrophobic and chemically inert polytetrafluoroethylene (PTFE - better known under the brand name Teflon of DuPont Co.) backbone which ensures mechanical stability. Second, onto this backbone, hydrophilic side chains made of perfluorinated ethers are chemically linked ending up with $HSO_3$ to make the material proton conductive.

![Chemical structure of a PFSA membrane (m=5-13; n=1-3).](image)

In the dry state of the membrane, the ionic side chains are isolated and ions cannot be conducted [18]. However, while exposing the membrane with liquid or water vapour, the hydrophilic regions of the membrane take up water - so called swelling of membrane - building up an interconnected network of the ion conductive polymer phase. Although in literature there is still an ongoing debate about the exact transport mechanism in a PFSA membranes, it is assumed that the ion transport is based on the combination of the Grotthus and vehicle mechanism. The Grotthus mechanism transfers the $H^+$ Ion because of the formation of hydrogen bridges in between the water molecules, followed by a rearrangement of the local molecular structure. The vehicle mechanism transports the $H^+$ Ion via diffusion as a bounded $H_3O^+$ molecule enclosed inside a hydration shell [19].

1.4.2 Catalyst layer

The catalyst layer (CL) provides the reaction sides for the electrochemical reactions - so called triple phase boundaries for electron, proton, water and gas transport. State of the art catalysts consist of a porous layer (approx. 50% porosity) with pore sizes in the range of 30 nm, composed of three main components: The electronically conductive support, catalyst particles, and electrolyte (see Figure 1.5). The support particles are the structural basis for the catalyst
nanoparticles and ensure the transport of electrons. The catalyst nanoparticles - commonly platinum - have the function to reduce the activation barrier between the oxidized and reduced species (see Equation 1.13). In order to ensure ionic transport, the CL is covered with an ionomer-film. To keep a sufficient diffusivity of the reactant gases without too dominant diffusion limitations, a certain pore space is maintained. In the research field of catalyst for fuel cells, various research groups are working on less expensive catalysts, more durable supports and maximized activities.

1.4.3 Gas diffusion layer

The gas diffusion layer (GDL) is a highly porous structure between the CL and the flow field, which for state of the art materials consists of two main components: micro-porous layer (MPL) and the substrate.

The micro-porous layer (MPL) is a layer of sintered carbon black and PTFE which is mostly coated on top of the substrate [21]. This layer has a much smaller pore size compared to the substrate (50-100 nm [22]), which results in an excellent electrical and thermal contact between CL and the GDL, while providing a sufficient diffusivity for the reactant gases. Based on the small pore size, relatively high capillary pressures are required to penetrate liquid water (see Equation 1.22). However, the water transport can be facilitated by cracks/imperfections induced by the sintering process, which serve as preferential pathways for the evacuation of product water from the CL [23].

The substrate itself is made of carbon fibres ensuring a good electrical, mechanical and thermal contact with a porosity of approx. 75% and a thickness of around 200 µm. This carbon

---

structure is coated with a hydrophobic agent (e.g. PTFE) in order to adjust the water transport properties. GDLs can be realized as carbon paper (see Figure 1.6 (a, b)), carbon cloth (see Figure 1.6 (d)) and carbon non-woven (see Figure 1.6 (c)). The production process of carbon cloth GDLs is rather expensive; hence carbon fiber GDL are favoured. The latter are commonly produced based on a Polyacrylnitril precursor, which is then spun into fibers, stabilized at around 200° C and carbonized at temperatures above 1000° C. As can be seen in Figure 1.6, the morphology of the substrate strongly varies according to its manufacturing process. A good overview about the different production processes of GDLs can be found in ref [24].

Inside a GDL liquid water propagates under the effect of capillary pressure and vapour diffusion from the CL to the flow channel [25]. For pore networks with certain wettability, the capillary pressure $p_c$ can be calculated according to the Young-Laplace equation [26, 27]:

$$p_c = p_{nw} - p_w = \frac{2 \lambda_{surface} \cos(\theta)}{r_{pore}},$$

where $p_{nw}$ depicts the partial pressure of the non-wetting phase, $p_w$ the pressure of water, $\lambda_{surface}$ the surface tension of water, $\theta$ the contact angle of water with the pore walls and $r_{pore}$ the radius of pore (assuming cylindrical pores). As can be deduced from Equation 1.22, the water pathways are created through pores with the lowest contact angle and the highest pore radius. After having created a certain number of pathways from the CL towards the flow channel, water will permeate along these preferential pathways.

![Figure 1.6: SEM radiographs of three different GDL substrates: Paper in (a) SGL, (b) Toray; Non-woven in (c) Freudenberg, Carbon cloth in (d).](image)
1. INTRODUCTION

In opposite direction, a sufficient diffusivity of the reactant gases has to be ensured to sustain the electrochemical reaction with limited mass transport losses (see section 1.3). As can be seen from Equation 1.22 and Equation 1.20, this concurrent two-phase flow can be adjusted by the material properties of the GDL such as hydrophobicity, porosity, or thickness. A hydrophobic coating affects the diffusion media in different ways: (i) by increasing the water contact angle and thus the capillary pressure, (ii) by modifying the diffusion structure of the dry material, and (iii) by affecting some characteristics such as the thermal conductivity. This effect will be studied in detail in chapter 5.

1.4.4 Flow fields

The flow fields contain small channels moulded, milled or stamped into a metallic or carbon composite plates to ensure the supply of the reactant gases across the active area. The arrangement of the flow channels highly affects the gas distribution and hence the performance of the cell. Mainly four different flow field layouts are utilized: (1) parallel, (2) serpentine, (3) interdigitated, and (4) their combination. In this thesis, the experiments are mainly performed on a flow field with parallel flow channels (see section 2.5) and in section 4.6 a flow field with 5 parallel serpentine flow channels is used.

In general, a flow field should be electrically conductive and serve as a mechanical support for the individual layers. Commonly, carbon composite is used for small series, whereas stamped stainless steel plates are used for mass production. In present work, aluminium flow fields are used, which are coated with a thin layer of gold preventing the oxidation of the surface. Aluminium was chosen to obtain a high transparency during the neutron experiments (see section 2.1).

1.5 Water management

During fuel cell operation, product water can be used to hydrate the polymer membrane to ensure a good proton conductivity. However, an excess of liquid water may block the pathways of the reactant gases which might induce mass transport losses. Hence, it is of crucial importance to understand and adjust the water transport in PEFCs.

1.5.1 Water balance

As can be seen from the overall reaction in Equation 1.3, water is produced inside the cathode CL of the PEFC. This product water is mainly transported in two ways (see Figure 1.7). First, water can be evacuated from the reaction sides via vapor diffusion or capillary transport of liquid water towards the flow fields of the cell, where it can be removed by the convective flow of...
the reactant gases. Second, water can diffuse across the membrane, induced by a concentration gradient of water between anode and cathode side, which is called back diffusion. Another water transport mechanism is the osmotic drag, which results from the proton transport from anode to cathode across the membrane. This results from the fact that water is not transported as a single $H^+$; it is transported in the form of a bounded species like e.g. a hydronium ($H_3O^+$) encased with a hydration shell of several water molecules.

Besides the intrinsic humidification of the PEFC by product water, additional humidification is commonly required to ensure a sufficient hydration of the ionomer. Technically, this is realized by the humidification of the inlet gas stream. By bringing water in vapor phase to the different half-cells of the fuel cell, the water balance can be adjusted according to the requirements of the individual operating condition.

### 1.5.2 Water management related overpotentials

In this subsection, the influence of the water management on the overpotentials will be presented:

- **Charge transfer losses:** The charge transfer losses have only a minor dependency on the water balance. However under very dry conditions with a really low hydration state of the membrane, the hydrogen protons cannot be transported as $H_3O^+$. Besides that,
1. INTRODUCTION

at very low partial pressures of water inside the CL, the Nernst potential can be affected according to Equation 1.8.

- **Ohmic losses:** As stated in previous section (see Equation 1.16), the proton conductivity of the polymer membrane is highly dependent on its hydration state \( \lambda_{\text{hydra}} \); the higher the amount of water, the higher the conductivity of the membrane. Consequently, the hydration state is strongly dependent on the equilibrated water balance inside the fuel cell. It has to be mentioned that with state of the art materials of a membrane thickness of 20 \( \mu \)m, the amount of ionomer inside the CL plays an increasing importance on the ohmic losses, particularly under dry conditions.

- **Mass transport losses:** As presented in previous paragraph, the water management highly affects the mass transport losses. Primarily, mass transport losses are related to liquid water condensation inside the PEFC, which reduces the effective diffusivity according to Equation 1.20. This concerns both, diffusion limitations inside the GDL as well as inside the CL.

1.5.3 Water management under freezing conditions

As liquid water risks to freeze at subfreezing temperatures, the water management becomes even more critical compared to normal operating conditions. Freezing of liquid water may lead to a blockage of the reactant gases, modification of the porous structures or shifting of sealings, which has to be prevented by all means.

In literature, several contradicting explanations about the freezing mechanism are published. It is widely accepted that the product water produced during the first minutes of subfreezing operation is primarily taken up by the hydrophilic polymer membrane, which can be identified by a decreasing membrane resistance. After this period, the ohmic resistance stabilizes, indicating an equilibration of the water amount inside the membrane. There is still an ongoing debate about the aggregate states of water inside the membrane. Differential scanning calorimetry (DSC) measurements [29–31] suggested a partial freezing of water, whereas contradicting results were found with X-Ray scattering [32, 33].

Besides product water which is diffusing back into the membrane, water is present in the CL. Concerning its aggregate state, contradictory findings were published. Some studies [34–38] claim that all product water produced during the startup freezes inside the CL of the cathode. After filling a certain amount of the pore space with ice, the reactant gases are blocked, leading to a breakdown of the electrochemical reaction. Such claims were contradicted by visualization

1.6 Scope of this work

experiments [39, 40], which identified liquid water inside the GDL and flow channels. Furthermore, if all the product water would be systematically frozen, a reproducible operating time proportional to the quantity of water needed to block the CL would be expected. However, during previous measurements of our group, [39] a stochastic freezing behaviour was observed with operating times ranging from 10 minutes up to more than two hours of operation. This variation can be explained by the production of supercooled water [40], which is in good agreement to studies performed with imaging [39, 41, 42] where supercooled water was undoubtedly identified inside the GDL and flow fields. Besides the proof by imaging, Oberholzer et al. [39] have shown that the phase transition could be triggered by a mechanical shock onto the PEFC.

Supercooled water is a well-known phenomenon, which describes liquid water below its thermodynamic melting point [43–46]. This aggregate state is metastable and its phase transition to frozen water occurs randomly [47]. The probability of freezing is dependent on the temperature of subcooling and the cluster/droplet volume. Furthermore, it has been reported that the phase transition can be released by agitation, mechanical shock or friction [48] as well as by facing a seed like a small ice nuclei, fiber breaks, asperities or micro cracks. The droplet size is particularly important for fuel cell research as shown in a recent publication of Ishikawa et al. [49]. They proved that the stability of supercooled water is ensured until the droplets reaches a critical size of around 10 nm at -10°C and 3 nm at -30°C. Hence, with state of the art CL with pores in the order of 30 nm, water may freeze in the CL [50, 51].

1.6 Scope of this work

The scope of the present PhD thesis is to enhance the understanding of the water transport inside PEFCs at technical as well as at subfreezing operating temperatures with neutron radiography. This PhD thesis follows the three dissertations performed at PSI by Dennis Kramer [52], Pierre Boillat [53] and Pierre Oberholzer [7], specifically targeting to a better understanding of the freezing mechanism inside fuel cells.

In general, the layout of the thesis follows a top-down approach, steadily refining the level of precision. A new imaging methodology to differentiate water and ice will be presented in chapter 3. The methodology is studied with three different energy selective neutron imaging techniques on a global scale of the PEFC. Subsequently, the influence of the active area size on the freezing behaviour is studied in section 4.6. This chapter is followed by investigations of different GDL materials at subfreezing temperatures, studied with neutron imaging on a macroscopic scale (section 4.7). In the last chapter (see chapter 5), the impact of hydrophobic coatings inside commercial GDL is studied with high resolution neutron radiography on the microscopic scale under technical operating conditions.
1. INTRODUCTION

In the subsequent chapter, the characterization methods used during this thesis are presented. First, an introduction about neutron imaging is given with fundamentals about the imaging setups, image processing and special adaptations for fuel cell research. This subsection is followed by the presentation of two different electrochemical techniques to study mass transport losses: The limiting current density and the pulsed gas analysis. The limiting current density technique is presented in section 2.2. This technique consists in operation at maximal current densities where the reaction is diffusion limited and the current independent on the cell voltage. The second technique is the pulsed gas analysis presented in section 2.3. The basic idea is to replace the cathode air by helox (21% O₂, 79% He) and pure oxygen to obtain information about diffusive mass transport limitations. In order to optimize the utilization of beamtime during neutron experiments, a specially adapted fuel cell setup was build, which enables the simultaneous operation of six individual differential PEFCs of 1 cm² with highly repeatable results (see section 2.5). It has to be mentioned that the pulsed gas analysis and the cell setup was developed in the PhD thesis of Pierre Oberholzer [7] and are only briefly summarized in chapter 2.

In chapter 3, a new methodology to differentiate ice from water is reported which relies on differences in the neutron cross section of water and ice at low neutron energies. The concept of the differentiation between water and ice is presented in section 3.4. This methodology is studied with three different techniques: Neutron filter in section 3.5, otime of flight in section 3.6, and velocity selector in section 3.7. A detailed discussion about the advantages and disadvantages of the three techniques is given in section 3.8.

In chapter 4, the use of these methods will be presented. First, the influence of the active area of a PEFC was studied based on two different cell sizes (section 4.6). Second, experimental results obtained from 1200 cold starts and neutron radiographs are presented (section 4.7) to study effects of different diffusion layer properties on the cold start capability of PEFCs. In chapter 5, the impact of hydrophobic coatings inside commercial GDL of PEFC was studied based on four different combinations of PTFE-loadings on both anode and cathode (see chapter 5). The thesis is concluded with a summary about the methodological improvements and in-situ results, as well as an outlook for further research of neutron radiography for PEFCs (see chapter 6).
Characterization methods

A basic introduction of arising overpotentials and their dependency on the water management was given in the introduction chapter. It was elaborated that ohmic losses and especially mass transport losses are highly affected by the water accumulation inside a fuel cell. A valuable tool to investigate the water distribution inside operating fuel cells is neutron radiography, which will be introduced in section 2.1. Subsequently, two electrochemical techniques to isolate the influence of mass transport losses on the overall cell voltage are presented: The Limiting Current Density technique (section 2.2) and the Pulsed Gas Analysis (section 2.3); a comparison of the two techniques is given in section 2.4. Most of the experiments were performed with an innovative cell setup, which allows the simultaneous operation of up to six small scale fuel cells. This cell setup is introduced in section 2.5.

2.1 Neutron radiography for fuel cells

2.1.1 Motivation

In literature, mainly four different imaging techniques are reported to visualize liquid water inside PEFCs: (1) Optical, (2) Magnetic resonance, (3) X-Ray, and (4) Neutron imaging, respectively. Optical access for fuel cells is achieved by exchanging the metallic or carbon composite flow field with a transparent flow field (including a current collector) to image droplets in the flow channels [54, 55]. Unfortunately, this modification strongly impacts the water transport, as e.g. the surface contact angle or the thermal behaviour changes. Magnetic resonance imaging (MRI) is mainly used to study the hydration state of the membrane. Similar to the optical imaging method, the cell housing needs to be exchanged to make the cell suitable for MRI [56–58]. During the past years, X-Ray tomography at synchrotron facilities has attracted increasing attention due to its high spatial and temporal resolution [59–62]. However, this technique has
2. CHARACTERIZATION METHODS

several major drawbacks like essential constraints on the choice of materials, cell design, as well as a risk of radiation damages [63].

The imaging method which overcomes most of these issues is neutron radiography. Its fundamental advantage compared to others is its high transparency for the constituent materials of fuel cells (e.g. steel, aluminium, carbon), whereas hydrogen containing molecules like water provide a high contrast. Furthermore, full flexibility is given regarding the field of views ranging from a few cm$^2$ to several hundreds of cm$^2$. Besides that, images can be acquired continuously without any impact on the cell performance at reasonable time and spatial resolutions. However, the major drawback of neutron radiography is the relatively low flux of common neutron sources, which highly affect the temporal resolution. Hence, typically temporal resolutions of radiographs are in the order of seconds and tomographs in the order of hours, which is several orders of magnitude higher compared to X-Ray tomographies at synchrotron light sources [64].

2.1.2 Literature overview

Research using neutron radiography or tomography of PEFCs is mainly executed at the following two research facilities (> 20 publications in the past 5 years) [65, 66]:

- National Institute of Standards and Technology (NIST), Gaithersburg, USA [67]
- Paul Scherrer Institute (PSI), Villigen PSI, Switzerland [53]

Additionally, research activities were occasionally performed at the following facilities (< 10 publication in the past five years) [66]:

- Hahn-Meitner Institute (HMI), Berlin, Germany [68]
- Japan Atomic Energy Research Institute (JAERI), Ibaraki, Japan [69]
- Kyoto University Research Reactor Institute (KURRI), Osaka, Japan [70]
- Pennsylvania State University (PSU), Pennsylvania, USA [71]
- Korea Atomic Energy Research Institute (KAERI), Dae-Jong, Korea [72]
- University of California (UC), Davis, USA [73]

To our knowledge, the first publication of neutron radiography of fuel cells was reported in 1999 by Bellows et al. [74]. In this study, water profiles across a 500 µm thick membrane were measured in in-plane configuration (membrane parallel to the beam axis). In 2002, work was published in through-plane configuration (membrane perpendicular to the beam axis) by Geiger et al. [75] and in 2003 by Satija et al. [76]. In the following years, several improvements regarding
the resolution - especially in in-plane configuration - were performed, with effective resolutions down to 10 µm (e.g., ref [77]). Tomographies of PEFCs are rarely reported in literature as significantly more beamtime is required compared to radiography [68, 73, 76, 78].

In general, the main focus of research targets three topics: water gradients inside the CCM, material comparisons of GDLs, and water accumulation inside flowfield. Due to limitations of the spatial resolution, investigations of water profiles across the CCM are rarely measured on state of the art materials with a thickness of less than 50 µm; most publications [79–81] deal with much thicker membranes like Naion® 117 which are primarily of scientific interest. In contrast, water gradients across GDLs can be properly resolved, as the thickness of usual GDLs is in the range of 200 µm. Exemplary papers are published by Owejan et al. [82], Hickner et al. [79], or Oberholzer et al. [83]. The third major activity of neutron radiography of PEFCs focuses on the optimization and analysis of flow field designs as published by Owejan et al. [84], Oberholzer et al. [85] or Turhan et al. [71]. Newly, growing interest is dedicated to questions regarding system integration [86] or the assembly procedure [87]. Recent overviews about neutron radiography of PEFCs were published by Mukundan et al. [88], Trabold et al. [65], and Boillat et al. (see bibliography in ref [21]).

2.1.3 Neutron Infrastructure

Neutron imaging of the PEFC water distribution is exclusively performed at two types of neutron sources: nuclear fission reactors and spallation sources, which is mainly related to the requirement of obtaining a high neutron flux for short exposure times. All experiments of the present thesis were executed at the Swiss Spallation Neutron Source (SINQ) at the Paul Scherrer Institut (PSI). In general, a spallation source is based on collisions of high-energy protons (in the range of 1 GeV) with heavy nuclei in a target. In the case of the SINQ, an array of lead rods, enclosed in zirconium alloy tubes cooled by heavy water is utilized. Following the collision of the high-energy particles with the target, fast neutrons are emitted, which are moderated by a heavy water tank. According to the experimental requirements, neutrons are provided continuously (e.g. SINQ) or pulsed (e.g. SNS, ISIS, or J-PARC) to the individual beamlines.

Subsequent experiments were mainly performed at the ICON [89] and some at the BOA [90] beamline. The two beamlines differ in their neutron flux, which is reduced by a factor of two at the BOA (1.7 · 10^8 cm^{-2}s^{-1}) compared to the ICON beamline (3.5 · 10^8 cm^{-2}s^{-1}). Furthermore, both beamlines provide polychromatic neutrons in the cold energy range (5 · 10^{-5}–0.025 eV) [91–93], with slightly colder neutrons at the BOA beamline. Further details about the individual properties can be found in ref [90] and ref [89].
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2.1.4 Basics of neutron radiography

In the following three subsections, the particular adaptations of neutron radiography for fuel cell research will be presented. As this work was mainly developed by Boillat [53], it will just be briefly summarized. The new methodological improvements of the present thesis can be found in chapter 3.

Neutron radiography is an imaging technique which is based on the exponential attenuation of the incident neutron beam by matter, which can be best described according to the Lambert-Beer-Law [91]:

\[ I = I_0 e^{-\Sigma \delta} = I_0 e^{-\sigma N \delta} = I_0 e^{\Delta}, \]  

(2.1)

where \( I \) and \( I_0 \) denotes the outcoming and incoming beam intensity respectively, \( N \) the molar density and \( \delta \) the water thickness. \( \sigma \) represents the energy dependent microscopic cross section. A cross section describes an effective area representing the likelihood of interaction between a neutron particle of a certain energy with the respective material and is commonly expressed as an area in barn (1 barn = \( 10^{-24} \text{ cm}^2 \)). \( \Sigma \) describes the macroscopic cross section in \( \text{mm}^{-1} \) of \( \text{cm}^{-1} \), being the product of \( \sigma \) and \( N \). \( \Delta \) describes the attenuation of the neutron beam and will be called optical density henceforth.

As the cross section of hydrogen is significantly higher than the constituent materials like aluminium (80 times) or carbon (20 times), optimal contrast is obtained for water inside fuel cells. For our experiments, the cross section of water was experimentally determined using a water scale. More details about the energy dependent interaction of neutrons will be given later on in section 3.2.

2.1.5 Imaging configurations

As has already been mentioned in subsection 2.1.2, mainly two imaging configurations are commonly reported in literature: through-plane mode and in-plane mode (see Figure 2.1). In through-plane mode the beam axis is perpendicular to the membrane and the water distribution across the active area of the PEFC can be imaged (see Figure 2.1 (a)). However, the resulting radiograph is just the integral amount of water inside the CCM, GDL, and flowfields and their individual contributions cannot be easily differentiated [94]. In order to overcome this drawback, the in-plane configuration was developed with the beam axis parallel to the membrane (see Figure 2.1 (b)). As the resolution is limited with the common through-plane detector setups, Boillat [53] refined the in-plane setup to a tilted in-plane setup (see Figure 2.1 (c)). By tilting the scintillator by an angle of \( \theta = 80^\circ \) (see Figure 2.1 (c)), the width of the cell \( d_{\text{cell}} \) is magnified to \( d_{\text{det}} \) by approx. a factor of 6. As either the through-plane mode or the
2.1 Neutron radiography for fuel cells

**Figure 2.1:** Imaging configuration used during the experiments: (a) through-plane imaging, (b) in-plane imaging, (c) tilted in-plane imaging

The *tilted in-plane* configuration was used, the latter will just be called *in-plane* configuration in the following.

With a regular detector setup, the resolution in *in-plane* is limited by (1) geometrical unsharpness induced by the divergent neutron beam, (2) the pixel size of the camera system, and (3) the inherent unsharpness of the scintillator [53, 95] (see Figure 2.1 (b)). These three terms lead to a blurring of the real object, which is illustrated in the edge-spread function in Figure 2.3.

**(1) Geometrical unsharpness**

As can be seen in Figure 2.2, the geometrical unsharpness $r_g$ can be adjusted according to the intercept theorem:

$$r_g = L_d \frac{e}{L},$$

with $L_d$ being the distance between the sample and scintillator, $L$ the distance between source and sample, and $e$ the slit width of the beam limiters. Hence, the geometrical unsharpness can be reduced by minimizing the distance between the sample and the scintillator as well as by
2. CHARACTERIZATION METHODS

Figure 2.2: Schematics of geometric blurring induced by the neutron beam.

reducing the width of the slit of the beam limiter. However it has to be mentioned that the latter implies a significant reduction of the neutron flux, which has considerable implications on the signal-to-noise ratio. The signal-to-noise ratio is defined as the ratio between the intensity of the signal \( I_{\text{Signal}} \) and noise \( I_{\text{Noise}} \) \[96\]. A more direct definition is the ratio between the average signal value \( \mu_{\text{signal}} \) and the standard deviation of the background \( \sigma_{\text{background}} \) according to subsequent equation:

\[
\text{SNR} = \frac{I_{\text{Signal}}}{I_{\text{Noise}}} = \frac{\mu_{\text{signal}}}{\sigma_{\text{background}}} \tag{2.3}
\]

According to Equation 2.3, the signal-to-noise ratio can be either increased by longer exposure times or by enhanced neutron flux which results in both cases to an increase of \( \mu_{\text{signal}} \). As a high resolution is only required across \((x\text{-axis)}\) and not along the layers \((y\text{-axis)}\), an anisotropic collimation is used with \( r_{g,x} >> r_{g,y} \) to ensure a maximal neutron flux (see Figure 2.2). For high-resolution \textit{tilted in-plane} imaging, \( r_{g,x} > 1000 \) is commonly chosen as good trade-off between spatial resolution and neutron flux. For \textit{through-plane} imaging, large \( e \) can be chosen to maximize the neutron flux to the expense of the spatial resolution.

(2) Pixel size \& (3) inherent unsharpness of scintillator

In order to overcome the limitations of the camera pixel size and intrinsic unsharpness of the scintillator, a rotated scintillator of 80° is used (see Figure 2.1). By tilting the scintillator by a certain angle \( \theta \), the cross section of the cell \( d_{\text{cell}} \) is magnified to \( d_{\text{det}} \) by a factor of \( \frac{1}{\cos(\theta)} \), which is 5.75 with our current setup. This results in high effective resolutions of 20 \( \mu \text{m} \) (FWHM) across the membrane with moderate resolutions of 200 \( \mu \text{m} \) along the membrane. The significant
2.1 Neutron radiography for fuel cells

Figure 2.3: Edge spread function with *through-plane* mode and *tilted in-plane* imaging configuration. As can be seen, the effective resolution in in-plane is increased by a factor of more than 10 compared to the *through-plane* configuration.

Improvement of the tilted imaging configuration on the resolution can be clearly observed in the Edge-Spread-Function in Figure 2.3.

### 2.1.6 Image processing

In the present section, the individual steps of image processing are shortly summarized. A schematic overview is depicted in Figure 2.4. More details about each individual step can be found in ref [53].

1. **Pixel-wise dark current correction**: A raw neutron radiography includes dynamic noise as well as faulty pixels superimposed to the effective signal. The latter results from e.g. defects of the camera chip. Hence, with the subtraction of the dark current signal of the camera this noise as well as the background of the camera can be removed from the images. Mathematically, this step can be written as follows:

   \[ I_{DC\text{ wrk,ij}} = I_{\text{wrk,ij}} - I_{DC\text{,ij}}, \]

   where \( I_{\text{wrk,ij}} \) denotes the intensity of a pixel \( ij \) of the working image and \( I_{DC\text{,ij}} \) a pixel \( ij \) of the dark background.

2. **Median filtering**: In the second step, white spots originating from \( \gamma \)-rays (e.g. resulting from inelastic neutron scattering) hitting the camera system are removed with a median
2. CHARACTERIZATION METHODS

Figure 2.4: Illustration of the individual steps of image processing: (1) Pixel wise dark-current correction, (2) Filtering, (3) Flat field correction, (4) Intensity and location correction, (5) Correction for scattered neutrons, and (6) Pixel-Wise referencing.

filter. Depending on the noise level, different sizes of median filter are applied. With the tilted in-plane configuration, the dynamic noise is significantly higher compared to the through-plane images, resulting from the considerably lower neutron flux and light intensity.

3. Flat field correction: After the removal of dynamic and static noise, the images are corrected for inhomogeneities of the neutron beam and the detector sensitivity by the division with the intensity of the open beam. This translates into the following equation:

\[ I_{DCOB,ij} = \frac{I_{DC_{work},ij}}{I_{DC_{OB},ij}}, \quad (2.5) \]

where \( I_{DCOB,ij} \) describes the intensity of a pixel \( ij \) being flat field corrected; \( I_{DC_{work},ij} \) and \( I_{DC_{OB},ij} \) the intensity of a pixel \( ij \) inside the working image and open beam being corrected for dynamic and static noise.

4. Intensity and location correction: Due to beam fluctuations, all images undergo an intensity correction. For this purpose, a region of bright \( I_{NCA} \) and dark \( I_{DNCA} \) intensity
2.1 Neutron radiography for fuel cells

are selected which are time-invariant during the entire experiment. Based on the average signal calculated inside the two areas, a linear interpolation is determined to correct for intensity fluctuations of the working image. Mathematically the intensity correction can be summarized as follows:

\[ I_{\text{Int},ij} = I_{\text{DCOB},ij} \frac{1}{a + b \cdot I_{\text{DCOB},ij}}, \]  

(2.6)

where \( a \) depicts

\[ a = I_{\text{DNCA,werk}} - b \cdot I_{\text{DNCA,ref}} \]  

(2.7)

and \( b \)

\[ b = \frac{I_{\text{NCA,werk}} - I_{\text{DNCA,werk}}}{I_{\text{NCA,ref}} - I_{\text{DNCA,ref}}} \]  

(2.8)

In addition, the images are corrected for translation, expansion and rotation within this step, which results from mechanical or thermal expansions. This correction is performed based on 2D correlation functions.

5. **Correction for scattered neutrons**: As the constituent materials lead to scattering of neutrons, the images have to be corrected for the scattered background. This value is experimentally measured with so called "black bodies" (boron carbide embedded in polyethylene), which are opaque for neutrons. The measured signal behind the black bodies \( I_{SBKG} \), is locally subtracted in the radiographs.

\[ I_{\text{sbkg,werk},ij} = I_{\text{Int,werk},ij} - I_{SBKG,ij}, \]  

(2.9)

where \( I_{\text{sbkg,werk},ij} \) denotes the intensity of a pixel \( ij \) which is corrected for background scattering, \( I_{\text{Int,werk},ij} \) the intensity of a pixel which underwent the first four steps of the image processing, and \( I_{SBKG,ij} \) the intensity of the scattered signal at a pixel \( ij \). In contrast to the constituent material scattering, sample scattering of water has only a minor influence [52].

6. **Pixel-Wise referencing**: In the final step, the images are referenced pixel-wise to their radiograms in the dry state to obtain the exclusive signal of water.

\[ I_{\text{refd,werk},ij} = I_{\text{sbkg,werk},ij} \frac{I_{\text{sbkg,ref},ij}}{I_{\text{sbkg,ref},ij}}, \]  

(2.10)

where \( I_{\text{sbkg,werk},ij} \) denotes the intensity of a working image at a pixel \( ij \) being corrected for scattered neutrons, \( I_{\text{sbkg,ref},ij} \) the intensity of the dry reference image at a pixel \( ij \) being corrected for scattered neutrons and \( I_{\text{refd,werk},ij} \) the attenuation of water at a pixel \( ij \). According to Equation 2.1 the water thickness can be locally calculated in these images at every pixel \( ij \).
2. CHARACTERIZATION METHODS

2.1.7 Experimental validation of water quantification

In order to validate the accuracy of the image processing and the calculation of the water thickness based on Equation 2.1, an in-situ calibration was developed [97]. In this experiment, a known quantity of water \( m \) was electrochemically produced with pure oxygen and hydrogen according to Faraday’s law:

\[
m = \frac{M}{z \cdot F} \cdot Q = \frac{M}{z \cdot F} \cdot \int_0^t I \, dt, \tag{2.11}
\]

where \( m \) represents the mass of water, \( M \) the molar mass, \( z \) the number of electrons transferred per ion, \( F \) the Faraday constant and \( Q \) the charge produced. By closing the exhausts of the fuel cell, water is neither brought to nor removed from the cell, which enables an accurate comparison of the electrochemically produced and experimentally measured water. Experimentally, this was realized by certain intervals of current production (1 minute current production, 30 minutes waiting, then drying) while neutron radiographs were continuously acquired.

![Figure 2.5](image.png)

**Figure 2.5:** Calibration experiment for water quantification in (a) through-plane and (b) in-plane image configuration. Good agreement is obtained in through-plane, whereas systematically deviating results are measured in the in-plane configuration.

As can be seen in Figure 2.5, the measurements in through-plane imaging show a good agreement with the electrochemically produced amount of water. However, with the in-plane image configuration, a certain underestimation of the amount of water can be observed. This deviation can be most likely explained by an error of the scattered background calculation. Although further experiments have to be executed to fully understand these deviations, a good repeatability including cell-to-cell variations and experiment-to-experiment variations is obtained. In

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1Part of the text was published in [97]: Boillat et al. "Accuracy of water quantification in fuel cells by neutron imaging" Annual report 2013, Laboratory of Electrochemistry, Paul Scherrer Institute, Switzerland
2.2 Limiting current density measurements

2.2.1 Concept

Limiting current density measurements are a well-established technique to study mass transport limitations inside fuel cells [10, 82, 99–101]. The limiting current density represents the current where the reaction is exclusively mass transport limited (convection, diffusion, and migration) and does not depend on activation- or ohmic overpotentials. In a polarization curve, limiting current densities can be identified, where the shape in the polarization curve bends vertically (see Figure 2.6) and no additional current can be extracted independently on the overpotential applied. Under technical operating conditions limiting currents are hardly reached, as the charge transfer and ohmic overpotential lead to a prior limitation. Furthermore, as limiting currents are reached above \(3 \text{ Acm}^{-2}\) under usual operating conditions (21% \(\text{O}_2\) in \(\text{N}_2\)), restrictions can arise from the thermal management or the electronic load setup.

Hence, limiting currents are typically measured under diluted oxygen concentrations (low \(c_{\text{O}_2,\text{ref}}\)), which results, according to Equation 1.18, in a significant reduction of the limiting current density (see Figure 2.6). Under these operating conditions, stable limiting currents are reached at cell potentials below 300 mV. According to Equation 1.18, the limiting current measured at diluted oxygen concentrations can be extrapolated to air operation at 21% oxygen.

As limiting currents in fuel cells are mainly relying on diffusion (migration and convection represents a neglectable contribution), 1D-Diffusion coefficients can be calculated according to Equation 1.18. Technically speaking, Equation 1.18 is only valid for flat surfaces and its applicability to porous materials is limited. However, as the thickness of the used CL (\(\approx 8 \mu\text{m}\)) is significantly smaller compared to the thickness of a GDL (\(\approx 200 \mu\text{m}\)), the equation can be applied in rather good approximation.

Another parameter which can be extracted based on the limiting current density, is the calculation of a one-dimensional oxygen transfer resistance \(R_{\text{oxygen}}\) according to Equation 2.12 [82, 102, 103]:

\[
R_{\text{oxygen}} = \frac{4 FC_{\text{O}_2,\text{ref}}}{\eta_{\text{lim}}} \cdot \frac{p - p_{w}^{\text{in}}}{RT},
\]  

(2.12)

where \(p\) denotes the total pressure and \(p_{w}^{\text{in}}\) the inlet water vapour pressure. This resistance is further subdivided as the sum of non-bulk \(R_{\text{non-bulk}}\) (e.g. Knudsen diffusion, Thin film diffusion)

2. CHARACTERIZATION METHODS

2.2.2 Technical implementation

In our experiments of chapter 5, the limiting current density measurements were carried out at three cell voltages of 0.4 V, 0.3 V, and 0.2 V, respectively. The limiting currents were determined only at 0.3 V and 0.2 V, where the current density remains essentially constant. Various gas concentrations were chosen (0.25, 0.5, 1.0, 2.0 %O₂ in N₂) to extrapolate to air operation. In order to investigate the differences in bulk and non-bulk diffusion, experiments with mixtures of oxygen in helium were performed, as the diffusion of oxygen in helium is significantly higher than in N₂ (see section 2.3). Consequently, higher limiting currents are obtained using this mixture; hence lower concentrations of 0.125, 0.25, 0.5, 1.0 %O₂ in He were chosen. With both gas compositions, a first measurement was done using relatively dry gases (Anode: 30 %RH / Cathode: 30 %RH) to obtain the limiting current density of the dry structure. Then, the cells were operated at 1 Acm⁻² and full humidity for 1 h, before performing a second measurement of the
limiting current density with fully humidified gases, intending to see the previously accumulated water in the GDLs.

2.3 Pulsed gas analysis

2.3.1 Concept

In previous publications of our group [85, 104–106], the pulsed gas analysis (PGA) method has shown its application for detailed studies of bulk and non-bulk mass transport losses. Bulk losses originate from diffusive transport limitations in the GDL and relies primarily on the binary/ternary molecular diffusion. In contrast, non-bulk losses result from Knudsen diffusion and thin film diffusion [107], which can be especially related to diffusive transport limitations in the CL (see subsection 1.3.3). However it has to be mentioned that the gas phase transport in the CL is not pure Knudsen diffusion; it is a mixed regime between bulk/non-bulk diffusion (see subsection 1.3.3).

The basic idea of the PGA is the replacement of the cathode air by helox (21% \(O_2\), 79% He) and pure oxygen. As the diffusivity of \(O_2\) in helium is higher by a factor of 2 to 3 compared to \(O_2\) in nitrogen [107], the bulk mass transport losses are reduced to nearly zero [104]. Consequently, a good estimation of the bulk mass transport losses can be obtained from the voltage difference between operation under air and helox. The non-bulk losses are obtained from the voltage difference between operation under pure oxygen and operation under helox, as the higher partial pressure of oxygen combined with the differential operation (see Figure 2.14) reduces the non-bulk diffusion losses to nearly zero with well defined CLs. However, a higher partial pressure also results in an increase of the cell voltage in absence of mass transport losses (due to the changes of the Nernst potential and improved oxygen reduction kinetics) estimated to 45 mV [107], which has to be corrected for. Although the use of helox and oxygen gain is quite often reported [100, 108, 109], the particularity of our method is the supply of helox and pure oxygen as short pulses of 1 s.

The motivation for using gas pulses instead of continuous operation is depicted in Figure 2.7, where three UI-curves were measured. In Figure 2.7 (a) the square symbols represent a UI-curve measured under continuous operation under \(O_2\); the other two curves depict the cell voltage during \(O_2\) gas pulses measured under continuous operation in air (circle) and Helox (rhombus). Similarly, Figure 2.7 (b) shows a UI-curve measured under continuous operation with helox in squares; the other two curves depict the cell voltage during helox gas pulses measured under

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2. CHARACTERIZATION METHODS

![Figure 2.7: Potential dependency of UI-curves and motivation of using gas pulses: (a) \(O_2\) UI-curves measured under (square) continuous \(O_2\) operation, (circle) oxygen pulse voltage during continuous air operation and (rhombus) oxygen pulse voltage during continuous Helox operation. (b) Helox UI-curves measured under (circle) continuous Helox operation, (square) Helox pulse voltage during continuous air operation and (rhombus) Helox pulse voltage during continuous \(O_2\) operation.](image)

continuous operation in air (circle) and oxygen (rhombus). It can be seen that significant differences arise along the entire current density range which can be explained as follows: It has been reported in literature [110–112] that the catalyst coverage by oxygenated species is potential dependent and lower potentials lead to a lower oxide coverage with a higher activity of the CL. As the cell voltage is increased under helox compared to air operation, a lower activity of the catalyst is obtained resulting in higher activation losses and vice versa under pure oxygen (see Figure 2.7 (b)); similar explanation holds for oxygen in Figure 2.7 (a). Besides the change in charge transfer overpotentials, the water vapour diffusivity in helox is significantly higher than in air, which results in a lower hydration state of the membrane and thus increased ohmic losses. To sum up, Figure 2.7 shows the crucial importance of performing measurements with helox and pure oxygen as short gas pulses and a continuous operation under helox or oxygen cannot be used to differentiate between bulk and non-bulk mass transport losses.

2.3.2 Technical implementation

In order to realize gas pulses of 1 s with different gas compositions, an advanced gas circuit is required (see Figure 2.8). The setup is realized based on two parallel gas streams: The cell flow, which is normally feed to the cell (MFC Air) and the gas mixture which is feed during a gas
2.3 Pulsed gas analysis

pulse (MFC He and O\textsubscript{2}). In order of being able to achieve a rapid transition between Air and the pulse gas, both gas circuits are flowing continuously and the exchange is realized based on two 3-way electric valves which switch from continuous to pulse mode.

Figure 2.8: Schematics of the gas circuit of the fuel cell testbench.

In this thesis, all experiments were performed in the so called suction mode. As can be seen in Figure 2.8 the cell flow before and after the cell has to be differentiated. The cell flow before the cell provides a high volumetric flow of reactant gases, which - in case no reactants are required inside the cell - is going directly via the bypass towards the exhaust without passing through the cell. In case a certain gas flow is required in the cell, the MFC\textsubscript{suc} branched off the required flow to the cell. This has the advantage that an excessive amount of reactants can be feed to the inlet of the fuel cell, without passing through the cells, which ensures a fast arrival of the new reactant gas after the switch.

Figure 2.9 depicts the transition of the cell voltage during a gas pulse. Initially (t = 0), the valves inside the testbench are switched (see Figure 2.8). As the piping between the valves and the cells is around 3 m, a certain delay of approximately 500 ms occurs until the pulse gas reaches the cell. 200 ms later, the reactant gases were completely exchanged within the cell and a higher cell voltage is obtained due to reduced mass transport losses. In order to minimize changes of the catalyst oxidation or membrane hydration state (see Figure 2.7), the cell voltage for the calculation of the mass transport losses is taken at the very beginning of the gas pulse. In the following, the voltage difference between the pulse and the base voltage of helox-air will be designated as indicator of bulk-diffusion losses and helox-O\textsubscript{2} as indicator of non-bulk-diffusion losses.
2.4 Comparison of limiting current density and pulsed gas analysis

If we compare the limiting current density technique with the PGA, both techniques have essential advantages and disadvantages (see Table 2.1). The major difference is the extraction of effective loss terms with the PGA versus generic component properties with the limiting current density technique. The mass transport losses of the PGA method are calculated as a voltage difference between Helox or \( O_2 \) pulses with the continuous air voltage at usual operating conditions (see section 2.3). This has the advantage that the impact on the cell performance can be directly extracted. In contrast, intrinsic material properties can be derived from the limiting current density technique, which are independent on ohmic and activation losses. Although more fundamental information of the materials are obtained, its impact on the overall cell performance requires advanced numerical simulations [82].

As already mentioned in section 2.3, the major advantage of the PGA is the direct measurement of a voltage loss under similar operating conditions with e.g. an identical water distribution and hydration state of the membrane, which is achieved by pulsing the gas as short pulses of 1 s. In contrast, the limiting current density is continuously measured under very low cell voltages and in a diffusion limited regime. Under these operating conditions, mainly two parameters differ: (1) the water distribution, (2) the current distribution between channel rib, and (3) the heat
Table 2.1: Comparison between the pulsed gas analysis and the limiting current density methodology.

<table>
<thead>
<tr>
<th>PGA</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Similar operating conditions</td>
<td>(1) Dependent on other overpotentials</td>
</tr>
<tr>
<td>(2)</td>
<td>Simple extraction of loss terms</td>
<td>(2) Challenging experimental setup</td>
</tr>
</tbody>
</table>

management. The redistribution of water can be observed in Figure 5.10, where an increased amount of water is measured inside the cathode GDL under the flow channel during limiting current operating conditions. Although the difference in water is rather small, these regions were identified of being critical concerning mass transport losses in chapter 5.

Regarding the channel-rib distribution at limiting currents, Reum [113] identified an increased dependency of current production under the channel with decreasing oxygen concentrations. This translates to the fact that more product water is produced under the channel [85], which explains the increased water accumulation in this region (see Figure 5.10).

Under limiting current densities, the heat management strongly differs compared to continuous operation, as the applied overpotential is maximal (operation at potentials between 0.1 - 0.3V), strongly rising the amount of heat released. Hence, the local temperature and thus the water transport may change significantly, as already reported previously.

As the reaction is exclusively diffusion limited, the major advantage of the limiting current density technique is its independence on other loss terms like ohmic and activation overpotentials. This has the significant benefit that isolated and characteristic component properties can be extracted. Another major disadvantage of the PGA is its very demanding experimental setup as described in section 2.3, with significant modifications of the testbench infrastructure; limiting current density measurements can be performed on every commercial testbench with a supply of diluted oxygen.

To sum up, both techniques are highly suited to investigate mass transport inside PEFCs. The limiting current density measurements elucidate mass transport limitations whereas mass transport losses can be studied with the PGA. Thanks to their different nature of both characterization techniques, complementary results are obtained (e.g. in chapter 5).
2. CHARACTERIZATION METHODS

2.5 Multicell

This section is divided in two main parts: (1) technical description of cell design and (2) recent improvements performed for validation of the setup. In the first part, the technical features of the Multicell are introduced in subsection 2.5.2, followed by the description of the cell design and the cell materials used. As this part was already introduced in the thesis of Pierre Oberholzer [7], it will just be briefly summarized. In the second part, recent improvements regarding the accuracy of the humidification, assembly procedure, operating conditions, and repeatability are presented.

2.5.1 Motivation

In order to perform precise studies of fuel cell materials, identical operating conditions and cell histories are required. Commonly [25, 87, 114], material investigations are exclusively realized as sequential testing of individual cells, which has significant drawbacks like uncertainties of the operating conditions (i.e. gas humidification), time consumption, and differences in the cell history. In order to overcome these disadvantages, the so called Multicell was developed by

Figure 2.10: Schematics of the Multicell housing. Reprinted from Oberholzer et al. [83] with permission of Elsevier. Copyright 2012 Elsevier.

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Pierre Oberholzer [7]. This cell setup allows the simultaneous operation of up to six differential fuel cells which comprises the following advantages: First, the testing time for six individual cells is highly reduced which is of particular interest during neutron beamtimes. Second, the measurement accuracy is increased, as the cells are fed with the same inlet gas streams of identical composition, humidification and temperature (see Figure 2.5.5). Another major advantage of this setup is its integration for neutron imaging as the cell is optimized for through-plane and in-plane imaging minimizing the amount of material in beam direction and using a specially developed scintillator.

A schematic of the Multicell is shown in Figure 2.10. In general, the cell consists of two external housings which include the thermal management, electric control, gas supply as well as the six individual cells.

2.5.2 Technical features

In this section, the following technical features of the Multicell are briefly summarized, which comprise: (1) thermal control, (2) gas supply, (3) cold start setup, (4) electrical control, as well as (5) the integration in the neutron beamline. Further details can be found in ref [7].

(1) Thermal control

The thermal management of the Multicell setup consists of three actuators: (1) liquid heating/cooling, (2) air cooling, and (3) electric heating. The external housings are temperature controlled via a thermostat (see figure Figure 2.10 red arrow). During the experiments at technical operating temperatures, liquid water was used; a mixture of 50 % Ethylen Glycol and water was utilized for cold start experiments in order to suppress the freezing point to -40°C. At technical operating temperatures, the heating liquid was set around 5 - 10°C higher compared to the desired cell temperature to prevent water condensation. As the individual cells are thermally connected to the housings, the cells are cooled down with an external cooling gas stream of air of around 30-50 L min⁻¹ (see figure Figure 2.10 blue arrow). In order to control the individual cell temperatures precisely, electric heaters on the anode and cathode housing maintain the cells at the desired cell temperature to ensure isothermal conditions in all six cells. Although the thermal concept is rather complicated, it offers full flexibility to operate the cells even under overhumidified operating conditions.

(2) Gas supply

One of the major advantages of the Multicell setup is the common gas supply of the six individual cells with identically gas composition and humidification. The gas supply can be easily switched between cell flow and bypass flow, which is integrated inside the external Multicell housing (see
2. CHARACTERIZATION METHODS

figure Figure 2.10 green arrow). From this cell-flow passing through the Multicell housing, the individual suction flows can be branched off through the single cells (see figure Figure 2.10 green arrow Out (MFC)).

(3) Cold Start setup

During cold start experiments, water vapour of the surrounding air condenses and risks to freeze inside the external housings of the Multicell. Frost would not only cause a damage of the electronic parts inside the cell housing; accumulation of frost in the field of view would result in an error of water quantification during neutron experiments. In order to prevent these effects, an additional aluminium housing was mounted around the cell, which was thermally decoupled and maintained at room temperature to prevent frost on its surface. Furthermore, the void space between cell and housing was continuously purged with dry nitrogen to remove any trace of water vapour.

(4) Electrical control

In the Multicell, the cells can be either operated in galvanostatic or potentiostatic operating mode. This is technically realized via printed circuit boards integrated inside the external cell housings, which are able to switch from a connection in series (galvanostatic / current controlled) to a connection in parallel (potentiostatic / voltage controlled). Furthermore, these printed circuit boards enable a compact interface to access the measurements of current, voltage, and temperature of each individual cell.

The membrane resistance is measured by superimposing an AC current signal of high frequency and low amplitude to the constant current signal of the cell, while measuring the resulting voltage response. The high frequency area resistance (HFR) resistance is calculated based on a Fourier-Transform of the voltage response of a sinusoidal incitation of the current signal at a frequency of 5 kHz. The indicator of ohmic losses is the product of the high frequency area resistance (HFR) and the individual current density of the cell.

(5) Integration in the beamline

The Multicell is specially built for neutron radiography providing special features for an optimized image quality. First, the material in direction of the beam axis is minimized in the housing as well as inside the cells to provide maximized transparencies. Second, the cells possess special positioning surfaces to ensure identical alignments of all six cells which is of particular interest in the in-plane configuration. Further details about the alignment surfaces can be found elsewhere [7].
As has already been mentioned, the Multicell is optimized for in-plane and through-plane imaging. For this purpose, an optimized scintillator was built for the ICON beamline, which enables the variation of the imaging configuration without a change of the scintillator. Further details can be found in ref [7, 115].

2.5.3 Cell design

The fuel cells used in this setup have an active area of 1 cm$^2$. The flow fields consists of 5 parallel channels (0.55 mm depth and 1 mm width), machined into an aluminium block to obtain the highest transparency for neutrons. In order to prevent the cells from oxidation, the housings were coated with a thin layer of gold. The compression of the cells can be fixed with stainless steel spacers between the anode and cathode housing, which can be stacked in steps of 10 µm. (see Figure 2.11).

2.5.4 Cell materials

For all experiments of this thesis, catalyst coated membranes (CCM) of type Primea 5710 (Gore Ltd., USA) were used with Pt-loadings of 0.1 and 0.4 mg Pt cm$^{-2}$ on the anode side and on the cathode side, respectively. If not mentioned specifically, a carbon paper GDL of type Sigracet 24BC (SGL Carbon Group, Germany) was used, which was coated with 23 wt% PTFE inside the MPL and with 5 wt% PTFE inside the substrate [116]. Experiments of GDLs with varying hydrophobic coating loads with and without MPL will be presented in section 4.7 and chapter 5.

2.5.5 Recent improvements of cell operation

Although first experiments were performed by Pierre Oberholzer [7], several improvements were applied to improve the repeatability under all conditions. In particular these improvements comprise the following four aspects: (1) Adjustment of cell assembly, (2) Verification of humidification concept, (3) Validation of operating conditions, and (4) Study of repeatability.
2. CHARACTERIZATION METHODS

(1) Cell assembly

As can be seen in Figure 2.11, the cell assembly consists in the placement of the individual fuel cell layers (GDL + CCM) plus two Teflon gaskets, followed by a defined compression based on precise stainless steel spacers. Consequently, the major variable influencing the performance and repeatability of the Multicell setup, is the choice of the right spacer thickness defining the compression of the cell assembly and in particular of the GDL.

![Figure 2.12: Influence of GDL compression on (a) overall cell performance, (b) ohmic losses, (c) bulk losses, and (d) non-bulk losses.](image)

The implications of the compression rate of GDLs on the performance are well-known and two major effects are reported [117–121]: First, with higher compression rates lower ohmic resistances are measured as the contribution of the contact resistance $r_{\text{contact}}$ decreases (see

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1This work was performed in the scope of the semester thesis of Muriel Siegwart "Effects of Gas Diffusion Layer Compression on the Performance of a Polymer Electrolyte Fuel Cell", Semester Thesis, ETH Zürich, June 2014, Supervised by J. Biesdorf
Equation 1.15). Second, with higher compression rates, the average pore size and hence $D_{eff}$ is reduced, inducing higher mass transport losses. However, both effects are highly dependent on the cell design (e.g. ratio rib/channel) and materials (e.g. GDL substrate) used. Hence, in order to achieve optimal operating conditions with our cell design, a systematic investigation of the compression rate was performed.

Figure 2.12 (a) depicts polarization curves of the cells with six different compression rates (18, 26, 37, 47, 58, 68%); Figure 2.12 (b-d) differentiates the individual contributions of the ohmic losses, bulk losses and non-bulk losses obtained with PGA at high humidification conditions (RH anode = 95%, RH cathode = 95%) and 2 bar$_{abs}$ operating pressure. As can be seen in Figure 2.12 (a), the differences of the compression rate on the overall performance have only a minor influence. However in Figure 2.12 (b) a significant decrease of the ohmic losses with higher compression of the cell is obtained, which can be explained by a decreasing contact resistance $r_{contact}$. In contrast, bulk losses (see Figure 2.12 (c)) are more pronounced under high compression rates, which can be explained by a reduction of the pore space, limiting the diffusivity of the reactant gases. Regarding the non-bulk losses in Figure 2.12 (d), no significant differences can be observed. This can be explained by the fact that non-bulk losses mainly occur inside the catalyst layers (see Equation 1.19) which are significantly less affected by compression. The best trade-off between decreasing ohmic losses and increasing bulk-diffusion losses were obtained at a GDL compression rate of 25%, which was fixed as optimal compression during all experiments.

(2) Validation of humidification concept

As the heating concept of the Multicell is rather complex (see subsection 2.5.2), a validation of the humidification and thermal concept of the cell setup is required to ensure a reliable operation. This can be evaluated with a simple calorimetric experiment (see Figure 2.13). Within this, the heating power of the individual cell heaters is measured two times; without and with humidified gas flow at several humidifications. The difference in heating power will be called released heat $Q_{release}$ henceforth.

Figure 2.13 depicts the released heat as a function of the measured dew point of the humidified gases. As long as the dew point of the gas stream is below the cell temperature ($T = 70^\circ C$), only little heat is released. This heat release results from the slightly higher temperature of the incoming gases, resulting from the gas feeding infrastructure (e.g. heated pipes). This temperature is assumed to be $73^\circ C$. At dew points above the cell temperature, the latent heat of condensation releases significantly more heat rising with overhumidification. According to the energy balance, the released heat can be calculated as follows:

$$P_{release} = P_{\Delta T} + P_{PC},$$  \hspace{1cm} (2.14)
2. CHARACTERIZATION METHODS

Figure 2.13: Experimental validation of thermal and humidification concept based on the measurement of the released heat of the humidified reactant gases.

with $P_{\Delta T}$ being the heat release of the humidified air which can be calculated as follows:

$$P_{\Delta T} = \dot{m}_{\text{Air}} \Delta T c_{p,\text{Air}} + \dot{m}_{\text{H}_2\text{O, in}} \Delta T c_{p,\text{H}_2\text{O}},$$  \hspace{1cm} (2.15)

where $\dot{m}_{\text{Air}}$ denotes the mass flow of air, $\Delta T$ the temperature difference of the instreaming gas and the cell temperature (typically 3°C), $c_{p,\text{Air}}$ the heat capacity of air, $\dot{m}_{\text{H}_2\text{O, in}}$ the mass flow of water vapour, and $c_{p,\text{H}_2\text{O}}$ the heat capacity of water vapour.

The heat release by the condensation of water vapour $P_{PC}$ can be calculated as follows:

$$P_{PC} = (\dot{m}_{\text{H}_2\text{O, out}} - \dot{m}_{\text{H}_2\text{O, in}}) q_{\text{latent}},$$  \hspace{1cm} (2.16)

where $\dot{m}_{\text{H}_2\text{O, in}}$ and $\dot{m}_{\text{H}_2\text{O, out}}$ denotes the mass flow of in- and outstreaming mass flow of water vapour, and $q_{\text{latent}}$ the lattent heat of phase transition from vapour to liquid water. The results of the mass balance are shown as the dotted line of Figure 2.13, where a good agreement can be found with the experimental data. Based on this experiment, the humidification system of the testbench and $Multicell$ has been calibrated and validated for further experiments with an accuracy of $\pm 0.5^\circ\text{C}$ of the dew point.
(3) Operating conditions

Figure 2.14 illustrates the three different types of fuel cells, which are typically used for scientific studies: (a) Fuel cell stack, (b) single cell, and (c) small scale cell. Although studies of fuel cell stacks include all technical relevant effects, the distinction of their individual contributions is very demanding. Therefore, the predominant number of fuel cell studies is performed on lab scale single cells (typically 50cm$^2$) as good trade-off between technical relevance and level of understanding. However, even with these downscaled systems, local effects are strongly superimposed by global effects (see section 4.6) and further downscaling is required. This downscaling can be performed in two ways: (1) By maintaining the lengths of a single flow channel or (2) by adaptation of the local gas velocity representative to a middle segment of a technical fuel cell. In the first case, gradients along one single flow channel can be studied by squeezing a straight channel of a technical cell into a serpentine shape. Unfortunately, by the implementation of a certain number of bends along the channel, the gas and water transport is highly affected.

In the second case, a small portion inside a technical fuel cell is simulated by feeding gases with high stoichiometry and realistic gas velocities into straight flow channels. In order to be comparable to a middle segment of a fuel cell, experiments are typically operated at stochiometries of around 60 at 1 Acm$^{-2}$. Under these operating conditions, the water distribution, oxygen concentration, and gas velocity can be assumed to be constant along the channel. This is of particular interest for imaging studies in *in-plane* configurations, where gradients cannot be imaged.

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\textsuperscript{1}Part of the text was published in [245]: Biesdorf et al. "Influence of operating temperature and pressure on the water management inside gas diffusion layers" Annual report 2014, Laboratory of Electrochemistry, Paul Scherrer Institute, Switzerland
2. CHARACTERIZATION METHODS

Figure 2.15: Pressure and temperature dependency of (a) raw voltage, (b) ohmic losses, (c) bulk losses, and (d) non-bulk losses under operation at 1 A cm$^{-2}$ and 80%RH on anode and cathode side.

In this direction. To investigate the mass transport on a local scale, all subsequent experiments were performed under these so called differential operating conditions.

In order to find a reference condition for optimal operating conditions, a systematic investigation of the operating temperature and pressure was performed. Figure 2.15 depicts the (a) raw voltage (b) ohmic, (c) bulk and (d) non-bulk losses as a function of pressure and temperature distinguished with the PGA. The raw voltage (see Figure 2.15 (a)) shows variations in the order of 100 mV between the different operating points. An increase in pressure and temperature leads to significant improvements of the cell performance even after correction of the different Nernst potentials at the individual temperatures and pressures. The ohmic losses (see Figure 2.15 (b)) seem to be independent on the operating pressure, whereas a significant decrease can be identified with increasing temperatures. The indicator of bulk diffusion losses (see Figure 2.15 (c)) is strongly dependent on the temperature as well as on the pressure. Non-bulk diffusion losses (see Figure 2.15 (d)) show a more homogeneous distribution with slightly reduced values at high operating temperatures and pressures. The best performance is obtained with our cells at 70°C.
and 2 bars, which will be defined as our reference condition in the subsequent experiments.

(4) **Repeatability**

After having optimized the cell assembly procedure, validated the humidification concept, and identified the optimal operating conditions, the reliability of the data is checked by reproducibility measurements. With strongly reduced active areas (e.g. 1 cm$^2$) unrepeatabilities resulting from material manufacturing and cell assembly procedures translate into substantial variations of the performance. With the *Multicell* setup, uncertainties resulting from operating parameters or cell operating history are highly reduced and unrepeatabilities are mainly ascribed to cell-to-cell differences.

To analyse the source of these differences, the previously presented methods were applied to compare three identical cells in a so called RH-Map: (a) PGA (see section 2.3), (b) membrane conductivity measurement (see subsection 2.5.2), (c) high-resolution neutron radiography (see section 2.1), as well as the (d) limiting current density technique (see section 2.2).

A RH-Map consists of asymmetric variations of the anode and cathode humidification (see humidification profiles in Figure 2.16). Every operating point was held 15 min, as the equilibrium of the water distribution is obtained after 3 minutes. The PEFCs were operated at a constant current density of 1 A cm$^{-2}$. The cell temperature was set to 70°C at a pressure of 2 bar$_{abs}$ on both sides. The cell flows were 0.4 Nl min$^{-1}$ on the anode and 1 Nl min$^{-1}$ on the cathode side, translating into stoichiometries of approximately 60. The measurement protocol is shown in the humidification profiles in Figure 2.16. All experiments presented hereafter were performed at the ICON beamline of the SINQ in order to study also the repeatability of the water accumulation inside the PEFC.

(a) **Pulsed gas analysis** & (b) **Membrane conductivity measurement**

Figure 2.16 shows the performance of the three identical PEFC at various humidifications of the anode and cathode gas stream. The uncorrected raw voltage of the fuel cells is illustrated in Figure 2.16 (d). It can be seen that the absolute voltage difference between the three different cells accounts for less than 20 mV at all operating points. Only a small portion (less than 10 mV) can be attributed to differences of catalyst activity, which are reflected in the voltage during oxygen operation corrected for ohmic losses (see Figure 2.16). At low humidifications of the anode gas stream, the raw voltage is highly reduced. This can be attributed to a reduced hydration state of the membrane, leading to highly increased ohmic losses (Figure 2.16 (e)).

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\[ \text{Part of the text was published in ref [246]: Biesdorf et al. "Reproducibility of performance and water distribution of small scale differential fuel cells." Annual report 2013, Laboratory of Electrochemistry, Paul Scherrer Institute, Switzerland} \]
2. CHARACTERIZATION METHODS

Figure 2.16: Repeatability measurements of three differential PEFCs based on (d) the cell voltage, (a) the bulk and (b) non-bulk mass transport losses, (c) ohmic losses, (e) IR free $O_2$ voltage, measured under various humidifications defined in (f).

As the operating conditions (humidification, temperature, pressure) are identical for all three cells inside our experimental setup, the indicator of ohmic losses (see Figure 2.16 (c)) shows negligible deviations. Non-bulk diffusion losses (Figure 2.16 (c)) were identified to occur mostly inside the ionomer of the catalyst layer on the cathode side [85]. In contrast to non-bulk losses, the indicator of bulk diffusion shows moderate variations between the three cells. A possible reason could be the inherent irregularity of the porous diffusion layers, even if all three cells were built out of a single sheet of GDL.

(c) Neutron radiography

Figure 2.17 shows the water distribution inside the different layers of the cell during the same experiment. The water content in the membrane region (Figure 2.17 (a)) is strongly dependent
on the humidification of the anode gas stream. As expected, a good correlation is obtained with the trend of the ohmic losses presented in Figure 2.17 (a). Inside the gas diffusion layers (Figure 2.17 (a) and (b)), the amount of water is highly dependent on the humidification level of the fed gases. As a dynamic equilibrium between humidification and product water is reached after approx. 3 min, repeatable water distributions are obtained between the three cells. A good agreement is obtained with the indicator of bulk diffusion losses (Figure 2.16 (a)): higher water content in the cathode GDL results in increased diffusion losses. Figure 2.17 (d) and (e) depict the water accumulation inside the anode and cathode flow field. The water accumulated inside the flow channels is established as an equilibrium between water production, drag-out

![Figure 2.17](image-url): Repeatability measurements of water quantification of three differential PEFCs based on water distribution inside (a) the membrane, (b) GDL anode, (c) GDL cathode, (d) Channel anode, (e) Channel cathode, measured under various humidifications in (f).
mechanisms of droplets by the gas stream in liquid phase and water uptake of undersaturated
gas in the gas phase. Although the water transport includes stochastic processes, the amount
of water is repeatable from cell-to-cell.

(d) Limiting current density

Figure 2.18 depicts the limiting currents as function of the oxygen concentration in nitrogen
for three identical cells. According to Equation 1.18, \( i_{\text{lim}} \) is proportional to the oxygen concen-
tration. Under dry conditions, moderate repeatabilities are obtained, as a systematically lower
limiting current density is measured with cell 2. In contrast, minor deviations are achieved
under full humidification (dotted lines in Figure 2.18). This particular behaviour of cell 2 was
also observed with the PGA in Figure 2.16 and highlight the complementary of both techniques.

![Figure 2.18: Repeatability measurements of the limiting current density methodology under dry and fully humidified conditions for three identical cell configurations.](image)

In summary, highly repeatable results were obtained with all characterization methodologies
presented. Using the pulsed gas method combined with neutron radiography, remaining devia-
tions could be attributed to differences in bulk mass transport losses. Possible reasons for these
differences are most probably variations in the local characteristics of gas diffusion layer, which
are strongly pronounced with small scale fuel cells.
2.6 Summary of chapter 2

In the present chapter, the characterization methods used in this thesis were presented. The key findings can be summarized as follows:

• In section 2.1, the fundamentals of neutron radiography were introduced. First, a literature overview about neutron radiography for fuel cells was given, succeeded by the presentation of the neutron infrastructure at PSI and the basic principles of neutron radiography. In subsection 2.1.5 the three existing image configurations and the different steps of image processing were presented. The chapter was concluded by a validation experiment of the water quantification.

• A brief introduction to two electrochemical methods to identify mass transport losses were reported: limiting current density and the pulsed gas analysis. A comparison of both techniques is given in section 2.4.

• Furthermore, several improvements regarding the cell assembly procedure, operating conditions, validation of the humidification concept and repeatability measurements were presented in subsection 2.5.5. Operation with the Multicell setup has shown excellent repeatabilities for small scale PEFCs.
2. CHARACTERIZATION METHODS
In the present chapter, a new methodology to distinguish water and ice will be presented. In section 3.1, the motivation of developing a new methodology to distinguish water and ice for fuel cells is given. Consecutively, the new energy selective measurement concept is presented in section 3.2, followed by the presentation of the commonly used energy selective neutron imaging techniques in section 3.3 and the technical implementation for fuel cell research will be presented in section 3.4. In the three following sections, the experiments performed with the neutron filter (see section 3.5), time of flight (see section 3.6), and velocity selector setup (see section 3.7) will be introduced. The different results will be discussed in detail in section 3.8. The chapter will be summarized in section 3.9 and an outlook is given in section 3.10.

3.1 Motivation

As has already been explained in subsection 2.1.2, neutron imaging methods, mainly neutron radiography (NR), are widely used to investigate the water distribution inside polymer electrolyte fuel cells (PEFC), due to its high contrast for hydrogen containing molecules and, at the same time, high transparency for structural materials such as aluminum [73, 83, 95, 124, 125]. As PEFCs will be used in an ambient environment, increasing interest is dedicated to their operation at subfreezing temperatures [39, 40, 124]. Under these conditions the water produced by

the electrochemical reaction risks to freeze, leading to a failure and/or to a damage of the fuel cell. Contrary to expectations, water does not condense as ice but is produced in its supercooled state under subfreezing conditions and freezing occurs randomly (see subsection 1.5.3).

Figure 3.1: Illustration of freezing inside (a) a geometry with defined cross section, (b) a geometry with defined height, and (c) a porous material. In (a), freezing can be identified as a change in volumetric density and increase in height. The phase transition cannot be identified in (b) as the number of molecules remains identical in direction of the beam. The combination into a two dimensional volume expansion is depicted in (c), where 3D imaging is required with sufficient resolution to identify the phase transition in the pore structure.

In this context, the ability to distinguish the aggregate state (liquid or solid) of water is highly valuable. Figure 3.1 shows three schematics of water accumulation inside (a) a geometry with defined cross section (e.g. cylindrical water column), (b) a geometry with defined height, and (c) a porous structure (e.g. gas diffusion layer). If water accumulates inside a volume with defined cross section (see Figure 3.1 (a)), the aggregate state transition can be measured in two different ways: First, water undergoes a volume expansion of around 10% [126], which can be measured as an increase in height. Second, the change in volumetric density decreases the number of atoms \( N \) in direction of the beam which leads to a higher transmittance according to Equation 2.1. Hence, the aggregate can be clearly identified in this configuration. On the
3.2 Concept

contrary, if the volume expansion occurs in perpendicular orientation (see Figure 3.1 (b)), the number of water molecules remains identical in direction of the neutron beam and no change in transmittance nor in height can be measured.

Figure 3.1 (c) represents water accumulation inside a partially saturated porous material (e.g. GDL inside a PEFC) in form of highly tortuous water cluster, where the volume expansion becomes 3-dimensional. Under these circumstances, the identification of changes in height or density becomes impossible, unless 3D imaging is used with sufficient resolution to image the pore structure (e.g. X-Ray Tomography [41]). Consequently, a new methodology is required to distinguish liquid water from ice independently on the morphology of the water cluster.

3.2 Concept

We propose a novel technique which relies on the energy dependency of the neutron cross section of water and ice. In the cold energy range [92], the kinetic energy of the incoming neutrons are in the same order of magnitude as the molecular excitations (translation, rotation, vibration) of liquid water and ice [127]. As the molecular energy content varies between the two aggregate states, the resulting interaction behaviour differs, causing a change in the total cross section [128, 129] (see Figure 3.2).

**Figure 3.2:** Schematics of deviating total neutron cross section of liquid water and ice above neutron wavelengths of 4 Å / 5.1 meV. The gray shaded area represents the contrast between both aggregate states.

The Lambert-Beer equation presented in section 2.1 describes the situation for monochromatic beams. In order to study energy dependent neutron interactions, the scintillator conversion
3. ENERGY SELECTIVE NEUTRON RADIOGRAPHY TO DISTINGUISH WATER AND ICE

efficiency η_{scint}(E), the energy spectrum Ω(E), and the total neutron cross section σ(E) need to be considered as function of the neutron energy E. Consequently, Equation 2.1 translates into the following equation [91]:

\[ \Delta = -\ln \left( \frac{I}{I_0} \right) = -\ln \left( \frac{\int_0^\infty \Omega(E) \eta_{scint}(E) e^{-\delta \sigma(E)} N dE}{\int_0^\infty \Omega(E) \eta_{scint}(E) dE} \right), \] (3.1)

The underlying data for Ω(E), η_{scint}(E), and σ(E) was measured experimentally. As can be identified in Equation 3.1, most parameters - but especially the microscopic neutron cross section σ(E) - are energy dependent (see Figure 3.2). The total neutron cross section σ(E) is composed by the following additive contributions [130]:

- **Elastic coherent scattering** results from collisions without exchange of energy and preserves its phase relationship. This type of interaction gives information about the equilibrium structure at the theoretical location without thermal motions and its contribution to the total neutron will be named σ_{co,el}(E) subsequently.

- **Inelastic coherent scattering** exchanges energy with the interacting nucleus but preserves the phase relationship. Based on this type of interaction, the collective motions of the structure due to thermal movements inside the structure can be studied. The contribution to the cross section will be defined as σ_{co,inel}(E).

- **Elastic incoherent scattering** scatters neutrons without exchange of energy, but changes its phase relationship. This interaction results in a nearly isotropic scattered intensity and its cross section will be named σ_{ico,el}(E) in the following.

- **Inelastic incoherent scattering** exchanges energy and changes its phase relationship. This type of interaction results from an interaction with the same atom at different positions and at different times, which enable the study of atomic diffusion processes inside a structure. Subsequently, the respective cross section will be called σ_{ico,inel}(E).

- **Absorption** of neutrons lead to the formation of heavier nuclei. Typical absorption materials for neutron interactions are any kind of boron containing composites, which are typically used as neutron shieldings. The representative cross section will be called σ_{ab}(E) in the following.

These five terms are additive and can be summarized to a total cross section σ(E) as follows [130]:

\[ \sigma(E) = \sigma_{co,el}(E) + \sigma_{co,inel}(E) + \sigma_{ico,el}(E) + \sigma_{ico,inel}(E) + \sigma_{ab}(E). \] (3.2)

In order to study changes of the aggregate state of water and ice in a small temperature range between ± 15°C, coherent interactions as well as incoherent elastic interactions will not change
significantly. However, the incoherent inelastic interaction is expected to be reduced in the frozen state, as the molecular diffusion is lowered in solid compared to its liquid state. This assumption is in good agreement with Harling et al. [131] and Edura et al. [132], who attributed the differences in the total neutron cross sections of water and ice to a different inelastic incoherent interaction between neutrons and water molecules, leading to a reduced total neutron cross section in frozen state. Other hydrogen containing materials like benzene [128], mesitylene [133, 134], methane [135] and toluene [134] show similar scattering behaviours. According to our knowledge, full energy spectra of liquid and frozen water are only published by Torres et al. [128], measuring ice at very low temperatures of 115 K. As can be seen in Figure 3.2, similar tendencies are obtained with our measurements.

Table 3.1 shows exemplary values of the macroscopic cross sections in the thermal energy range (≈ 0.025 eV) for selected elements used in this thesis [136]. As can be seen, hydrogen is a strong incoherent scatterer and has a significantly higher total neutron cross section compared to the other materials, which results in a good contrast for water.

<table>
<thead>
<tr>
<th></th>
<th>$\Sigma_c$</th>
<th>$\Sigma_{ic}$</th>
<th>$\Sigma_{ab}$</th>
<th>$\Sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1.757</td>
<td>80.26</td>
<td>0.3326</td>
<td>82.3</td>
</tr>
<tr>
<td>O</td>
<td>4.232</td>
<td>0.0008</td>
<td>0.0002</td>
<td>4.2</td>
</tr>
<tr>
<td>Al</td>
<td>1.495</td>
<td>0.0082</td>
<td>0.231</td>
<td>1.7</td>
</tr>
<tr>
<td>C</td>
<td>5.551</td>
<td>0.001</td>
<td>0.0035</td>
<td>5.6</td>
</tr>
<tr>
<td>Be</td>
<td>7.630</td>
<td>0.0018</td>
<td>0.0076</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Table 3.1: Selected neutron cross section in the thermal energy range extracted from the NIST database [136, 137]. As can be seen, the cross section of hydrogen is significantly higher compared to other commonly used materials.

3.3 Energy selective methods for fuel cell applications

Three different techniques are commonly used for energy selective neutron radiography: (1) Double-crystal monochromator methodology, (2) Time of flight technique, and (3) Velocity selector methodology. Although these techniques share a high energy resolution, the neutron flux is strongly reduced. Therefore, a new imaging concept with (4) a motorized neutron filter will be proposed. As all four techniques strongly differ in their energy resolution, neutron flux, as well as its spatial resolution (see Table 3.2), a brief comparison will be given hereafter:

1. **Monochromator:** In general, a monochromator relies on diffraction according to Bragg’s law. For neutron research, typically double crystal monochromators are used, which have a precise energy resolution of 0.05 Å at the expense of neutron flux. As the reduction of the
neutron flux would require exposure times in the order of 1 h for reasonable signal-to-noise ratios at one single energy, this technique cannot be used for studies of dynamic water transport inside fuel cells and no experiments will be presented with this technique.

2. **Time of flight:** The time of flight technique takes advantage of differences in the velocity of neutrons with different energies; neutrons of high energy propagate with increased velocity and will be detected prior compared to neutrons of low energy. Hence, based on the effective time of arrival at the detector, the energy of the neutrons can be differentiated. Although the neutron flux is strongly reduced in our experiments by pulsing the continuous neutron beam, a complete energy spectra can be measured with a single exposure, which makes this technique very attractive for time resolved measurements. Furthermore, these measurements serve to evaluate the potential of performing these experiments at a pulsed neutron source (e.g. Raden beamline at J-Park, Japan [138] or the IMAT beamline at ISIS, UK [139]) with a significantly higher neutron flux. The experiments with this technique are presented in section 3.6.

3. **Velocity selector:** Similarly to the time of flight technique, a velocity selector selects neutrons according their propagation speed with a rotating turbine inserted into the neutron beam. Dependent on its rotation speed, neutrons are transmitted or blocked. Hence, single captures are required at each energy. More details about the technique and experimental results are given in section 3.7.

4. **Motorized neutron filter:** Experiments with a neutron filter are typically not an energy selective technique as long as the filter is not motorized. With a motorization, the energy spectrum with and without filter can be compared. This enables the access to radiographs acquired at two distinct energy spectra with high neutron flux and is of particular interest for dynamic studies of water transport. Further details about this new methodology are given in section 3.5.

### 3.4 Methodology

As the time resolution is of particular interest for in-situ studies of fuel cells, an attractive alternative to the time consuming recording of full energy spectra will be presented in this section. According to Equation 2.1, the aggregate state cannot be identified inside fuel cells with a single capture, as neither the water thickness $\delta$, the cross section of ice or water $\sigma$, nor the molar density $N$ is known a priori. Hence, we propose a unique technique, which relies on the comparison of exposures in energy bands at low energy (LE) and high energy (HE), being independent on the water thickness and molar density. For this reason, we introduce a parameter
### 3.4 Methodology

<table>
<thead>
<tr>
<th></th>
<th>Energy resolution</th>
<th>Neutron flux</th>
<th>Spatial resolution (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monochromator</td>
<td>High</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td>Time of flight</td>
<td>Adjustable</td>
<td>Adjustable</td>
<td>Low</td>
</tr>
<tr>
<td>Velocity selector</td>
<td>Medium</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Neutron filter</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

**Table 3.2:** Comparison of the energy resolution, neutron flux, and spatial resolution of three commonly used energy selective neutron radiography techniques. Energy selectivity with a neutron filter is obtained by comparing energy spectra with and without filter. (*) dependent on detector setup used at beamlines / indicators given for commonly used detectors at PSI.

called *relative attenuation* \( \sigma_{rel} \), which represents the ratio between the optical density \( \Delta \) (see Equation 3.1) at LE and HE (see Figure 3.2):

\[
\sigma_{rel} = \frac{\Delta_{LE}}{\Delta_{HE}} = \frac{\sigma_{LE} \cdot N \cdot \delta}{\sigma_{HE} \cdot N \cdot \delta}.
\]  

(3.3)

If the radiographs at the two spectra are taken with a short time delay, the molar density \( N \) and the water thickness \( \delta \) can be assumed to be constant and the equation can be simplified as follows:

\[
\sigma_{rel} = \frac{\sigma_{LE}}{\sigma_{HE}}.
\]  

(3.4)

Hence, \( \sigma_{rel} \) is expected to be independent on the water thickness \( \delta \) and molar density \( N \), describing simply a ratio of two cross sections at LE and HE. This fact is of particular interest for dynamic studies of the water saturation inside fuel cells, where the water thickness is not known a priori. As the cross section of water and ice differs at LE, \( \sigma_{rel} \) varies for water and ice. From ref [128, 129] and Figure 3.2 it can be seen that the higher the energy spread between HE and LE, the higher is the absolute difference between \( \sigma_{rel} \) for water and ice. The ratio \( \sigma_{rel} \) for ice and liquid water is expected to be above 1 as the relative attenuation at LE is higher compared to HE. Consequently, the relative attenuations in liquid state is inferior with respect to the frozen state.

For fuel cell applications, three more parameters are of high importance: Neutron flux, spatial resolution and the time of energy spectrum change. First, a high neutron flux is required, in order to record radiographs with fast exposure times to investigate dynamic water transport inside the PEFC. Second, high spatial resolutions are needed to study the local water transport (e.g. distinction between the different layers of a fuel cell). Third, Equation 3.3 assumes a constant water distribution inside the cell, which requires a very fast energy transition between LE and HE. Consequently, the choice of an appropriate energy selective neutron imaging technique becomes challenging, as most of these requirements are contradictory. In order to find the best trade-off between these parameters for fuel cell applications, we present experiments with ex-situ and in-situ measurements of PEFC with three energy selective neutron imaging techniques:
3. ENERGY SELECTIVE NEUTRON RADIOGRAPHY TO DISTINGUISH WATER AND ICE

Motorized neutron filter (NF) in section 3.5, Time of flight (TOF) in section 3.6, and neutron velocity selector (VS) in section 3.7, which will be discussed and compared in section 3.8.
3.5 Neutron filter (NF)

The working principle of a neutron filter will be introduced in subsection 3.5.1, followed by the experimental description in subsection 3.5.2. In subsection 3.5.3, the ex-situ and in-situ results are presented, followed by a short conclusion of the measurements. The discussion of the results and the comparison with the two other energy selective imaging techniques can be found in section 3.8.

3.5.1 Working principle

The principle of a polycrystalline NF is based on coherent scattering of neutrons on the atomic structure (so called Bragg scattering); neutrons with a low energy pass the filter, whereas neutrons above the bragg-energy are scattered [140–143]. The cutoff energy can be calculated based on the atomic distance of the lattice planes \(d_{hkl}\) according to Bragg’s-law [140]:

\[
n \lambda = 2d_{hkl} \sin(\theta), \quad n = 1, 2, 3, \ldots
\]

(3.5)

The maximal wavelengths fulfilling Equation 3.5 is obtained at \(\sin(\theta) = 1\) and \(n = 1\), which will be defined as the Bragg-cutoff-wavelengths \(\lambda_c\):

\[
\lambda_c = 2d_{hkl,max},
\]

(3.6)

with \(d_{hkl,max}\) being the maximal distance between two lattice planes. For neutrons with a wavelengths \(\lambda < \lambda_c\), there is statistically at least one grain in the polycrystalline crystal,

Figure 3.3: Schematics of working principle of polychristaline neutron filter adapted from [140]. Neutrons with a low energy pass the filter, whereas neutrons above the cutoff wavelengths are scattered.
3. ENERGY SELECTIVE NEUTRON RADIOGRAPHY TO DISTINGUISH WATER AND ICE

<table>
<thead>
<tr>
<th>Material</th>
<th>Cutoff wavelength [Å]</th>
<th>Average total thermal σ [barn]</th>
<th>Average total residual σ [barn]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beryllium</td>
<td>3.95</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>Magnesium</td>
<td>5.55</td>
<td>3.5</td>
<td>0.7</td>
</tr>
<tr>
<td>Bismuth</td>
<td>6.50</td>
<td>9</td>
<td>0.8</td>
</tr>
<tr>
<td>Graphite</td>
<td>6.69</td>
<td>5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 3.3: Comparison of different neutron filter materials measured at room temperature [143].

which has the correct orientation θ and lattice distance dhkl to scatter the incoming beam (see Figure 3.3). For λ > λc, Equation 3.5 cannot be fulfilled and the incoming beam is not scattered while passing the filter.

During all our experiments, a Beryllium filter was used. The advantage of Beryllium is its relatively small atomic distance of ≈ 200 pm, which results in a low cutoff wavelength of 3.95 Å (with n = 1 and θ = π/2) of the 101 plane [142]. Furthermore, the cutoff energy of Beryllium coincides with a region of high neutron flux at both, the ICON and BOA beamline. Other cheaper materials (e.g. graphite) have a rather high cutoff wavelengths and are not suited for the energy spectrum at both beamlines, as the neutron flux strongly reduces above wavelengths of 5 Å / 3.27 meV (see Figure 3.4).

Figure 3.4: Experimentally determined energy spectrum of the BOA and ICON beamline. Furthermore, the cutoff edges of different filter materials are included into the figure.
3.5 Neutron filter

Figure 3.5: Experimentally and theoretically determined transmission of a 30 mm thick beryllium filter used during the experiments. Additionally, two supplementary curves of a thinner and thicker filter are included in the figure.

According to values published in ref [143], the total neutron cross sections of Beryllium are 5 barn for $\lambda < \lambda_c$ and 0.5 barn for $\lambda > \lambda_c$. Based on these values, the filter thickness could be adjusted in that way to obtain a good trade-off between low transmittance at high energies and high transmittance at low energies. For subsequent experiments, we decided to work with a filter of 30 mm (see Figure 3.5), where the transmission is expected to be 15% at high energies and 83% at low energies. As can be seen in Figure 3.5, this theoretical calculation is in very good agreement with the experimentally measured transmission values of the neutron filter. The reduction of the integral neutron flux is around 50% at the BOA and 34% at the ICON beamline.

The transmittance of the filter in Figure 3.5 was measured with the time of flight technique at the BOA beamline (see section 3.6); the theoretical transmittances for the three filter thicknesses are based on data published by Egelstaff et al. [143]. As predicted from Equation 3.6, the transmittance strongly increases above a wavelength of 3.95 Å / 5.1 meV. At $\lambda > \lambda_c$ approximately 85% of the neutrons pass the filter, as the residual cross section of a beryllium filter is rather small (0.5 barn). This contribution can be minimized by either decreased temperatures or by a thinner filter material. Decreased temperatures require a rather complex technical infrastructure which was avoided to maintain full flexibility for the motorization of the filter material. Hence, we decided to maintain the filter at a constant temperature of 35°C to keep the characteristic constant during the entire experiments. Regarding the filter thickness, a reduction would not
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only lead to a higher transmittance at low energy but also at high energy (see Figure 3.5). At wavelengths below $\lambda_c$, Bragg scattering dominates the total cross section and strongly reduces the transmission of the neutron filter. As Bragg scattering is mainly dependent on $d_{hkl,\text{max}}$, the temperature dependence is limited.

Based on a theoretical calculation according to Equation 3.1, a relative attenuation of 1.14 for frozen and 1.18 for liquid water is expected with the ICON spectrum, resulting in a theoretical contrast of 3.50%. The maximal potential of improvement with this technique would be obtained with a perfect filter, transmitting 100% at low and 0% at high energies. With this perfect filter, an enhanced contrast of 5.5% would be obtained.

3.5.2 Technical implementation

As already mentioned in section 3.4, the aggregate state cannot be identified from the filtered image only, because the thickness $\delta$ and molar density $N$ of water is not known a priori (see Equation 2.1). Therefore, two radiographs with and without neutron filter were acquired. Technically this was realized by a linear motor which moves and removes the filter from the beam axis (see Figure 3.6).

From Figure 3.5 it can be observed that the integral neutron flux is strongly reduced with the neutron filter. In order to keep constant image quality, the lower neutron flux of the filtered beam was compensated with higher exposure times [53]. This was realized by acquiring radiographs with a similar neutron dose with and without filter, while the ratio between the exposure times of images with and without filter was set to 3:1. To exclude artefacts from changes in the saturation levels, images with and without filter were recorded in an interleaved fashion (cf. Figure 3.6), with cycle periods listed in Table 3.4. Hence, for images merged over longer periods (e.g. 10 minutes), the distribution for the images with and without filter can be considered identical.

For the individual experiments, different exposure times were used which are summarized in Table 3.4.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Sample</th>
<th>Ex/In-Situ</th>
<th>Beamline</th>
<th>Exposure time / s</th>
<th>Cycle period / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water cylinder</td>
<td>Ex-situ</td>
<td>ICON</td>
<td>30</td>
<td>120</td>
</tr>
<tr>
<td>2</td>
<td>Water droplet</td>
<td>Ex-situ</td>
<td>BOA</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>Fuel cell</td>
<td>In-situ</td>
<td>ICON</td>
<td>30</td>
<td>120</td>
</tr>
<tr>
<td>4</td>
<td>Fuel cell</td>
<td>In-situ</td>
<td>ICON</td>
<td>2</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 3.4: Overview of samples measured with the neutron filter.
In this thesis, four different types of samples (see Table 3.4) were measured with the Beryllium Filter setup at the BOA [90] and ICON [89] beamlines of PSI (further details about the differences of the beamlines can be found in subsection 2.1.3) which will be described subsequently:

1. A **cylindrical water column** (⌀ 1.7 x 10 mm) was used as reference object with a known thickness of water. This sample facilitates the observation of phase transitions due to volumetric expansions and changes in density (see Figure 3.1 (a)). The measurement protocol for this sample consisted of freezing at -15°C, subsequent heating up to 3°C in 1 hour steps, and finally cooling down to -5°C and -7.5°C in order to produce supercooled water. This protocol allowed the comparison of liquid water and ice at the same temperature, as an influence of the temperature on inelastic neutron scattering cannot be excluded [129].

2. **Droplets of water** were manually injected with a micro-syringe into a fuel cell flow field. The experimental protocol was similar to previous experiment, with a freezing at -15°C and a subsequent heating up with steps of 1 h.

3. The third sample was a **small scale fuel cell** (active area 0.5 cm$^2$) similar to ref [39]. The cell was operated at different temperatures (-7.5°C, -5°C and -2.5°C) with a current density of 0.1 A cm$^{-2}$ during 10 minutes, after which it was kept with the produced water in supercooled state during 1 hour. The water in the cell was then frozen by cooling the cell down to -15°C and the cell was finally heated up to the same temperature as during the

---

**Figure 3.6:** Technical implementation of dual spectrum measurements based on a polycrystalline beryllium filter. By motorizing the filter, consecutive images with (continuous line) and without (dashed line) filter were acquired. The time sequence depicts an example with an exposure time of 30 s. Reprinted from Biesdorf et al. [42] with permission of the American Physical Society. Copyright 2014 American Physical Society.
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1 hour hold in which supercooled water is present. Unlike in the cylindrical water column, freezing in the fuel cell cannot be detected with volumetric expansion (see Figure 3.1). However, the event of freezing can be detected by an increase of the cell electrical resistance (further informations are given in section 4.3), which allowed to confirm the aggregate state of water (liquid during the first 1 hour hold, frozen during the second). An overview of the experimental protocol is depicted in Figure 3.7.

![Experimental protocol to compare supercooled and frozen water inside fuel cells at identical temperatures. The freezing event was identified based on a sudden increase of the membrane resistance.](image)

**Figure 3.7:** Experimental protocol to compare supercooled and frozen water inside fuel cells at identical temperatures. The freezing event was identified based on a sudden increase of the membrane resistance.

4. The **in-situ experiments** were performed on fuel cells of an active area of $1 \text{ cm}^2$. These cells were operated with the multicell setup [83] described in section 2.5. The experimental protocoll was identical to the experiments executed in section 4.3.

The image processing was accomplished according to the procedure described in subsection 2.1.6. In case of the NF experiments, $\sigma_{\text{rel}}$ is calculated as the ratio between the filtered and unfiltered attenuation:

$$\sigma_{\text{rel}} = \frac{\sigma_{\text{filter}} N \delta}{\sigma_{\text{nofilter}} N \delta} = \frac{\sigma_{\text{filter}}}{\sigma_{\text{nofilter}}} \quad (3.7)$$

Due to the interleaved measurements (see Figure 3.6), both the thickness $\delta$ and molecular density $N$ can be considered the same for the exposures with and without filter. They cancel out as shown in Equation 3.7 and $\sigma_{\text{rel}}$ only depends on the ratio of the differing cross sections. As the cross section at lower neutron energies is enhanced compared to higher neutron energies, $\sigma_{\text{rel}}$ is above 1 and is smaller for ice than for water. According to Equation 3.1, a relative attenuation
of 1.14 is expected for ice and 1.18 for liquid, resulting in a contrast of 3.5%. Unless specified otherwise, analyses are based on images averaged over a period of 10 minutes. Therefore, the subsequent definition of working image refers to an average image over 10 minutes.

### 3.5.3 Results

In this section, the experimental results of the four different samples will be presented: (1) Cylindrical water column, (2) Water droplet inside flow field, Small scale fuel cell experiments: (3) In-Situ/non-operando, and (4) Operando.

#### (1) Cylindrical water column

In Figure 3.8, the measured relative attenuation $\sigma_{rel}$ is plotted as a function of the optical density for different positions in the cylindrical water column. As the optical density is proportional to the molar density and thickness of water, it is well suited to illustrate a contrast between water and ice, which is purely based on changes of the relative attenuation. Each point in the graph represents an average value of a horizontal matrix with 19 segments of a surface of 90 x 7000 µm (see scheme Figure 3.8 bottom right). The graph contains four measurement points in the frozen state and five measurement points in the liquid aggregate state (see temperature ramp Figure 3.10). The classification of the aggregate states is based on analysis of the vertical volume expansion in the cylinder. According to Equation 3.1, the optical density is proportional to the thickness of water. As expected, $\sigma_{rel}$ values higher than 1.0 are obtained, because the attenuation of H$_2$O is higher for low energy neutrons. Contrary to what is expected from Equation 3.7, the

![Figure 3.8:](image)

Relative attenuation ($\sigma_{rel}$) as a function of the optical density without filter. Averaging over 1 hour is used to reduce the noise. Reprinted from Biesdorf et al. [42] with permission of the American Physical Society. Copyright 2014 American Physical Society.
measured relative attenuation slightly depends on the water thickness. A detailed explanation is given in subsection 3.8.5.

However, as the corresponding curves of Figure 3.8 clearly do not overlap, we can conclude that the change of $\sigma_{rel}$ is the result of a change in the cross section $\sigma$ and the aggregate state of water can be obtained from the dual spectrum measurements without any a priori knowledge of the water thickness with a contrast of 1.6% within a cylindrical water column of a diameter of 1.7 mm.

(2) Water droplet inside flow field

In order to prove that this measurement technique can also be applied on small water clusters, a similar measurement was performed with water droplets injected manually inside a flow field (see Figure 3.9 (a)) undergoing a temperature ramp from -15 to 5°C; Figure 3.9 (b-d) depicts the temporal evolution of the relative attenuation parameter of droplets of three different sizes.

Figure 3.9: Temporal evolution of $\sigma_{rel}$ undergoing a temperature ramp from -15 to +5°C of three different droplets inside a flow field.
First, the phase transition can be identified in all three droplets, even of small water slugs in (b) and (c). In (c) and (d), the phase transition clearly occurs at a temperature of 1°C, whereas in (b) the phase transition cannot be clearly identified at this temperature. This fact can be most likely explained by a temperature gradient along the flowfield, which might be induced by the liquid coolant (see Figure 3.9 (a)). Second, the signal of $\sigma_{\text{rel}}$ in Figure 3.9 (b-c) is much noisier compared to Figure 3.9 (d), which can be explained by the differences of the water quantity. Third, the absolute values of the relative attenuation fully agree with the tendencies observed in Figure 3.8, increasing with increasing water thickness.

However, similar to previous measurements, clear steps can be observed during the aggregate state transitions during freezing and melting of the water slug which proves that the technique is also applicable on small water clusters of a few microliters.

(3) In-Situ/non-operando

The previous three measurements have clearly validated the methodology of the dual spectrum technique for bulk water and small droplets. For fuel cell applications, the identification of the aggregate state as well as the phase transitions is of high importance. The latter can be determined based on the temporal evolution of $\sigma_{\text{rel}}$; the absolute aggregate state only based on a calibration curve. Hence, we propose a calibration based on the curve presented in Figure 3.8. This can be done in practice by defining a liquid fraction parameter $f_{\text{LQ}}$ as follows:

$$f_{\text{LQ}}(\sigma_{\text{rel}}, \Delta_{\text{nofilter}}) = \frac{\sigma_{\text{rel}} - m \cdot \Delta_{\text{nofilter}} - a_{\text{ice}}}{a_{\text{water}} - a_{\text{ice}}}$$  \hspace{1cm} (3.8)

The values of the slope $m = 0.04$, $y$-intercept of ice $a_{\text{ice}} = 1.109$ and liquid $a_{\text{water}} = 1.127$ were obtained from a linear fitting of the experimental data in Figure 3.8, so that the value of $f_{\text{LQ}}$ is 0.0 for ice and 1.0 for liquid water.

The temporal evolution of the liquid fraction parameter $f_{\text{LQ}}$ is illustrated in Figure 3.10 during the temperature ramp from -7.5°C to 3°C. The measurement points are merged over 10 minutes and over a small region of 5 mm$^2$. The phase transition at 0°C is clearly visible and exceeds the noise level significantly. As expected, no phase transformations are observed during the last two measurements at -3°C and -7.5°C, where supercooled water is present. The error bars represent $2.57 \times 99 \%$ of measurement values) times the standard deviation of $f_{\text{LQ}}$ for the corresponding temperature. The obtained absolute values of $f_{\text{LQ}}$ range from 0.0 to 1.0, which is obvious because the parameters in Equation 3.8 were fitted using the same underlying data. The possibility of obtaining spatial information on the aggregate state is illustrated in Figure 3.11, for images averaged over 1 hour. The measurements with the water column (see Figure 3.11 (a)) resulted in clear high resolution images of the aggregate state represented using the value
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Figure 3.10: Temporal evolution of the liquid fraction parameter $f_{LQ}$ during a temperature ramp (spatial averaging over a surface of approximately 1 x 5 mm). Reprinted from Biesdorf et al. [42] with permission of the American Physical Society. Copyright 2014 American Physical Society.

of $f_{LQ}$. However, the calculated $f_{LQ}$ values for the flow channels of the fuel cell (see Figure 3.11 (b)) are strongly scattered and will be discussed subsequently.

Figure 3.11: Spatial distribution of the calculated liquid fraction parameter for images of the water column at (a) 1°C and (b) 1°C of the water column and the cathode flow channels (c) 1°C and (d) 1°C. Figure (e) illustrates the spatial distribution of the water content inside the fuel cell. All images are averaged over 1 hour to reduce the noise. Reprinted from Biesdorf et al. [42] with permission of the American Physical Society. Copyright 2014 American Physical Society.

In Figure 3.12, the temporal evolution of the calculated liquid fraction parameter averaged over the entire flow channels of the cathode of the small scale fuel cell is presented. In these
experiments, water was electrochemically produced during the first 30 minutes and has then been maintained at subfreezing temperatures for 1 h. Afterwards, the cells were cooled down to \(-15^\circ\text{C}\) to induce the freezing within the cells (see Figure 3.7). The last experiment was followed up by a temperature ramp (see temperature ramp in Figure 3.12). The first striking observation is that the liquid fraction parameter calculation based on the water scale calibration in Figure 3.8 gives values which are largely out of the expected range (0.0 - 1.0), despite the fact that the measurements on both objects were performed with the very same imaging setup. Possible reasons include the different morphologies of water between the two objects (filled reservoir vs. water droplets) or different interferences from the container material (aluminum for the water column and graphite for the fuel cell). Despite the fact that a meaningful absolute value of \(f_{LQ}\) cannot be extracted, it must be noted that the phase transitions (freezing of supercooled water during the three experiments at \(-2.5^\circ\text{C}\), \(-5^\circ\text{C}\) and \(-7.5^\circ\text{C}\) and melting of ice during the following temperature ramp) can clearly be identified as a step of the \(f_{LQ}\) value. Thus, we could confirm the presence of supercooled water as a product of the PEFC reaction with a direct measurement method.

**Figure 3.12:** Temporal evolution of the calculated liquid fraction parameter \(f_{LQ}\) inside the flow channels of a small scale fuel cell (average over 4 channels corresponding to a total area of \(2\text{mm}^2\)). Reprinted from Biesdorf et al. [42] with permission of the American Physical Society. Copyright 2014 American Physical Society.

(4) Operando

As the aggregate state was not identified in an absolute fashion in previous measurements, we resign from utilizing the parameter of \(f_{LQ}\) in the following experiments. Subsequent measurements will be exclusively based on the temporal evolution of the relative attenuation \(\sigma_{rel}\) to identify phase transitions. Figure 3.13 shows an in-situ cold start experiment studied with a neutron filter averaged over the entire active area of \(1\text{cm}^2\) in through-plane mode. During this
example, the fuel cell was able to be operated during almost 1 h until its failure (black dotted line in Figure 3.8 (b)). In Figure 3.8 (a), the relative attenuation parameter requires approximately 15 minutes until its stabilization. This observation can be explained both by the requirement of reaching a certain water thickness and by getting to a dynamic equilibrium of the water saturation inside the GDL, which is typically reached at a saturation level of 30% (or 60 µm of water) inside a GDL (see Figure 3.8 (c)). However, the decrease of the relative attenuation is clearly coupled with the cell failure. Hence, this indicates that a phase transition can be directly measured inside an operating fuel cell with this new methodology, as long as the cell can be operated longer than 15 minutes under subfreezing conditions.

![Graph](image_url)

**Figure 3.13:** In-situ experiments of PEFC measured with the motorized neutron filter averaged over the entire active area of a 1 cm² fuel cell in through-plane image configuration at -7.5°C.

In order to validate the methodology on growing in-situ water droplets, Figure 3.14 shows the temporal evolution of the relative attenuation measured of a water droplet inside the flow field during a cold start. From the water thickness in (c) it can be observed that the droplet is created after around 15 minutes, which is in good agreement with previous experiment in Figure 3.13. This particular droplet was chosen because the phase transition can be observed visually as a
volume expansion and an inversion of the meniscus. Correlating the optical observations with the relative attenuation parameter, only limited information can be gained, as the signal is highly fluctuating. However, at the cell failure, a small drop of the relative attenuation can be identified, which might be attributed to the change of the aggregate state. Nevertheless, the fluctuations of the relative attenuation are more dominant than the differences of the relative attenuation induced by the freezing. Regarding the other droplets where the volume expansion cannot be observed visually, the phase transition cannot be identified with high certainty.

\[ \text{Relative attenuation} \]

\[ \text{Cell voltage / mV} \]

\[ \text{Water thickness / mm} \]

\[ \text{Operation time / h} \]

**Figure 3.14:** In-situ experiments of PEFC measured with motorized neutron filter of a droplet of a 1 cm² fuel cell in *through-plane* image configuration at -7.5°C.

### 3.5.4 Conclusion

A novel method called dual spectrum neutron imaging was developed with a beryllium filter in order to determine the aggregate state and phase transitions of water (liquid to ice and vice versa) inside fuel cells without any prior knowledge of the water thickness. The following key findings were obtained during the measurements with the neutron filter:
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- The proposed methodology was validated using a cylindrical water column. A contrast of about 1.6% was obtained between frozen and liquid water.

- The applicability of this methodology was shown for water droplets (in the range of µl) and bulk water (in the range of ml).

- The identification of aggregate states inside a fuel cell are only possible after operating time inferior to 30 minutes as a certain water thickness is required.

- The experimental contrast of around 1.6% is the limiting factor of this methodology. An increased contrast would strongly enhance the signal-to-noise ratio and the identification of phase transitions.

- Aggregate state transitions from supercooled to ice were unambiguously identified in operating PEFCs, which proves the presence of supercooled water as a product of the PEFC reaction under subfreezing temperatures.
3.6 Time of flight (TOF)

Similar to previous section, the working principle is introduced in subsection 3.6.1, followed by the experimental description in subsection 3.6.2 and the results in subsection 3.6.3. A detailed discussion of the results with its comparison to the two other energy selective neutron techniques can be found in section 3.8.

3.6.1 Working principle

Time of flight measurements can be either performed at a pulsed neutron source or by pulsing a continuous neutron source [91]. Imaging beamlines at pulsed neutron sources are currently under construction at the Japan Proton Accelerator Research Complex (J-Park) (Raden beamline [138]), at the ISIS Neutron and Muon Source in the United Kingdom (IMAT beamline [139]) and at the European Spallation Source (ESS) in Sweden (ODIN beamline [144]). As these beamlines are still not in user operation, all experiments presented in this thesis were performed at the continuous neutron source SINQ at PSI. The working principle of a typical TOF setup is depicted in Figure 3.15. In general, the setup consist of a pulse chopper, which transforms the continuously provided polychromatic neutron beam into short neutron pulses. Neutrons of high energy will propagate with a high velocity and will be detected prior compared to neutrons of low energy. Hence, based on the effective time of arrival, the energy of the neutrons can be calculated according to a simple energy balance:

\[
v_0 = \frac{d}{\Delta t} = \sqrt{\frac{2E}{m}},
\]

where \(v_0\) depicts the velocity of the incoming neutron, \(d\) the distance between the pulse chopper and detector, \(\Delta t\) the time between the trigger signal of the pulse chopper and the detection on the detector, \(E\) the kinetic energy, and \(m\) the neutron mass.

![Figure 3.15: Working principle of a time of flight setup at a continuous neutron source. Based on the effective time of arrival of the neutrons at the detector, the neutron energy can be differentiated.](image)

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3.6.2 Technical implementation

The experiments with the TOF setup were performed at the BOA beamline [90]. The neutron beam was pulsed by a disk made of Boral (alloy of boron and aluminium) comprising a radial slit of 17° (duty cycle of 4.7 %). The rotation frequency of the disk was set to 20 Hz, which results in short repetition periods of 50 ms. With a distance of 7.8 m between pulse chopper and detector, measurements in an energy spectrum between 1-9 Å (1 - 80 meV) could be performed. Based on the chosen rotating speed and travel distance, no pulse overlap chopper was required.

The detector was a 2D 3He-filled wire chamber counting device (EMBL-detector [145]), with 256 x 256 pixels over a field of view of 10 x 10 cm² [90]. With this type of detector, an additional reduction of the neutron flux was required; hence a small hole aperture was introduced into the beam axis. Measurements were acquired with an energy resolution of 0.05 Å. In order to increase the image quality, the energy resolution was reduced to 0.5 Å, by averaging the energy resolution by a factor of 10 in the post-processing. A pixel resolution of around 1 mm/pixel was achieved with the detector setup. Detailed information about the TOF imaging setup can be found in ref [90].

Similarly to previous measurements with the neutron filter and TOF, $\sigma_{rel}$ is calculated based on the integrated radiograms in the energy ranges between 6 - 7.5 Å (1.45 - 2.27 meV) for LE and 2 - 4 Å (5.1 - 20.5 meV) for HE as follows:

$$\sigma_{rel} = \frac{\sigma_{6-7.5\text{Å}}}{\sigma_{2-4\text{Å}}}$$

(3.10)

According to Equation 3.1, a relative attenuation of 1.45 is expected for liquid water and 1.54 for ice in this energy range, resulting in a theoretical contrast of 6.2 %.

3.6.3 Results

Based on the experimental setup used, the neutron flux had to be significantly reduced, which prohibited the study of dynamic measurements with TOF. Hence, only ex-situ samples were measured with this methodology. Figure 3.16 shows the total neutron cross section of a scale filled with water ($\delta = 1.4$ mm) measured at several temperatures around 0°C (-9, -3.5, -0, 3.5, 7, 11°C) and hold during 1 h at each temperature. As the water thickness and the molar density are known a priori inside the scale, the cross section can be calculated at every wavelengths and temperature. In order to increase the signal-to-noise ratio, the two overlaying curves represent the spectrum averaged over 3 temperatures above and below 0°C. It can be clearly seen that the cross section of liquid water and ice diverges at wavelengths above 5 Å / 3.3 meV which is in good agreement with literature [128, 129]. Furthermore, no significant temperature dependency is measured in our temperature range.
3.6 Time of flight

Figure 3.16: Total neutron cross section of liquid water and ice measured in an energy range between 0.5 and 9 Å. The underlying curves represent the spectra for the individual temperatures (-10, -4.5, -1, 2.5, 6, 10°C).

According to Equation 3.10, relative attenuations can be calculated for every single temperature, which are plotted in Figure 3.17; the gray dotted lines represent the theoretical values calculated according to Equation 3.1. At a first glance, the contrast between liquid and ice is significantly enhanced compared to previous measurements with the neutron filter, which can be explained by the strongly increased energy spread between low (LE) and high energy (HE). This leads to the fact that the phase transition between frozen and liquid water is identifiable with an

Figure 3.17: Relative attenuation parameter as a function of the temperature measured in a water scale of 1.4 mm; the gray dotted lines depict the theoretical values according to Equation 3.1. With this technique, a contrast of 6.2% is obtained between ice and water.
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experimental contrast of around 6.2%. The values of $\sigma_{rel}$ are rather stable in the frozen state, whereas significantly higher fluctuation can be observed above the melting temperature of ice; especially at 10°C. A possible explanation can be given by a change of the water thickness due to evaporation or leakage of water inside the water scale during the 3 h of experiment above the melting point. Nevertheless, these measurements clearly show the ability to distinguish water and ice with TOF.

![Figure 3.18](image)

**Figure 3.18:** Temporal evolution of (a) relative attenuation with a time resolution of 10 minutes undergoing a temperature ramp specified in (b) measured with time of flight. Based on the relative attenuation parameter, the aggregate state transition can be clearly observed.

In Figure 3.18 the temporal evolution of the (a) relative attenuation parameter is plotted with a time resolution of 10 minutes undergoing a temperature ramp specified in (b). Figure 3.18 (a) clearly highlights the strongly reduced neutron flux compared to previous measurements with the neutron filter, which leads to a strong reduction of the signal-to-noise ratio from 14.712 with the neutron filter to 2.213 with the present technique. Nevertheless, even with the rather noisy signal, the aggregate state transition is clearly identifiable at temperatures above 0°C.

To sum up, the TOF measurements have shown its great potential to study phase transitions with a high contrast at time resolutions down to 10 minutes, even with the highly reduced neutron flux of the TOF detector at PSI. In order to make this technique suitable for fuel cell investigations, two significant enhancements need to be performed in subsequent measurements. First, these experiments should be repeated at an imaging beamline of a pulsed neutron source (e.g. the Raden beamline at J-Park [138] or the IMAT beamline at the ISIS [139]), due to the higher neutron flux and a enhanced detector setup. As the neutron flux is expected to be 2-3 orders of magnitudes higher compared to current TOF setup at PSI, the exposure time and
3.6 Time of flight

hence the signal-to-noise ratio should be significantly improved. According to Boillat [53], the relationship between neutron flux and exposure time is related via the root function; hence an increase of 2-3 orders of magnitudes in neutron flux results in an increase of the time resolution by 1.4-1.7 orders of magnitudes. Furthermore, the IMAT beamline provides a Micro Channel Plate (MCP) detector which will not only be able to capture the full neutron flux (high flux cannot be captured with current detector at PSI) but also higher spatial resolutions. Second, the current design of the rotating disk of the TOF setup at PSI can be optimized for subsequent measurements. This can be achieved by maximizing the neutron flux at the expense of the energy resolution which is not needed for present experiments.

3.6.4 Conclusion

During the experiments with the TOF setup, the following key findings were obtained:

- A significantly higher contrast compared to the neutron filter experiments was obtained.
- Although the neutron flux was strongly reduced with the TOF setup, the aggregate state transition was clearly identified, even at high time resolutions of 10 minutes
- The TOF setup has a high potential for improvements for further fuel cell investigations. This can be either performed by executing the experiments at a pulsed neutron source or by utilization of optimized rotating disks of the TOF setup at the BOA beamline.
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3.7 Velocity selector (VS)

This section is split into the description of the working principle in subsection 3.7.1, the technical implementation in subsection 3.7.2, results in subsection 3.7.3 and conclusion in subsection 3.7.4. Similar to previous measurements, the discussion and comparison with previous results can be found in section 3.8.

3.7.1 Working principle

The working principle of the neutron velocity selector is depicted in Figure 3.19 [146, 147]. In general, the neutron velocity selector consist of a rotating turbine of length $L$ which is opaque for neutrons. In order to transmit neutrons of selected energies, the VS needs to rotate with a certain rotating speed $\omega$ to pass neutrons in between the turbine blades. If the turbine blades have a phase angle $\beta$ between the inlet and the outlet plane, only particles with the velocity $v_0$ are able to pass through the velocity selector, fulfilling the following equation [148]:

$$\frac{L}{v_0} = \frac{\beta}{\omega}. \tag{3.11}$$

![Figure 3.19: Working principle of neutron velocity selector at the ICON beamline at PSI [148]. (a) Velocity selector rotates with a certain rotating speed $\omega$ and passes neutrons with a certain energy according to Equation 3.11. (b) Temporal evolution of a duty cycle with stabilization intervals of approximately 1 minute in between each wavelengths.](image)

3.7.2 Technical implementation

The experiments with the neutron velocity selector were performed at the ICON beamline of the SINQ at PSI [89]. The spectral resolution of the VS of the ICON beamline is $\Delta \lambda/\lambda = 15\%$. Radiographs were taken at $3\,\text{Å} / 9.1\,\text{meV}$ (HE), $4.5\,\text{Å} / 4.0\,\text{meV}$ and $6\,\text{Å} / 2.3\,\text{meV}$ (LE) to calculate
3.7 Velocity selector

Figure 3.20: Experimentally determined relative attenuation parameter measured in two different cells with a velocity selector at the ICON beamline. As can be seen, a clear difference between ice and liquid water can be identified with a clear step at the melting temperature of water.

\[ \sigma_{rel} = \frac{\sigma_{6A}}{\sigma_{3A}} \]  

(3.12)

Six radiograms were taken with an exposure time of 30 s at each energy, which results in a cycle time of approximately 12 minutes (see Figure 3.19 (b)). The camera was a Andor iKon-L with 2048x2048 pixels with a pixel resolution of 60 \( \mu \)m/pixel in through-plane configuration [83]. The aperture was set to 40 mm. According to Equation 3.1, a relative attenuation of 1.34 is expected in liquid state and 1.28 in the frozen state, which results in a contrast of 4.68 \%.

All experiments with the VS were performed on 1 cm\(^2\) fuel cells of the Multicell setup described in section 2.5. The following two experiments were carried out with the VS:

- **(1) Temperature ramp:** During this experiment, PEFCs were electrochemically filled with around 70 \( \mu \)m of water according to the experiment described in subsection 2.1.7. Afterwards, the cell current as well as gas flows were stopped and the remaining water was imaged during 1 h at each temperature (-7.5, -2.5, -1, 0, 1, 2.5, 5\(^\circ\)C).

- **(2) In-Situ experiments:** The in-situ experiments were performed with the identical protocol which will be presented in section 4.3.
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3.7.3 Results

Figure 3.20 shows the temporal evolution of the relative attenuation measured at 7 different cell temperatures for two different cells (cell 1 in (a) and cell 2 in (b)). The individual measurement points represent median values calculated during 1 h of measurements (see Figure 3.21). Three major observations can be drawn from both graphics. First, a significant step around 0°C can be identified in both cells which can be clearly attributed to the aggregate state transition from frozen to liquid water. Second, the absolute value of the relative attenuation is significantly different in between the two cells and strongly deviates from the theoretical values of 1.34 for liquid and 1.28 for ice. Similar to previous measurements, this deviation can be explained by several mechanisms like thickness dependency of the relative attenuation or error in the scattered background (see subsection 3.8.5). Another interesting point is the poor repeatability of both cells regarding the temperature dependency and the experimental contrast between the two aggregate states.
In order to understand the poor repeatability, the temporal evolution of $\sigma_{rel}$ is plotted in Figure 3.21 undergoing the very same temperature ramp but with a time resolution of 12 minutes (10 minutes could not be achieved as the cycle time was 12 minutes). At first glance, a distinct aggregate state transition can be clearly identified at 0°C with cell 1, whereas no significant trend of cell 2 can be observed, as the signal is superimposed by a significant contribution of noise. Hence, the observed temperature effect in Figure 3.20 (b) results from averaging effects and has no scientific meaning. This qualitative observation can be quantified by the calculation of the signal-to-noise ratio according to Equation 2.3, resulting in a value of 3.824 for cell 1 and 1.596 for cell 2. In both cases, this value is significantly lower compared to measurements with the neutron filter (value of 14.712) but in a similar range compared to the TOF measurements (value of 2.213). A possible explanation for the strongly reduced signal-to-noise ratio of cell 2 might result from the thickness dependency of water (see Figure 3.8). As can be seen in Figure 3.21 (c), the water thickness of cell 1 is stable during the entire 7 h of the experiments, whereas cell 2 shows a decreasing water thickness, which might be related to evaporation processes. Furthermore, it has to be mentioned that previous measurements have shown in Figure 3.8 and Figure 3.18 were measured on samples with a water thickness of approximately 1.5 mm compared to 70 μm in present experiment. By a reduction of the water thickness by more than one order of magnitude, the signal is strongly affected. Another reason might result from the cycle time in the range of 12 minutes (Figure 3.19 (b)); changes in the water thickness can induce significant errors in the calculation of the relative attenuation. The fluctuations of the water thickness in the range of $<10\mu$m can be related to limitations of the image processing (e.g. intensity correction).

Figure 3.22 illustrates the temporal evolution of (a) $\sigma_{rel}$ during a cold start averaged over the entire active area; the cell voltage is depicted in (b). As can be seen, the cell fails after approximately 45 minutes of operation (black dotted line). Similar to previous in-situ measurements with the Beryllium Filter (see Figure 3.13), no stable value is obtained during the first 15 minutes. This can be explained by the fact that the amount of water is still very little and highly time-variant. With a cycle time of 12 minutes, the imaging of dynamic water transport is rather challenging. However, after a certain operating time, a reasonable parameter can be calculated. However, no sharp increase of $\sigma_{rel}$ can be measured at the point of cell failure which might also be explained with the duty cycle time of 12 minutes with the VS.

3.7.4 Conclusion

With the VS setup, the following key findings were obtained:

- The neutron filter provides a sufficient contrast between water and ice for measurements which do not require a high time resolution.
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Figure 3.22: In-situ measurements of PEFC measured with neutron velocity selector averaged over the entire active area of a 1 cm$^2$ fuel cell in through-plane image configuration at -7.5°C.

- Although the cycle time can be reduced in further measurements by just measuring at 3 Å / 9.1 meV and 6 Å / 2.3 meV, the time of energy change between HE and LE will limit its application for dynamic studies of water transport inside fuel cells.
3.8 Discussion

In the three previous sections, the applicability to distinguish water and ice was studied inside ex-situ and in-situ samples with the neutron filter, neutron velocity selector and TOF setup. In general it was observed that all three methods are able to distinguish water and ice, with significant differences in its contrast and time resolution. In the subsequent sections, the advantages and disadvantages of the three different techniques regarding temporal (see subsection 3.8.1), spatial (see subsection 3.8.2) and energy resolution (see subsection 3.8.3) will be discussed. Furthermore, explanations are given regarding the contrast between water and ice (see subsection 3.8.4), the absolute value of the relative attenuation parameter (see subsection 3.8.5), the minimal water thickness (see subsection 3.8.6), concluded with limitations of the method for fuel cell applications (see subsection 3.8.7).

3.8.1 Temporal resolution

For fuel cell research, the temporal resolution is of particular interest to study dynamic water and ice accumulation. Figure 3.23 summarizes previous measurements with (a) time of flight, (b) neutron filter, and (c) velocity selector with a time resolution of approximately 10 minutes per data point (time resolution of VS is 12 minutes due to limitations resulting from the duty cycle). In general it can be observed that the highest SNR is obtained with the neutron filter. These differences can be explained by two effects: (1) neutron flux and (2) the time of energy change.

(1) Neutron flux

According to ref [53], the SNR scales with the neutron flux. This effect can be clearly observed in the experimental data summarized in Table 3.5, where highest SNRs are obtained with high neutron fluxes. With our experimental setup during the TOF measurements, the neutron flux was strongly reduced due to limitations of the detector setup, resulting in the lowest SNR of around 2. In contrast, an excellent SNR ratio is obtained with the neutron filter as the minimal neutron flux did not went below 33% of open beam. Similar explanation holds for the measurements with the VS, where moderate SNR are obtained. However, it has to be mentioned that the water thickness during the measurements with the VS was more than one order of magnitude smaller compared to both other techniques.

(2) Time of energy change

Another important parameter concerning the SNR is the time of energy change. The TOF setup has the fundamental advantage that a full energy spectrum can be measured with a single
3. ENERGY SELECTIVE NEUTRON RADIOGRAPHY TO DISTINGUISH WATER AND ICE

Figure 3.23: Comparison of relative attenuation parameter undergoing temperature ramps measured with (a) time of flight, (b) neutron filter, and (c) velocity selector. It can be clearly seen that the signal-to-noise ratio scales with neutron flux. Hence, the best temporal resolution is obtained with the neutron filter.

capture. Hence, no time is required to change the energy between LE and HE, which perfectly fulfils the boundary conditions of Equation 3.4.

In contrast, measurements with a NF require a certain time for the alternation of the energy spectrum, in order to place or remove the filter from the beam axis. This movement was automatized by a linear motor; hence the transition accounted for less than 1 second. According to the experimental requirements, different cycle times were chosen, ranging from 8 - 120 s (see Table 3.5: Overview of neutron flux and spatial resolution with the three different energy selective imaging techniques. (*) 33% OB at the ICON beamline, 50% OB at the BOA beamline; (**) Between 2-10%OB according to the energy chosen [89]; (***) water thickness is one order of magnitude smaller compared to NF and TOF measurements.)
3.8 Discussion

Table 3.4), during which the amount of water can be assumed to be constant. However, especially in the in-situ experiments, variations or redistribution of the local water saturation can affect the analysis.

The maximal time to vary the energy between LE and HE is required with the VS, as the rotation speed needs to stabilize during approximately 1 minute. Consequently, duty cycles of around 12 minutes are obtained, in which the water distribution can hardly be assumed to be constant. Hence, dynamic studies of fuel cells cannot be performed with this technique (see Figure 3.22).

3.8.2 Spatial resolution

The three imaging techniques have significant differences in their spatial resolution (see Table 3.5). The setup with the NF and VS can be utilized with the so called "midibox", having full flexibility on the imaging configuration, scintillator material or camera used [89]. During presented experiments, a pixel resolution of 60 \( \mu \text{m} / \text{pixel} \) with an effective resolution in the order of 200 microns was achieved. High resolution imaging was also used for the NF and could be used for the VS.

In contrast, the present TOF detector at the BOA beamline is highly optimized for fast readout times, resulting in a rather low resolution of around 1000 \( \mu \text{m} / \text{pixel} \). However, a new generation of TOF detector by Tremsin et al. [149] exists, which strongly improves the spatial resolution. In future experiments, these kind of detectors would enable local investigations of freezing inside fuel cells.

3.8.3 Energy resolution

As already mentioned, the three imaging techniques strongly differ in their energy resolution. The motorization of the neutron filter is the simplest energy selective technique, measuring at two distinct energy spectra. Hence, the energy resolution is very limited, but enables measurements with a maximal neutron flux. The energy selectivity of the VS is adjusted by the rotating speed of the velocity selector, enabling the precise measurement in a small energy range between 2-9 Å (1.0-20.5 meV) at the ICON beamline. Major drawback of this energy selective technique is the long stabilization time of the turbine-motor, which requires up to 1 minutes to change between the different energy ranges. The energy technique of choice of high energy resolutions is the TOF technique, measuring a full energy spectrum in one single capture.

3.8.4 Contrast between water and ice

Another important parameter is the contrast between water and ice (see Table 3.6); the higher the energy spread between HE and LE, the higher the difference of \( \sigma_{rel} \) between the two aggregate
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<td>$\sigma_{rel,\text{frozen}}$</td>
<td>1.14</td>
<td>1.28</td>
<td>1.536</td>
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<td>Theoretical contrast</td>
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<td>4.68%</td>
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<td>1.15</td>
<td>1.16</td>
<td>1.45</td>
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<td>$\sigma_{rel,\text{frozen}}$</td>
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<td>1.54</td>
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<tr>
<td>Experimental contrast</td>
<td>1.6%</td>
<td>10.4%</td>
<td>5.7%</td>
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Table 3.6: Theoretical calculations of relative attenuation and contrast between water and ice for the three imaging techniques according to Equation 3.1.

Table 3.6: Theoretical calculations of relative attenuation and contrast between water and ice for the three imaging techniques according to Equation 3.1.

states. Consequently, the TOF setup has shown the highest contrast between water and ice, as $\sigma_{rel}$ was calculated between 6 - 7.5 Å (1.5 - 2.3 meV) (LE) and 2 - 4 Å (5.1 - 20.5 meV) (HE). With the comparison of the filtered and the white beam with the NF, a rather low contrast is obtained (1.6% in Figure 3.8), as the white beam includes the contribution of the filtered image. Even by using an ideal filter material with no transmission at high energies and full transmission at low energies, the contrast would only be theoretically improved from 3.5 to 5.51%. Regarding the VS, the difference was calculated based on the ratio of 3 Å / 9.1 meV (HE) and 6 Å / 2.3 meV (LE), in a relatively thin energy band of $\Delta \lambda / \lambda = 15\%$. According to theory, this ratio would result in a contrast of around 6.2%, which is in a similar range as obtained in Figure 3.21.

3.8.5 Absolute value of $\sigma_{rel}$

As can be seen in Table 3.6, significant differences are obtained between the theoretical calculation and the experimental values of the relative attenuation parameter. Furthermore, a thickness dependency of this parameter was identified in Figure 3.8 which is contradictory to Equation 3.4. These differences can be explained by three undesired effects: (1) beam hardening, (2) error in background calculation, (3) sample scattering, and (4) interference with enclosing materials.

(1) Beam hardening

The experiments were either executed at the ICON or the BOA beamline with polychromatic energy spectra and a single average attenuation is calculated according to Equation 2.1 over the radiograms. By simplifying Equation 3.1 to Equation 2.1, beam hardening effects have to be taken into account. In case of the experiment with the neutron filter, the energy distribution of a filtered image is reduced based on the cutoff energy of the beryllium filter. Consequently beam hardening affects the filtered image at LE less than the unfiltered image at HE, resulting in a thickness dependency of the relative attenuation (see Figure 3.8). Based on Equation 3.1, relative attenuations can be determined by calculating the attenuation with and without filter.
Figure 3.24: Numerical calculation of thickness dependency of the relative attenuation during the measurements with the NF resulting from beam hardening. Reprinted from Biesdorf et al. [42] with permission of the American Physical Society. Copyright 2014 American Physical Society.

The resulting thickness dependency for liquid water is shown in Figure 3.24, which strongly reproduces the trend observed in Figure 3.8.

Besides the width of the energy spectrum, $\sigma_{LE}$ is generally more affected by beam hardening compared to $\sigma_{HE}$. As the widths of the energy spectrum is similar in the LE and HE range for the VS and the TOF setup, an inverted thickness dependency is obtained with these techniques. This effect can clearly be observed in Figure 3.17 as well as in Figure 3.21, where a reduction of the water thickness leads to an increase of the relative attenuation parameter.

(2) Error in background correction

Besides beam hardening effects, other possible reasons are uncertainties in the background correction of scattered neutron done during the image processing. As reported in subsection 2.1.6, the scattered background is subtracted pixel-wise according to Equation 2.10. Figure 3.25 depicts the thickness dependency which is obtained in the most inappropriate case assuming an error of $\pm 1\%$ of $I_{bkg}$, calculated on the example for the neutron filter. Hence, even a minor error of $\pm 1\%$, leads to a substantial impact on the thickness dependency which can be seen in Figure 3.25. Although Figure 3.25 is just calculated for the experiments with the neutron filter, similar explanation holds for the TOF and VS technique.
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Figure 3.25: Calculation of thickness dependency on the relative attenuation resulting from errors of the background correction. Reprinted from Biesdorf et al. [42] with permission of the American Physical Society. Copyright 2014 American Physical Society.

(3) Sample scattering

Another possible source of error is the fact that some neutrons scattered by water hit the detector. Figure 3.26 (a) depicts the angular distribution of neutron scattering after scattering by the cylindrical water column. These values were calculated using a Monte Carlo simulation based on an in-house code with $10^8$ neutrons, sample-detector distance of 20 mm, mean free path of neutrons in water assumed to be 2 mm. As can be seen from the angular distribution of the single scattering distribution, we assume isotropic scattering of neutrons by water. According to this simulation (see Figure 3.26 (b)), the scattered neutron intensity represents less than 0.17% of the open beam intensity and, although multiple scattering has a large impact in neutron scattered in certain directions (in particular, in the axis of the water column), the amount of neutrons scattered in the forward direction is only marginally higher. Figure 3.26 (c) shows the probability of scattering events as a function of the number of scattering events. Almost 2/3 of the scattered neutrons undergo only single scattering. Hence, the sample scattering with less than 0.2% of the open beam represents only a minor effect.
Figure 3.26: Influence of sample scattering correction: (a) Angular distribution of sample scattering (b) Horizontal profile of the scattered neutrons intensity relative to the open beam intensity (average over a vertical distance of 7 mm). (c) Histogram of the scattering events occurring inside the cylindrical water scale. Reprinted from Biesdorf et al. [42] with permission of the American Physical Society. Copyright 2014 American Physical Society.
(4) Interference with enclosing materials

As was reported in literature [150] aluminium has a distinct Bragg-edge at around 4 Å / 5.1 meV, which softens the beam with increasing thickness of aluminium. During the ex-situ measurements, 3 cm of aluminium were utilized vs. 4.5 cm during the fuel cell measurements with the Multicell. Hence, the neutron beam has a slightly colder spectrum, which results (according to Equation 3.3) in an increased $\sigma_{rel}$. This effect might explain the differences between Figure 3.23 and Figure 3.13. The differences between Figure 3.21 and Figure 3.22 might result from the thickness dependency identified in Figure 3.8, where a higher $\sigma_{rel}$ is identified with higher water thickness. Regarding the discrepancies between the theoretical calculations and the experiments in a fuel cell with the VS, the same explanations holds (beam-softening and thickness dependency). Based on this fact, a reliable identification of the absolute aggregate state cannot be achieved with the present measuring setup.

To sum up this subsection, the absolute value of the relative attenuation parameter is highly dependent on various undesired effects, which can explain the absolute differences as well as the thickness dependency of the relative attenuation.

3.8.6 Minimal water thickness/cluster volume

Inside fuel cells, water accumulates in the form of small cluster of several µl inside the different layers [62]. Consequently, the knowledge of the detection limit of the minimal water thickness/cluster volume is of high interest. As was shown with the ex-situ samples in Figure 3.23 (a-b) and Figure 3.8, the distinction between water and ice is straightforward. However, with reduced water thickness like inside a non-operating fuel cell (see Figure 3.21 and Figure 3.12), the differentiation becomes already more challenging.

This effect can be explained by several contributions: First, the water thickness in through-plane configuration of Figure 3.21 and 3.22 was reduced by 1-2 orders of magnitudes compared to the water scales of Figure 3.23 as well as the in-plane measurements in Figure 3.12. Furthermore, the results of the water scales (see Figure 3.23) are averaged over a homogeneous thickness and interconnected cluster of water, whereas the water thickness inside PEFCs is highly inhomogeneous (e.g. over entire active area in Figure 3.13 and Figure 3.22). In Figure 3.8 it was shown that although $\sigma_{rel}$ should be independent on the water thickness according to Equation 3.3, a certain thickness dependency was measured, attributed to beam hardening, error in background correction, sample scattering, and interference effects with the enclosing materials. In the range of 1-2 mm, this dependency shows an almost linear trend, whereas it becomes non-linear below 1 mm (see Figure 3.8). As the water thickness inside a PEFC is highly inhomogeneous and below 1 mm, averaging over the active area may induce a certain error. However, if the analysis
is based on the local scale (see Figure 3.11), the SNR decreases significantly. Hence an optimum averaging area has to be chosen for each individual case. Another important difference compared to the experiments with ex-situ samples is the partial saturation of liquid water inside a porous system compared to bulk water in the water scales. Consequently, the neutron interaction between the water-air-interface may induce unknown contributions.

Figure 3.27 illustrates the effect of the cluster volume on the contrast between water and ice. The data is based on a water slug which was injected with a syringe into a flow field undergoing a temperature ramp imaged with a NF (see Figure 3.9 (d)). The cross section in direction of the beam of the water slug is around 1 x 0.5 mm$^2$ and segments with an increasing length of 2 mm are plotted in Figure 3.27. The error bars represent 2.57 times the standard deviation calculated based on merged images during 10 minutes in frozen and liquid state. As can be seen, the contrast between water and ice remains almost constant independently on the cluster volume. However, the error bars clearly highlight that liquid water and ice can only be differentiated at a cluster volume above 4 µl. This fact can be explained by the decreasing signal-to noise ratio with increasing cluster volume.

Figure 3.27: Influence of cluster volume on distinction between water and ice.

### 3.8.7 Limitations of method for fuel cell application

As was shown in the previous sections, all experimental techniques have certain advantages and disadvantages. The TOF setup has the highest contrast between water and ice while having the lowest neutron flux and resolution. Hence, in the current status this technique is not suited for in-situ investigations. However, with several improvements regarding the neutron flux (e.g. measurements at pulsed neutron sources or with optimized pulse chopper) and improvements
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regarding the spatial resolution (e.g. detector presented in ref [149]), this technique can be highly suited for fuel cell application.

The VS offers the advantage of having a higher neutron flux compared to TOF with high spatial resolutions. However, a significant drawback is the rather high alternating time between LE and HE, which translates into a poor time resolution with this technique. A possible improvement for this technique would be the motorization of the VS with a linear motor, which enables the insertion and removal of the VS from the beam centre similar to the motorization of the neutron filter. However, as the weight of the VS is rather heavy, this motorization would only result in a slight improvement.

The best result was obtained with the NF, having a good trade-off between energy, spatial and temporal resolution for fuel cell applications. However, the major drawback of the method is the relatively poor contrast between LE and HE which leads to a low SNR of $\sigma_{rel}$ (see Figure 3.13). However by cooling the filter to lower temperatures, the contrast can be improved by a factor of 2-3.

3.9 Summary of chapter 3

A novel method called dual spectrum neutron imaging was developed in order to determine aggregate state changes and phase transitions of water (liquid to ice and vice versa) inside fuel cells. This method is based on arising differences of the cross sections of water and ice in the low energy range. The following key findings were obtained with this chapter:

- For the first time, the phase transition between water and ice was directly measured inside an operating fuel cell. This unambiguously proves the presence of supercooled water as a product of the polymer electrolyte fuel cell reaction.

- It was emphasised that the time, spatial and energy resolution are critical parameters to distinguish water and ice inside fuel cells. The time to alternate between high and low energy was identified to be the most critical parameter.

- Time of flight setup has the highest contrast between water and ice, whereas it has a rather poor spatial resolution in the present setup. Further modifications of the chopper design or measurements at a pulsed neutron source makes this technique suitable for in-situ investigations of water transport inside fuel cells.

- The neutron velocity selector has shown the slowest alternating-time between the two energy spectra, while having a rather low neutron flux. Hence this technique is not suitable for studies of dynamic water transport in PEFCs with the current setup.
The neutron filter has shown the best applicability for fuel cells, as it has the best trade-off between spatial, temporal and energy resolution.

3.10 Outlook

The presented experiments depict the great potential of energy selective neutron radiography to study freezing of product water inside fuel cells. However, several improvements are required to further develop the current technique.

- **Absolute value of \( \sigma_{rel} \):** In presented measurements, several undesired effects like beam hardening, error in background calculation, sample scattering, and interferences with the enclosing materials were identified to affect the absolute value of the relative attenuation parameter. Further theoretical and experimental investigation should be performed in order to isolate the individual contributions of these effects. A fundamental understanding of all effects would provide the possibility to identify the aggregate state in an absolute fashion.

- **Time of flight setup:** Although the time of flight setup at PSI is strongly limited by its neutron flux, the aggregate state transition was able to be identified with a time resolution down to 10 minutes. By increasing the flux either by an optimized pulse chopper at PSI or by measuring at a pulsed neutron source, promising results can be expected. Furthermore, by using a new generation 2D TOF detector [149], reasonable spatial resolutions can be obtained.

- **Other fields of application:** Especially the application of the motorized neutron filter, is not only suited for the differentiation of liquid and frozen water: it could also be used as a faster alternative for energy selective neutron imaging in applications requiring limited spectral information. Thus, basic information about deviations in the atomic motions of hydrogen can be easily obtained with the dual spectrum neutron radiography. In the field of fuel cells, this technique might be valuable to distinguish water in phosphoric acid during operation of high temperature fuel cells, as the atomic diffusion of hydrogen is expected to be different, the cross section should differ.
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4

Operation at subfreezing temperatures

A new methodology to differentiate water and ice was introduced in the previous chapter, whereas the present chapter targets on the understanding of the freezing mechanism itself. The chapter starts with section 4.1, motivating the requirement of having a fundamental understanding of the freezing mechanism inside PEFCs. In section 4.2 a literature review is given, followed by the experimental procedure applied during all subfreezing experiments (see section 4.3). In the subsequent sections, experimental results about the influence of the size of active area (section 4.6) and the effect of different GDL materials (section 4.7) are studied with respect to the freezing behaviour. The chapter is summarized with a general conclusion and outlook regarding the technical applicability of these scientific findings.

4.1 Motivation

The first generation of commercial fuel cell vehicles (FCV) has entered the automotive market. Although the freezing mechanism is poorly understood and various contradictory findings are reported in literature (see subsection 1.5.3), the car manufacturers (e.g. Toyota [152, 153]) promise a cold start capability down to -30°C without failure [154]. Performance targets defining the cold start capability at a certain temperature for FCV are formulated by the US department of Energy [155]: (1) Deliver 50% of rated power within 30 s and (2) utilization of less than 5 MJ auxiliary energy. In order to fulfil these requirements, various approaches have been patented:

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- **Catalytic burning** of the reactants: Either via diffusion of hydrogen through the membrane [156] or by controlled injection of hydrogen in the air stream [157, 158].

- **Exothermal hydride formation** inside special fluid modules to heat up reactants [159].

- Cell operation with reduced power to feed electronic **cell heaters** [160, 161].

- **Short circuiting** of the fuel cell to heat via the overpotentials of the cell components [162].

- Heating up by **waste heat** of electrochemical reaction [161, 163].

- Special **purging** strategies in order to prevent freezing inside the fuel cell [164].

In general, all these techniques target a rapid heating of the fuel cell in order to quickly overcome the melting point of water. Furthermore, catalytic burning of reactants via diffusion or injection represents a considerable safety hazard. Hence, the methodology of choice for automotive applications is the heating by the waste heat of the electrochemical reaction.

This concept can be implemented in two ways: (1) Rapid heating by operation under high power densities with large overpotentials or (2) smooth heating under moderate operating conditions but with substantially longer operating times under subfreezing conditions. The major advantage of the first approach is that the melting point of water is quickly exceeded and the operation under subfreezing temperatures is minimized. However, a fast heating leads to significant thermal stress of the cell materials which might result in mechanical deformation and long-term degradation. Although, a smooth increase of the temperature is favoured with respect to the thermal behaviour, it requires a fundamental knowledge about the freezing mechanism inside PEFCs due to its longer operation below 0°C.

In a previous study of our group [39], we observed the possibility of operating small scale fuel cells for more than 1 h below the melting point of water. These long operating times were explained by the production of supercooled water, which was demonstrated indirectly by the water distribution inside the PEFC [39] and directly by energy selective neutron radiography (see chapter 3 of this thesis). However, fuel cells with increased active area (>10 cm²) show generally shorter and more deterministic operating times [165–167], whereas unrepeatable but longer operating times were measured with small scale fuel cells. In order to understand the deviations between the different sizes of the active area, experiments and simulations will be presented in section 4.6. This different startup behaviour also strongly contributes to the ongoing debate about the aggregate state of product water inside fuel cells, where supercooled water was mainly identified inside small scale cells and direct freezing of product water in technical fuel cells (see subsection 1.5.3).
The probability of the phase transition from supercooled to frozen water is dependent on several parameters such as the pore size or the hydrophobic coating [49]. In order to understand the parameters inducing the phase change, the cold start capability of different GDLs with different coating loads and MPLs will be presented in section 4.7.

4.2 Literature review

Experimental investigations of cold starts have been widely reported in the past years [39–41, 73, 168, 169]. Mainly two experimental protocols are used: (1) Free-heating and (2) isothermal startups. Free-heating startups are used to investigate the cold start capability by heating up the cell with the waste heat of the electrochemical reaction [170]. This technique is mainly used for commercial applications and has been mostly studied on technical fuel cells or fuel cell stacks [168, 170–175]. Such measurements usually aim to validate if the full subzero startup strategy is valid, i.e. if the stack reaches temperatures above zero degrees before failure occurs due to the blocking of the cell by frozen water. However, they give little information about the actual failure mechanisms and are strongly dependent on the individual cell design.

Therefore, isothermal startups in moderate sub-freezing temperatures are often reported [34, 39–41, 73, 167, 176–179], where the PEFC is maintained at a constant subfreezing temperature during its operation, targeting a better scientific understanding of the freezing mechanism. The freezing capability of isothermal startups can be judged based on the operational time [39], which is the time from start of current production / water production until the cell voltage drops below 0.2 V (see Figure 4.5). Other similar definitions such as the specific accumulated charge [165, 166, 180] or the specific amount of water produced [36, 169] during the cold start are also reported.

Free heating as well as isothermal startups are often combined with electrochemical and imaging characterization techniques. Electrochemical characterization is mainly performed by cyclic voltammetry [166, 178, 181, 182] or impedance spectroscopy [166, 181, 182]. Characterization with imaging is executed with light [40, 49, 178, 179, 183], electrons [166, 170, 181, 184, 185], x-rays [41, 186] and neutrons [38, 39, 42, 67, 124, 182].

The cold start capability of fuel cells has been widely studied on lab-scale [37, 39, 40, 42] as well as technical fuel cells [171, 172]. It has been reported that water does not deposit as ice inside fuel cells; it is produced in its supercooled aggregate state [39, 40, 42, 171] and the phase transition to ice occurs randomly. This was proven indirectly based on the location of water condensation (see ref [39, 40, 171]) but also directly by dual spectrum imaging in chapter 3. Furthermore, Oberholzer et al. [39] have shown that the freezing can be triggered by a mechanical shock onto the PEFC.
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The influence of the operating temperature on the cold start capability was studied [39, 41, 176]. Tabe et al. [176] have performed isothermal startups at two different cell temperatures (-20°C, -10°C) with a fuel cell of 25 cm². They obtained reduced operating times with decreased temperatures. This is in good agreement with refs [39, 41], where shorter operational times were identified at lower cell temperatures. These findings are also consistent with the existence of supercooled water, as the phase transition between supercooled water and ice is more probable at lower temperatures [187].

4.3 Experimental procedure

All experiments which will be presented in the present chapter are isothermal cold starts. Unless otherwise noted, the experiments with the Multicell were performed with a slight overpressure of 100 mbar with cell flows of 0.1 Nl/min on both sides. The subsequent protocol was used; an overview of the individual steps can be found in Figure 4.1, where (a) depicts the cell voltage, (b) the membrane resistance, and (c) the cell temperature.

1. **Drying**: In order to obtain identical boundary conditions for every cold start, the cells

![Figure 4.1](image-url)  
**Figure 4.1**: Temporal evolution of the (a) cell voltage, (b) membrane resistance, and (c) cell temperature during the cold start protocol used. The cold start itself can be found in step no. (5).
were dried with nitrogen on both sides, until the high frequency area resistance (measured at 5 kHz) reached 0.5 Ohm cm$^2$. Afterwards, this condition was held for 3 additional minutes.

2. Preconditioning: As has been explained in subsection 1.4.1, the PFSA membrane requires a certain hydration state to be proton conductive. Consequently, the membrane was preconditioned under nitrogen humidified with 50%RH on both sides for 20 minutes.

3. Cool down: While the cells were cooled down to the desired temperature, the gas flows were stopped in order to maintain the hydration state of the membrane.

4. Feed gas: After stabilization of the temperature, unhumidified reactant gases (hydrogen and air) were fed until the cell voltage reached values above 0.9 V during 5 s.

5. Apply current: The current was linearly increased during the first 60 s to 0.1 A cm$^{-2}$ (see Figure 4.5). Afterwards, the cells were operated in galvanostatic mode until the cell voltage dropped below 0.2 V when the current of the individual cells was stopped. The step was interrupted after 1 or 2 hours, depending on the experiment.

6. Heat up: In the final step, the cells were heated up stepwise to 25°C and the protocol was restarted from the beginning.

Taking a closer look at the 5th step, the characteristic behaviour for isothermal galvanostatic cold starts can be observed. In the first minute of operation, the current is linearly increased, resulting in a decreasing voltage response. In this time frame, the membrane resistance decreases as product water is taken up by the polymer membrane. After several minutes of operation, the membrane resistance as well as the cell voltage stabilizes and remains constant. However, after a certain operating time, an increase of the ohmic resistance is measured, followed by a steep decrease of the cell voltage. After approximately 2-4 minutes, the cell voltage reaches 0.2 V, where the current is stopped and the cell voltage rises to OCV. This evolution of the cell voltage and resistance is characteristic for all cold starts performed in the present chapter.

An increase of the membrane resistance was previously observed during isothermal cold starts (see ref [39, 41, 177]). Several explanations like (1) the partial freezing of water inside the membrane, (2) the formation of ice shells affecting the contact resistance between MPL and CCM, or (3) the change of saturation pressure of air above ice compared to liquid water are proposed. As has already been mentioned in subsection 1.5.3, DSC measurements [29-31] suggest a partial freezing of water in the membrane, whereas more recent measurements with X-Ray scattering [32, 33] contradict these findings. Regarding the formation of ice shells, Tabe et al. [176] assumed the formation of ice at the interface between MPL and CL, which increases
4. OPERATION AT SUBFREEZING TEMPERATURES

the contact resistance between the two layers. Although, this effect could explain the stepwise increase of the ohmic resistance during the freezing of the fuel cell, another stepwise decrease of the cell resistance would be expected at the melting temperature of ice. This explanation strongly contradicts the experimental findings of Figure 4.1, where a continuous decrease of the cell resistance is obtained with increasing temperatures.

Figure 4.2 shows the temperature dependency of the High Frequency area resistance under sub-freezing conditions in a cell with frozen and supercooled water. These measurements were acquired by operating the cell during 20 minutes at -10°C without failure. Afterwards the current was stopped and a temperature ramp until -2°C was performed to obtain the temperature-resistance dependency with supercooled water. Subsequently, the remaining water was frozen at -15°C and the same temperature dependency was acquiring with frozen water. In general, it can be observed that with decreasing temperatures increasing differences are measured between the membrane resistance of a cell with supercooled and frozen water. This effect clearly disproves the effect of contact resistance, as a constant offset between the two graphs would be expected including a stepwise decrease at 0°C. Consequently, the most probable explanation of the increase of the high frequency resistance during freezing is the effect of the decreased saturation pressure of water vapour above ice compared to liquid water (e.g. at -15°C: 2.0 mbar supercooled water

![Figure 4.2](image.png)

**Figure 4.2:** Temperature dependence of membrane resistance inside a cell with supercooled and frozen water. The arising differences at low temperature can be most likely explained by changes in the water saturation pressure above liquid water and ice.
4.4 Degradation

In literature, degradation of fuel cells resulting from freezing is widely reported [37, 188] and is either explained by the volume expansion of water or the depletion of oxygen after freezing. In order to validate that the utilized protocol does not interfere with degradation effects, the cell voltage and the membrane resistance is depicted in Figure 4.3 shortly before the cell failure. As can be clearly seen, no significant degradation effects can be identified on the cell voltage and on the membrane resistance even after more than 50 freezing cycles. These experimental observations are in good agreement with ref [39, 189].

![Figure 4.3: Cell voltage and membrane resistance shortly before cell failure as a function of the freezing cycle. As can be clearly seen, no significant degradation effects can be identified on both, the cell voltage and the membrane resistance, even after more than 50 freezing cycles.](image)

Regarding subsequent statistical analysis in section 4.6 and section 4.7, the individual operating times of five identical fuel cells are plotted in Figure 4.4 for more than 50 cold starts. As can be seen, no correlation between the number of previous freezing cycles and the operating time can be identified. This does not necessarily mean that no degradation occurs inside the fuel cell; in fact our characteristic parameters (operating time, accumulated charge) are not affected
4. OPERATION AT SUBFREEZING TEMPERATURES

**Figure 4.4:** Operating time of five different fuel cells as a function of the freezing cycle. During our experiments no correlation between the number of previous freezing cycles and the operating time can be identified.

by degradation. However, it is not excluded that at higher current densities degradation effects in terms of increased mass transport losses might appear.
4.5 Data evaluation

In this chapter the cold start capability is analysed according to the specific charge produced until the cell potential drops below 0.2 V (see freezing event in Figure 4.5) as well as on the operating time. The specific accumulated charge $q_c$ is calculated based on the current density $i$ during the operating time $t$ (shaded area in Figure 4.5):

$$q_c(T) = \int_0^t idt$$  \hspace{1cm} (4.1)

In order to get a characteristic indicator, the median value of the operating time and accumulated charge are calculated for each temperature. The error bars represent the lower and upper quartiles (interval between 0.25 and 0.75 of all measurements values) in subsequent graphics (e.g. Figure 4.7).
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4.6 Influence of size of active area on Cold Start capability

4.6.1 Introduction

As has already been mentioned in section 4.2, strongly deviating results are obtained with small scale fuel cells compared to large scale fuel cells. In literature, subfreezing startup experiments have been reported with various sizes of active areas ranging from 0.16 cm$^2$ [41], 0.5 cm$^2$ [39, 42], 2.5 cm$^2$ [38], 5 cm$^2$ [177], 13 cm$^2$ [40], 25 cm$^2$ [36, 169, 170, 176], 33 cm$^2$ [180], 40 cm$^2$ [168], 46 cm$^2$ [165, 166] up to 220 cm$^2$ [167]. Interestingly, the studies identifying liquid water inside the GDL and flow field, concern exclusively experiments with relatively small fuel cells (active areas below 15 cm$^2$), whereas high reproducibility and freezing inside the CL was found for larger size fuel cells. This indicates that the freezing process might be related to the size of the active area. In the present chapter, we present experimental results of subzero isothermal startup experiments with two different cell sizes of 1 and 50 cm$^2$. Using the statistical distribution of operating time for small cells (1 cm$^2$) we calculate the operating time as a function of the cell area, closing an important understanding gap between the stochastic operating time of small cells and the deterministic operating times of larger cells.

4.6.2 Experimental

Cell setup

The experiments were performed on the following two cell designs with our base materials presented in subsection 2.5.4:

- **Cell type 1** were differential fuel cell described in section 2.5. In order to investigate cell-to-cell variations, 5 identical cells were studied.

- **Cell type 2** is a 50 cm$^2$ fuel cell operated under technical stoichiometries. The bipolar plates are made of graphite with a single serpentine flow field. The bipolar plates are compressed between aluminium endplates with integrated cooling channels and additional electrical heaters for a fine control of the temperature. Further details can be found in ref [87].

The sub-freezing temperature was controlled via a thermal bath, operated with a mixture of 50% Ethylene-Glycol and water. A precise temperature control was achieved with several local heaters on both PEFCs.

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4.6 Influence of size of active area on Cold Start capability

Experimental protocol

All tests were performed with gas pressures slightly higher than 1 bar\textsubscript{abs}. The differential cell was studied at 1.1 bar\textsubscript{abs} on both sides, whereas the 50 cm\textsuperscript{2} cell was operated at 1.15 bar\textsubscript{abs} at the anode and 1.25 bar\textsubscript{abs} on the cathode side, respectively. The cell flows were set to 0.1 Nl/min on the anode and cathode side for both cell designs which translates into stoichiometries of \(140/60\) for the 1 cm\textsuperscript{2} cell and \(2.8/1.2\) for the 50 cm\textsuperscript{2} cell.

The previously presented experimental protocol was applied at various temperatures with the two different cell sizes. As identified during the experiments, the differential cell shows highly scattered operating times, whereas the lab-scale PEFC gives more repeatable results. Consequently, a certain number of repetitions were performed on the small scale PEFC in order to get statistical information. The exact number of cold starts at each temperature is listed in Table 4.1.

4.6.3 Simulation

In order to get a deeper understanding of the influence of the active area on the operating time, a Monte Carlo simulation was performed. The simulation parameters were fitted to the experimental data obtained with the differential fuel cells at \(-7.5\, ^\circ\text{C}\) (see Figure 4.6), as the highest numbers of repetitions were performed with this configuration (see Table 4.1). As five different cells with identical materials were tested, the simulation accounts for local variations of the material composition (e.g. specific points in the carbon fibers which can act as a seed for the freezing) which influences the cold start capability.

This distribution can be used for calculations of increased cell sizes under two assumptions: every 1 cm\textsuperscript{2} portion of the larger cells has the same probability distribution to freeze as a 1 cm\textsuperscript{2}

\[
\begin{array}{|c|c|c|}
\hline
\text{Temperature} & \text{Cell type 1:} & \text{Cell type 2:} \\
\text{\degree\text{C}} & \text{1 cm}^2 & \text{50 cm}^2 \\
\hline
-15 & 9 & \\
-10 & 33 & \\
-7.5 & 284 & \\
-7 & 1 & \\
-6 & 1 & \\
-5 & 72 & 1 \\
-4 & 1 & \\
-3 & 1 & \\
-2 & 1 & \\
\hline
\end{array}
\]

\textbf{Table 4.1:} Number of cold starts performed at the individual temperatures.
4. OPERATION AT SUBFREEZING TEMPERATURES

fuel cell; the water is considered to form a continuous network, thus the freezing in any of
the portions of the cell will propagate to the entire cell [168, 190]. This assumption is based on
theoretical percolation studies [191] which describe the capillary water transport inside the GDL
as being independent on the direction, resulting in highly interconnected water cluster inside the
GDL. These theoretical studies are in good agreement with high resolution X-Ray Tomography
data of operating fuel cells [62].

Under these circumstances, it is reasonable to assume that each small section of the cell is
independent from the other in terms of freezing probability, and the operating time of a cell with
an area of n cm$^2$ is calculated as the minimum value of n independent variables following the
probability distribution of freezing in the 1 cm$^2$ cell. If the event of freezing is considered to have
a constant probability for a given time interval, the corresponding probability distribution on the
operating times should be an exponential. However, the probability of failure of fuel cells cannot
be assumed to be constant and two types of failures have to be distinguished. The first type of
cell failure occurs during the first 10 minutes with a high probability, as the amount of water
inside the GDL and CCM increases. The second type occurs after 10 minutes of operation with
a much lower probability (further information is given in section 4.7). Hence, this probability

![Figure 4.6: Experimental probability distributions of cell failure of fuel cells with an active area of 1 cm$^2$ at various subfreezing temperatures. Reprinted from Biesdorf et al. [28] under the terms of the Creative Commons Attribution 4.0 License (CC BY).](image)
4.6 Influence of size of active area on Cold Start capability

distribution can be best modelled as a sum of two exponentials:

\[ p = a \left( 1 - e^{-\frac{t-t_0}{t_1}} \right) + (1-a) \left( 1 - e^{-\frac{t-t_0}{t_2}} \right), \]  

(4.2)

with \( a, t_0, t_1, t_2 \) being fitting constants. In order to get sufficient statistics, 100'000 cold starts were simulated for each of the six cell sizes (1, 2, 5, 10, 25, 50 cm\(^2\)) chosen for the simulation. The simulation was run on the average probability distribution of the five individual cell as well as on the best (cell 05) and worst (cell 03) performing cell. The fitting parameters can be found in Table 4.2.

<table>
<thead>
<tr>
<th></th>
<th>( a )</th>
<th>( t_0 )</th>
<th>( t_1 )</th>
<th>( t_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall</td>
<td>0.479</td>
<td>300</td>
<td>348.743</td>
<td>7687.044</td>
</tr>
<tr>
<td>Cell 03</td>
<td>0.872</td>
<td>300</td>
<td>180.564</td>
<td>3075.107</td>
</tr>
<tr>
<td>Cell 05</td>
<td>0.072</td>
<td>300</td>
<td>1</td>
<td>6416.205</td>
</tr>
</tbody>
</table>

Table 4.2: Fitting parameters used for the Monte Carlo simulation.

4.6.4 Experimental results

Figure 4.7 depicts the experimental results obtained with the two different cell setups as a function of its isothermal startup temperature. The calculated points inside the graphic represent the median values over all cold starts performed for a certain cell size and temperature. It can be seen that the median value of the charge produced during the cold start decreases with decreasing temperatures. The differential cell shows at all temperatures the highest operational times and charge produced, whereas the cell with 50 cm\(^2\) shows a significantly lower cold start capability. In Figure 4.6 it can be seen for the small scale PEFC that more than 25% of the cells at -7.5°C and more than 75% of the cells at -5°C did not fail within 1 h. In contrast, the 50 cm\(^2\) PEFC failed before less than 15 min of operation for all temperatures even with temperatures as high as -2°C. These results highlight that the size of the active area has a significant influence on the cold start capability.

Furthermore, it is worth noticing that the differences between the two cell configurations are amplified with increasing temperatures, whereas the cells converge to a lower limit of the accumulated charge with decreasing temperature. Interestingly, this limit is already reached at around -6°C at a cell size of 50 cm\(^2\), whereas the small scale cell reaches this lower limit not before -10°C. From Figure 4.6, it can be seen that the minimum operating time of the 1 cm\(^2\) cell decreases with decreasing temperatures.

The trends observed also agree with literature [39, 168, 176]. Oberholzer et al. [39] performed measurements with a 0.5 cm\(^2\) differential PEFC with similar operational times compared to the
4. OPERATION AT SUBFREEZING TEMPERATURES

1 cm$^2$ in Figure 4.6 and Figure 4.7. Tabe et al. [176] obtained operational times of around 3 minutes at -10°C with a 25 cm$^2$ PEFC; Jiao et al. [168] operated a cell of 40 cm$^2$ for less than 3 minutes at -10°C, which perfectly fit into the data of Figure 4.7. The cell of 0.16 cm$^2$ of Mayrhuber et al. [41] was operated for longer operational times compared to the experimental data of the 1 cm$^2$.

![Figure 4.7](image)

**Figure 4.7:** Experimental results of the cold start capability of two different cell sizes at various subfreezing temperatures. The points show median values, error bars indicate the upper and lower quartiles. Reprinted from Biesdorf et al. [28] under the terms of the Creative Commons Attribution 4.0 License (CC BY).

The cell of 50 cm$^2$ shows a smooth temperature dependency of the accumulated charge without any significant outliers (see Figure 4.7). Although only one experiment at each temperature has been performed with this cell size (see Table 4.1), the continuous trend indicates a more repeatable startup behavior. In contrast, the small scale cell shows a high variability especially at higher subfreezing temperatures (see Figure 4.6), whereas more reproducible data is obtained at lower temperatures.

In order to understand the influence of cell-to-cell variations on the overall probability distribution, the individual distributions of the five 1 cm$^2$ fuel cells are shown in Figure 4.8. It can be seen that significant differences are obtained between the cells with median values ranging from less than 15 minutes to more than 1 h. However, all cells except cell 5 show a minimal operating time of 5 minutes, which corresponds to 27 C cm$^{-2}$. Consequently, the cell-to-cell variations have a strong influence on the freezing behaviour of cells with an active area of 1 cm$^2$.
4.6 Influence of size of active area on Cold Start capability

4.6.5 Modelling results

In order to understand the impact of cell size on subzero startup capability, a Monte Carlo simulation was performed based on the experimental data obtained with the five identical 1 cm² cells at -7.5°C. Figure 4.9 shows the results of the simulation based on the statistics obtained with all five cells, and compares the results to the same simulation based on the statistics obtained with the cells having the best (cell 5) and worst (cell 3) startup capabilities. As the model assumes that the probability curve of 1 cm² holds for every cm² inside a fuel cell of increased cell size, the probability of failure increases with increasing size of the active area. At cell sizes above 10 cm², the operating times converge towards a lower limit of 5 minutes, which corresponds to the parameter $t_0$ of the fitting curve of the experimental data (see Equation 4.2). In order to account for the influence of material variations of the 1 cm² portions in large size fuel cells, the simulation based on all five cells represents the most realistic case for larger fuel cells. However, the curve of cell 5 represents the distribution with the highest startup capability found in our experiments. It can be seen that the startup capability is increased for cell sizes below 10 cm², whereas no improvement can be obtained at bigger cell sizes. Nevertheless, all these simulations are in good agreement with the experimental results obtained with the 50 cm² in Figure 4.7, where operating times around 3 minutes were obtained.

Furthermore, Figure 4.9 clearly shows that the variability of the cold starts decreases with increasing cell size. At a size of 1 cm² a difference between 25 and 75% of cell failure of 540 C cm⁻² is obtained, whereas 0.6 C cm⁻² is obtained at 50 cm². This correlates with our experimental data obtained in Figure 4.7, where more repeatable isothermal startups have been measured with the lab-size fuel cell, whereas highly scattered operational times were obtained with the differential cell above -10°C.

4.6.6 Discussion

Operating time

As has been visualized in Figure 4.6 and in Figure 4.7, cells with reduced dimensions can be operated significantly longer at subfreezing conditions. This tendency can be explained by the phase transition of supercooled water into ice. As has already been shown in literature on small scale fuel cells [38, 39], water is condensing in its supercooled aggregate state under subfreezing conditions. This aggregate state is metastable [43, 47] and its phase transition can be induced in different ways (e.g. agitation, mechanical shock, or friction [48]). One of these transition mechanisms was shown for fuel cells in ref [39], where the freezing of a fuel cell was triggered by inducing a mechanical shock onto an operating fuel cell. As a water cluster extends over a large volume inside the cell [62], the initiated freezing propagates along the entire water cluster and
4. OPERATION AT SUBFREEZING TEMPERATURES

Figure 4.8: Probability distributions of cell failure measured on five identical 1 cm$^2$ fuel cells at -7.5°C. Significant cell-to-cell variations can be measured in-between the individual cells. Reprinted from Biesdorf et al. [28] under the terms of the Creative Commons Attribution 4.0 License (CC BY).

the cell fails after a short time. However during our experiments, the cells were not exposed to any kind of mechanical shocks. Hence, the phase transitions observed during our experiments are purely related to a spontaneous phase transitions. Consequently, large fuel cells comprising a larger quantity of water inside the cell have a much higher probability of cell failure.

The results of our simulation indicate that the stochastic nature of the water-ice transition is not incompatible with the more repeatable operating times observed with larger cells: above a critical size of approximately 10 cm$^2$, the freezing probability become high enough so that the operating time is given by deterministic factors (accumulation of water in the membrane, filling of the catalyst layer). This is in good agreement with literature where stochastic freezing times are obtained with small scale fuel cells [39, 41] and deterministic operating times with larger fuel cells [36, 165, 166, 168-170, 176, 180].

Figure 4.6 and Figure 4.7 show a decreased cold start capability with decreasing subfreezing temperatures. This effect can be explained with the higher probability of an aggregate state transition with decreasing temperature [43, 44, 46]. As the probability distribution reaches its maximum already at an early state, the differences between the cell sizes become smaller. In contrast, under relatively small subfreezing temperatures, the differences of the probability distributions become more dominant.
4.6 Influence of size of active area on Cold Start capability

![Graph showing accumulated charge and operating time for different cell sizes at -7.5°C and 0.1 A cm⁻². Reprinted from Biesdorf et al. [28] under the terms of the Creative Commons Attribution 4.0 License (CC BY).]

**Cell-to-cell variations**

During our experiments we have identified significant cell-to-cell variations. These variations may result from various sources. One potential explanation might be inhomogeneities of the coating, which strongly affect the nucleation rate [49]. Another explanation is the presence of seeding points like fiber breaks, asperities or micro cracks. These inhomogeneities can act as seeds for crystal growths [192]. In large size fuel cells, these variations are spread across the active area leading to an increased probability encountering a seed. However, the simulation of larger cells - based on the statistical data obtained with the best of our differential cells - indicates clearly improved startup capability for sizes up to 10 cm². It must be reminded that state of the art materials are not optimized for the stability of supercooled water, and that an optimized material might have far better properties that the best sample measured here. By understanding which feature of the material promotes the freezing and how to avoid such features, there is a huge potential of improvement of the cold start capability possibly also for larger fuel cells.

**Lower limit of charge produced**

In our experiments (see Figure 4.7), a minimal operating time was identified for both cell configurations. A possible explanation is the water uptake of the membrane and the ionomer inside the catalyst layer. However, as can be seen in Figure 4.5, the ohmic resistance stabilizes already
after around 1.5 minutes corresponding to a production of $6 \text{ C cm}^{-2}$. The remaining part can be explained by the fact that a certain time is necessary until the catalyst layer is filled with enough ice to block the access of reactants. This mechanism can be observed in the voltage profile in Figure 4.5 where a progressive voltage drop can be identified after the freezing event occurs. However, the time until the catalyst layer is filled with ice is dependent on the saturation pressure and the gas flow. As the water uptake of the gas is reduced at lower temperatures, less water/ice can be removed in the gas phase which results in a decreased operating time (see Figure 4.7). Furthermore, the cell with $50 \text{ cm}^2$ was operated under technical stoichiometries, which results in a reduced water uptake along the channel. This effect can be clearly identified in Figure 4.7, where water tends to freeze immediately below $-7.5^\circ \text{C}$ at a cell size of $1 \text{ cm}^2$ and $-3^\circ \text{C}$ at a cell size of $50 \text{ cm}^2$. For technical applications, high stoichiometries may extend the minimal cold start capability to several minutes in technical PEFCs [170].
4.7 Effect of PTFE Coating and MPL on Cold Start capability

4.7.1 Introduction

In the previous section, the considerable influence of the size of the active area was highlighted. However, these studies were performed with state of the art materials which were not optimized for the stability of supercooled water. As was explained previously in subsection 1.5.3, Ishikawa et al. [49] pointed out that the transition of supercooled to frozen water is dependent on several parameters like e.g. the water cluster volume, the hydrophobicity of the substrate as well as its microstructure. This is in good agreement with the previous section (section 4.6), where local variations of the material were identified to play a significant role on the cold start capability. If these features which promote the freezing can be identified and removed, the cold start capability can be significantly improved for lab-scale as well as for technical fuel cells. In order to identify factors improving the cold start capability of fuel cells, two parameters of GDLs are studied in this chapter: (1) the influence of a hydrophobic coating and (2) the presence of an MPL.

Although various studies investigated the cold start capability, the influence of material properties is rarely reported [38, 176, 184, 193, 194]. Nakajima et al. [193] studied the impact of the hydrophobic coating and MPL on a lab-scale 13 cm$^2$ cell with two different coating loads as well as with and without MPL. They have shown that the combination of a hydrophobic coating with an MPL results in the best startup capability. Tabe et al. [176] have studied the effect of an MPL inside the fuel cell of 25 cm$^2$. They concluded that the amount of water inside the catalyst layer (CL) of cells with MPL is strongly reduced resulting in a better startup capability. Hirakata et al. [184] concluded that the cold start performance slightly increases by including a supplementary hydrophilic GDL between MPL and the ordinary GDL inside a cell of 30 cm$^2$. The slightly better performance is explained by a more effective water removal from the CL. Mishler et al. [38] investigated the influence of the PTFE loading (5 and 23 wt% PTFE) inside the MPL. They found out that the degradation inside cells with low amounts of PTFE is significantly higher which can be attributed to the water accumulation at the interface GDL-CL. Ko et al. [194] increased the thickness of the CL. This results in a larger pore space for water accumulation during cell failure and has shown its potential to increase the cold start capability. Another finding has been published by Oszcipok et al. [166] who reported that the hydrophobicity might degrade during the experiments. These studies highlight that the water distribution affected by the different materials inside the PEFC has an important impact on the cold start capability.

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1 Part of the text was submitted to the Journal of The Electrochemical Society [151].
4. OPERATION AT SUBFREEZING TEMPERATURES

Although a few publications [38, 176, 184, 193, 194] reported about effects resulting from fuel cell materials on the cold start capability, two crucial characteristics were not considered up to now: Cell-to-cell variations and in-situ water distribution. Thus, we present a statistical investigation of the cold start capability combined with high resolution neutron radiography. The statistical investigation is based on around 1000 cold starts performed on five different cell configurations with at least two repetitions each (see Table 4.3). As has been shown in the previous section, experiments with small scale fuel cells enable the disclosure of hidden effects inside technical fuel cells. In order to obtain an unprecedented insight of different material properties, the investigations in the present chapter are performed on 1 cm$^2$ cells. Furthermore the experiments of cell-to-cell variations are of particular interest for fuel cell stacks with active areas in the order of hundreds of cm$^2$. Imaging by neutron radiography serves to interpret the results of the statistical analysis and to understand the implications of the water distribution for the five cell configurations at subfreezing temperatures.

4.7.2 Experimental

Cell materials

The following experiments were performed with 15 different fuel cells operated with the Multicell setup presented in section 2.5. Five different configurations with 0, 5, 20 wt% PTFE coating and with and without MPL were used (see Table 4.3), which are commercial materials from the SGL Carbon Group Series 24 [116]. The materials were varied symmetrically on anode and cathode side. The GDL with MPL accounts for additional 40 µm (230 µm) compared to the GDLs without MPL (190 µm). During the experiments, the standard material Primea 5710 (Gore) was used as CCM (see subsection 2.5.4). In order to study statistical effects of the material distribution, several samples of each configuration were measured. The statistical analysis was performed at a temperature of -7.5°C, as the failures of the cells were distributed within 2 h of operation (see section 4.6). The detailed numbers of cold starts executed at -7.5°C with each cell configuration can be found in Table 4.3.

<table>
<thead>
<tr>
<th>Configuration</th>
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<th>2</th>
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<th>4</th>
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</tr>
</thead>
<tbody>
<tr>
<td>MPL</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>PTFE / % wt</td>
<td>0</td>
<td>5</td>
<td>20</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>No. of samples</td>
<td>3</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>No. of cold starts</td>
<td>169</td>
<td>284</td>
<td>183</td>
<td>71</td>
<td>72</td>
</tr>
</tbody>
</table>

Table 4.3: Material definition and number of experiments performed with the five cell configurations used during the experiments at -7.5°C.
4.7 Effect of PTFE Coating and MPL on Cold Start capability

Imaging setup

The neutron experiments were performed at the ICON beamline [89] of the Swiss Spallation Neutron Source of PSI. The cells were imaged in in-plane configuration with a tilted imaging setup. With this imaging setup, a pixel size of 5 x 60 µm/pixel with an effective resolution (FWHM) of approximately 30 µm across and 200 µm along the membrane was obtained. The exposure time was set to 20 s. The camera was an Andor iKon-L with 2048 x 2048 pixels. The image processing was performed according to subsection 2.1.6.

4.7.3 Results

Statistical analysis

Figure 4.10 shows the accumulated probability of failure as function of the operating time for GDLs with (a) 0 wt%, (b) 5 wt%, (c) 20 wt% of PTFE with MPL at -7.5°C. The individual graphs

![Diagram](image_url)

**Figure 4.10:** Accumulated probability of failure during a 2 h cold start at -7.5°C operated with GDLs with MPL and (a) 0 wt%, (b) 5 wt% and (c) 20 wt% PTFE coating. The solid lines in the graphic depict individual cells, the dotted line the probability distributions of all cells.
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(a-c) share a common x-axis. The solid lines depict the histograms of the individual cells, the dashed line represents the probability distribution of all cells. In general, three interesting effects can be observed:

First, the data clearly indicates that the cold start capability differs strongly between the individual cells of 0 and 5 wt% PTFE, whereas the cells with 20 wt% PTFE show a more repeatable behaviour. Consequently, the dashed lines in Figure 4.10 (a-b) are not representative for material comparisons with low coating loads as the cell-to-cell variations are more dominant.

Second, a tendency of reduced probability of cell breakdown can be identified with increasing hydrophobic coating of the GDL; after 2 h of operation the cells with 20 wt% PTFE fail with a probability of around 50%; cells with lower coating load around 75%.

Third, mainly two scenarios of cold start can be classified: Type I occurs during the first 10-15 minutes of operation with a high risk of cell failure. After this period, the probability is significantly decreased and this category of cold start will be named Type II henceforth. As has already been observed in Figure 4.6, no cell failures occur during the first 3-5 minutes (temperature dependent), which can be explained by the water uptake of the membrane and the CL.

Figure 4.11 shows the accumulated probability of failure as a function of the operating time for GDLs with (a) 0 wt% PTFE, (b) 5 wt% of PTFE without MPL at -7.5°C. In general, similar trends with highly dominant cell-to-cell variations (especially Figure 4.11 (b)) are observed.

![Figure 4.11: Accumulated probability of failure during a 2 h cold start at -7.5°C operated with GDLs without MPL and (a) 0 wt% and (b) 5 wt% PTFE coating. The solid lines in the graphic depict individual cells, the dotted line the probability distributions of all cells.](image-url)
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However, a significant difference can be identified during the first 10 minutes of operation compared to the cells with MPL. The cells without MPL seem to reach the lower quartile (25% of cell failure) significantly later (around 15 minutes) compared to the cells with MPL (around 8 minutes). Furthermore, no cell failures are measured during the first 7 minutes with all cells.

Voltage peaks

Figure 4.12 shows the detailed temporal evolution of the cell voltage during three cold starts of type I at -10°C with three different coating loads (0, 5, 20 wt% PTFE) including a MPL. In general, almost identical trends are obtained with minor variations in voltage and time between the three configurations. It can be observed that the evolution of the cell voltage can be subdivided into three phases. During the first period, the cell voltages stabilize and an electrochemical equilibrium is reached. This equilibrium is maintained during approximately 2 minutes and a voltage peak of 2-3 mV can be identified in minute 3. Afterwards, the cell voltage decreases with a slope of 150-200 mV min$^{-1}$ during 3-4 minutes until it drops below 0.2 V when the current is

![Figure 4.12: Three cold starts of type I at -10°C operated with GDLs including an MPL and (a) 0 wt%, (b) 5 wt% and (c) 20 wt% PTFE coating.](image-url)
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automatically stopped. Hence, operating times in the range of 7-8 minutes are obtained, perfectly fitting with the probability distributions presented in Figure 4.10. It has to be mentioned that a second voltage peak is observable 3-5 s after the previous peak, being almost one order of magnitude smaller compared to previous peak. The chosen cold starts in Figure 4.12 are representative for all Type I cold starts performed with the three configurations.

In case of a type II cold start (operating times >10 minutes) a similar voltage peak can be identified initiating the cell voltage drop (see Figure 4.13). Although the shape of the voltage peak is similar compared to a cold start type I, the height of the voltage peak is significantly increased (6 mV) which will be explained later on in the discussion part.

![Figure 4.13: Example of cold start type II at -7.5°C operated with a GDL with MPL and 0 wt% PTFE.](image)

Figure 4.13 depicts the cell voltage during a cold start of type I of PEFCs without MPL with (a) 0 wt% PTFE and (b) 5 wt% PTFE. At first glance, significant differences are measured between the cell with and without PTFE. It has to be mentioned that substantial cell-to-cell variations were identified during the breakdown of the cell configuration without MPL and without PTFE. Hence, no characteristic cold start could be identified representing all individual tests. Although the evolution of the cell voltage is rather unrepeatable, all cold starts have shown at least 2 distinct voltage peaks of similar height.

In contrast, the cell without MPL and 5 wt% PTFE (see Figure 4.14 (b)) shows a similar behaviour compared to the cells with MPL. However, two main differences can be observed: First, the voltage drop is initiated with two distinct peaks of heights above 1 mV and peak heights up to 6 mV are obtained at cold start of type I. Second, the operating time of a cold start of type I is significantly longer compared to the cold start performed with MPL. In contrast to previous configuration without MPL and PTFE, Figure 4.14 (b) represents a characteristic
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Figure 4.14: Two cold starts of type I at -10°C operated with GDLs without MPL and (a) 0 wt% and (b) 5 wt% PTFE coating.

cold start. In general, both cell voltages without MPL are significantly lower compared to the cell voltages with MPL.

Integral water distribution

Figure 4.15 depicts the integral amount of water in (a) the CCM, (b) the anode GDL and MPL, (c) the cathode GDL and MPL under the land of the flow field, (d) the cathode GDL and MPL under the channel of the flow field, (e) inside the flow channel of the cathode, and (f) the cell voltage during an isothermal cold start at -7.5°C of 30 minutes. The three line styles depict the different PTFE loadings (0, 5, 20 wt% PTFE) of the GDLs. During this experiment, all cells were able to run through the entire 30 minutes of operation (cold start type II).

The amount of water inside the CCM increases during the first 10 minutes and remains constant during the entire experiment for all three cell configurations (see Figure 4.15 (a)). It has to be mentioned that the integration area of the CCM accounted for only 8 pixel rows in horizontal direction, as the pixel resolution was 5 μm/pixel. Hence, the water thickness in this region will give us only an indication about the amount of water inside and around the CCM. However, as all five cell configurations are analysed with the identical procedure, comparisons
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Figure 4.15: Integral amount of water during a cold start of -7.5°C in the (a) CCM, (b) Anode GDL, (c) Cathode GDL under the channel, (d) Cathode GDL under the land and inside the (e) channel of the cathode flow field of three cell of different PTFE coating load with MPL. (f) depicts the temporal evolution of the cell voltage.

between the cells are suitable.

In the anode GDL and MPL (see Figure 4.15 (b)), only very little water accumulates, as the back diffusion is rather low at these temperatures, which is in good agreement with previous studies performed with neutron radiography [39] and in chapter 3. The amount of water inside the cathode GDL (see Figure 4.15 (c-d)) is significantly higher and increases continuously during
4.7 Effect of PTFE Coating and MPL on Cold Start capability

Figure 4.16: Integral amount of water during a cold start of -7.5°C in the (a) CCM, (b) Anode GDL, (c) Cathode GDL under the channel, (d) Cathode GDL under the land and inside the (e) channel of the cathode flow field of two cell of different PTFE coating load without MPL. (f) depicts the temporal evolution of the cell voltage.

As already been published [59, 195], water preferentially accumulates under the ribs. It requires around 15 minutes to reach the steady state of the water saturation, which is significantly longer compared to the stabilization inside the CCM. Although the GDL of the three cell configurations are coated with different amounts of PTFE, all three cell configurations show a similar integral quantity of water inside the GDL, which is in good
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agreement with subsequent measurements which will be presented in chapter 5. Regarding the accumulation of water inside the flow channel of the cathode, water starts to accumulate after 10 minutes of operation, which indicates that first preferential pathways of water are created inside the GDL. The cell with the highest coating load accumulates less water which can be explained by a better removal of water droplets on the surface of the GDL thanks to the increased surface contact angle.

In analogy, Figure 4.16 depicts the integral amount of water in the different layers of the two cell configurations without MPL. Unfortunately, no cell of configuration 4 (0 wt% PTFE, no MPL) was able to be operated through the entire 30 minutes of the experiment inside the beamline. Nevertheless, an increased amount of water can be measured around the CCM compared to the cells with MPL, which is in good agreement with literature [83]. Besides that, the water distributions and the times scales of equilibration in the different layers are very similar compared to the cells with MPL.

Local water distribution

Figure 4.17 shows the local water distribution after 30 minutes of operation at -7.5°C for all 5 cell configurations. The water thickness is depicted in a false colour code, representing 0 mm

![Local water distribution](image)

**Figure 4.17:** Local water distribution of the five different cell configurations after 30 minutes of operation at -7.5°C.
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of water (yellow) and 1 mm of water (blue). The dotted line in the middle of the radiograph represents the membrane, with its anode on the left and cathode on its right. The alternating structure on the left and right represents the flow field. The GDLs are located in between the dotted line and the bottom of the flow fields. As described in the experimental part, the effective resolution has been improved in direction perpendicular to the membrane. Hence, the radiographs are magnified by a factor of approximately 6 in x-direction. The images are merged in a time period of 15 minutes after the cell failure. The neutron radiographs presented hereafter are the resulting water distributions obtained from the cold starts of Figure 4.15 and Figure 4.16. As can be seen, the water distribution inside cells including a MPL is rather similar. Water preferentially accumulates under the lands of the flow fields, the region between the CL and GDL shows a relatively low amount of water. In contrast, the cell without MPL, show significantly more water accumulation in the region of the CCM. As has already been reported previously, no cell of the configuration without PTFE coating and without MPL was able to be operated for 30 minutes in the beamline to obtain reasonable saturation levels.

4.7.4 Discussion

Types of cold starts

In Figure 4.10 and Figure 4.11 two different time scales of freezing were identified: High probability during the first ten minutes, succeeded with a region of significantly reduced number of failures. The differences in the freezing behaviour can be explained as follows:

Cold starts of Type I occur during the first 10-15 minutes, meanwhile a steady increase of the saturation levels are measured inside the CCM and the MPL/GDL of the cathode side (see Figure 4.15 and Figure 4.16). After this timeframe, the amount of water stabilizes inside the porous layers and a linear growth of the water thickness can be identified inside the cathode flow field. According to the saturation levels, the following water transport mechanism can be deduced: During the rise of the water thickness inside the porous layers, water pathways are created from the CL towards the flow channels. First pathways are generated after 10 minutes, as initial water accumulation is identified inside the flowfield. The creation of the pathways is completed after 15 minutes, as the saturation levels stabilize inside the porous layers.

This water transport has a significant impact on the freezing probability. As has been explained in the introduction, the phase transition from supercooled water to ice can be triggered by a seed. In general a seed represents any kind of impurity or structure which increases the probability of triggering a heterogeneous nucleation of supercooled water. Inside fuel cells, these seeds can be either defects like e.g. fibre breaks, asperities or micro cracks but also any kind of boundary surfaces like e.g. carbon fibers. During the creation of the water pathways through the porous layers, two scenarios are possible: First, the water cluster does not pass a seed (see
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Figure 4.18 (a): no freezing occurs and the cell can be successfully operated during the first 15 minutes. Second, a seed is encountered during the growth of the water cluster (see Figure 4.18 (b)); the phase transition is induced and the cell fails during this time period. However, if the water pathways are created after 15 minutes of operation and the saturation levels reach a steady state, water permeates along these water clusters (so called preferential pathways) with a significantly reduced probability of facing a seed and hence cell breakdown. Consequently, these transport mechanisms identified by neutron radiography could clearly explain the statistical differences in Figure 4.10 and Figure 4.11 between cold start of type I and II.

![Figure 4.18](image)

**Figure 4.18:** Schematics of freezing inside (a) uncoated GDL without seed, (b) uncoated GDL with seed and (c) coated GDL with seed.

Period of zero-failure

During the experiments, a period of zero-failure was identified at all operating temperatures (see Figure 4.6) or GDL materials used (see Figure 4.10 and 4.11). This period can be explained by the following mechanisms: At the beginning of the cold start, product water is taken up from the hydrophilic membrane until a maximal hydration state is reached. According to literature values [34], a maximum amount of approximately 0.05 mg cm\(^{-2}\) of water can be taken up by the membrane (neglecting lateral diffusion of water under the sealings). According to our protocol which comprises a linear increase of current density to 0.1 A cm\(^{-2}\) during first minute of operation, enough product water is already present after 30 s to saturate the membrane. However, as can be clearly seen in Figure 4.5, more than 1 minute is required to stabilize the HFR and thus its hydration state, which can be explained by the differential operating conditions with gas flows of 100 Nml min\(^{-1}\) on both sides enabling the water uptake of up to 0.44 mg min\(^{-1}\) of water at -10°C (according to the Goff Gratch equation for partial pressures below 0°C [196]). Consequently,
the first 1.5 - 2 minutes of the present protocol can be mainly explained by the water uptake of the membrane.

Subsequently, liquid water starts to accumulate inside the void space of the CL. As can be seen in Figure 4.12, fuel cells undergoing a cold start type I can be operated for 1 - 2 more minutes until the freezing event can be identified based on the voltage peak and an increase in the membrane resistance. Similar to the water uptake of the membrane, this step is highly dependent on the evaporation rate, as up to 78% of the product water can be taken up by evaporation on the anode and cathode side. However with increasing operating time, the probability of supercooled water to freeze increases due to a higher likelihood of facing a seed as well as due to its increased cluster size [49].

Although these calculations are in good agreement with our experimental results (see Figure 4.6 and Figure 4.12), contradictory findings are reported in literature [34]. In these models, good agreement is obtained between experiments and models by coupling the cold start capability with the water uptake of the membrane and the CL void volume, neglecting the evaporation rate. These experiments have two major differences: First, these investigations were performed on lab-scale fuel cells operated at technical operating conditions ($\lambda_{stoeic} < 5$), where the evaporation rate plays a minor role. Second, as these experiments were performed on lab-scale fuel cells of 50 cm$^2$, cell failures occur in a repeatable manner with high probability after short operating times (see section 4.6). Based on these two differences, the freezing mechanism appears to be different on the global scale even though the freezing mechanism is identical on the local scale. For technical applications, a mitigation strategy of freezing would be the supply of reactant gases with high flow in order to decrease the water saturation inside the individual porous layers.

**Influence of MPL on period of zero-failure**

Besides the influence of the temperature, differences between the period of zero-failure of cells with and without MPLs were observed. During the first 5 minutes of operation, no cell failures were measured with cells including MPLs. This time period was slightly increased in cells without MPL being able to be operated during 7.5 minutes without any cell failure at -7.5°C. The difference can be explained by a different water accumulation inside the fuel cells. In cells without MPL, water is more concentrated around the CCM, whereas it is pushed throughout the MPL inside GDLs with MPL (see Figure 4.15 and Figure 4.16). As the water transport is more limited without a MPL, the probability of facing a seed is reduced. However, the remaining part of the probability distribution in Figure 4.10 and Figure 4.11 is looking rather similar between cells with and without GDL. This analogue behaviour can be explained by the water transport inside the MPL, which is mainly defined by the morphology (e.g. pore size, roughness, and
coating level) of the cracks [197]. Since the morphology of the cracks have a comparable pore size and roughness with respect to the GDL, a similar freezing behaviour is obtained.

Period of cell breakdown

The period of the cell breakdown (time between voltage peak until the cell voltage drops below 0.2 V) can be explained by the filling of the void space of the CL with ice after the first nucleation of supercooled water. Assuming a porosity of 50%, a maximal storage capacity of 0.4 mg cm\(^{-2}\) of water is obtained with our materials. At a current density of 0.1 A cm\(^{-2}\), 0.56 mg min\(^{-1}\) of water is produced, which would result in a maximal time-scale of around 40 s until failure. However, similar to previous explanations, the evaporation rate of water has to be taken into account. As first water/ice already condenses inside the porous layers of the cathode side of the fuel cell (see Figure 4.15), the gas stream is saturated and only little amount of water/ice can be removed via the cathode side; thus water removal is mainly driven by evaporation via the anode gas stream. Consequently a rate around 0.22 mg min\(^{-1}\) at -10°C and 0.33 mg min\(^{-1}\) at -5°C can be removed by evaporation. Thus, a voltage drop between 1 - 2 minutes can be explained in order to fill the entire pore space of the catalyst layer and thus block all active sides. This calculation is in good agreement with our experimental findings observed in Figure 4.6 and Figure 4.12.

Influence of coating on cold start capability

In the statistical analysis of Figure 4.10 the coating load has been identified as being a crucial parameter for repeatability; with low coating loads significant cell-to-cell variations were identified, which were considerably reduced with 20 wt% PTFE. These variations can be explained by the morphology of the used GDL materials. As has been observed with SEM (see Figure 5.1), the used GDLs comprise a highly porous carbon binder, which can act or host seeds for crystal growth during the cold start. With increasing coating load (> 10 wt% PTFE), this carbon binder is covered with a homogeneous layer of PTFE (see Figure 5.1) and the probability of encountering a seed is reduced (see Figure 4.18 (c)). With this model, the minor cell-to-cell variations as well as the reduced overall probability of cell failure of highly coated GDLs can be explained.

Explanation of voltage peaks

In our experiments, voltage peaks were identified shortly before cell failure. Variations of the cell voltage can be induced by e.g. temperature, pressure, or humidification. In the present experiments, these voltage peaks can be mostly likely explained by an increase of the local temperature resulting from the latent heat of freezing during the change of aggregate state from supercooled water into ice.
According to literature, the latent heat of freezing accounts for \( q = 336 \, \text{J g}^{-1} \) [198]. Based on the neutron radiographs, an average mass of 1.6 mg of water can be determined inside the GDL, which translates into a release of 0.538 J inside the GDL during the freezing. The amount of water inside the CL cannot be identified based on the neutron radiographs due to the limited spatial resolution. However, if we assume a saturation of 50% in the CL with a porosity of 50%, a mass of around 0.2 mg\( \text{H}_2\text{O} \) of water can be obtained.

Taking literature values for heat capacities \( c_p \) of the two layers [199] and assuming that all heat results exclusively in an temperature increase of the individual layer, the increase of the temperature can be calculated as follows:

\[
Q = (m_{\text{H}_2\text{O}} \cdot c_{p,\text{H}_2\text{O}} + m_{\text{struc}} \cdot c_{p,\text{struc}}) \cdot \Delta T
\]

Thus, a temperature increase of around 64.80°C is obtained inside the GDL and 59.68°C inside the CL without considering the thermal conductivity of the fuel cell materials. The thermal conductivity is calculated according to the heat equation, with the following general 1D solution:

\[
T = \frac{M}{2(\pi D t)^{0.5}} \cdot \exp \left( \frac{-x^2}{4Dt} \right),
\]

with \( D \) being the thermal diffusivity, \( t \) the time and \( x \) a coordinate across the layer, \( M \) being a constant. The exponential part of this equation represents the time dependency of the temperature profile across the layer. Having renamed \( \exp((-x^2)/4Dt) \) to \text{parameter of temperature deviation}, Figure 4.19 shows the temporal evolution of the parameter calculated inside a GDL of 200 μm thickness. At \( t = 0 \), significant temperature gradients are obtained, which converge after around 1 s towards 1, which represents a homogeneous temperature distribution across the layer. This effect could explain the duration of approximately 1 s of the voltage peaks.

It has been widely reported that the temperature strongly influences the overall cell voltage of a PEFC [3, 10, 200] (see Equation 1.10). The Nernst potential (see Equation 1.8) consists of a concentration independent term \( U_{\text{rev}}(T) \), which decreases with increasing temperature. Furthermore, the concentration dependent term of the Nernst-Equation also reduces with higher temperatures, as the change in partial pressure of water \( p_{\text{H}_2\text{O}} \) is more dominant than the proportionality with temperature. In our temperature range around 0°C, the overall Nernst-Potential decreases in the range approximately -0.7 mVK\(^{-1}\).

Besides the Nernst-Potential, the activation overpotentials \( \eta_{HOR} \) of the anode and \( \eta_{ORR} \) of the cathode are temperature dependent. In our current density range \( (i = 0.1 \, \text{Acm}^{-2}) \), the polarization of the anode is negligible. The temperature dependency of the kinetic losses of the cathode catalyst follows an Arrhenius relation and can be described according to the Butler-Volmer equation [10]. This equation highlights that the ORR-kinetics increases with increasing...
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Figure 4.19: Temporal evolution of the temperature deviation inside a GDL. As can be seen, the temperature stabilizes after 1 s inside the GDL.

Temperature. In our temperature range, this rise in kinetics translates into an improvement of the cell voltage in the range of $2\text{ mVK}^{-1}$ (calculated according to equation (5) in ref [201]).

The ohmic losses $\eta_{IR}$ are dominated by the hydration state of the ionomer inside the CL and the membrane. The temperature dependency of the proton conductivity can be modelled with an Arrhenius relation [13] and rises exponentially with temperature. However, in this temperature range and a current density of 0.1 Acm$^{-2}$, the temperature effect of the ohmic losses is much smaller compared to the improvement in kinetics. A slope in the order of $0.08\text{ mVK}^{-1}$ is obtained and can thus be neglected. Similar explanation holds for the bulk $\eta_{bulkMTL}$ and non-bulk $\eta_{non-bulkMTL}$ mass transport losses.

Consequently, an overall improvement of around $1.48\text{ mVK}^{-1}$ can be expected under these operating conditions. In Figure 4.12, the voltage peaks in the order of 1 - 2 mV translate into a temperature rise of around 1°C; the voltage of around 6 mV in Figure 4.13 into around 4°C.

Explanation of multiple voltage peaks

The second voltage peak observed in Figure 4.12 and Figure 4.14 can be most likely related to the interconnectivity of the water cluster. These peaks were mainly identified in Type I cold starts with failures below 10 minutes of operation. As has been observed in the neutron radiographs, the water pathways are not fully created and a maximal saturation level in the
GDL is not reached in this timeframe. Hence, the full interconnectivity of the water cluster in the GDL might not been established, which might lead to a separate freezing with two distinct voltage peaks.

This assumption would also be able to explain the differences between the cells with and without MPL. As has been observed with X-Ray tomography [62], the water is more clustered inside GDLs without MPL, which might lead to an independent freezing with more distinct voltage peaks. Furthermore, the disappearance of the second voltage peak in cold starts of Type II can be nicely explained with this phenomenon. Based on the neutron radiographs, a steady state condition of the saturation level is reached which is assumed to be highly interconnected [191]. This fact might not only explain the disappearance of the second voltage peak but also the significantly higher voltage peak compared to separate water cluster in Type I cold starts.

**Influence of water distribution on freezing**

As has been explained in section 4.6, the size of the cluster volume and hence the water distribution has a significant impact on the freezing behaviour of PEFCs. The neutron radiographs in Figure 4.17 have clearly shown that the amount of water around the cathode CL is significantly reduced in cells with MPLs. However, the water clusters are not expected to be entirely separated between water inside the CL and the GDL. More likely, the water volume of a water cluster in cells with MPL is expected to be increased, as liquid water is transported only via a certain number of cracks of the MPL (≈ 100 cracks cm$^{-2}$), similar to a point-like injection [202]. This assumption is in good agreement with X-Ray tomography measurements of operating fuel cells without MPL [64], where water cluster are not entirely connected with each other.

Hence, it is expected that the propagation of the freezing of cells including a MPL occurs instantaneously. This behaviour can be clearly observed in Figure 4.12, where one distinct voltage peak is measured; the second voltage peak is significantly smaller. In case of locally separated water cluster, several voltage peaks of similar height would be expected. This effect might explain the particular behaviour of the cell without MPL and PTFE in Figure 4.14 (a). Two voltage peaks of comparable amplitude have been identified after a very short operating time, where the water cluster can be assumed of not being interconnected in the GDL, as only little amount of water was accumulated (see Figure 4.16 (a)).

**Thermodynamic transition from supercooled to frozen water**

As has been reported previously [40], the free energy change of phase transition from water to ice is more positive (less spontaneous) with higher coating loads of Teflon at a critical cluster size below 5 nm. This calculation is based on a spherical droplet accumulating on a flat surface. The critical cluster size is obtained by an equilibrium of a superficial (dG>0) and volumetric
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term \((dG < 0)\). As has been shown in several publications [62, 203], water is not accumulating in the form of droplets but rather as a continuous water cluster across the different porous layer of the PEFC. Consequently, in reality water accumulates more as a network of cylinders than spheres. This results in a completely different surface-to-volume ratio which is more favourable to maintain supercooled water. Hence, this can explain the rather stable occurrence of this metastable phase.

Technical application

In order to evaluate whether the significantly improved performance of the GDL with high coating load can be used for technical applications (see Figure 4.10), previously presented Monte-Carlo simulation was applied to the experimental data (see section 4.6); the numerical results are plotted in Figure 4.20. Although significant differences are identified between the different materials with small scale fuel cells, the simulation clearly shows the limited impact for cell sizes above \(10\text{ cm}^2\).

![Figure 4.20: Modelling results from Monte-Carlo simulation: Comparison between two GDL materials with different hydrophobic coating load as a function of its cell size at \(-7.5^\circ\text{C}\) and \(0.1\text{ Acm}^{-2}\).](image)

4.8 Summary of chapter 4

In the present chapter, the cold start capability was studied regarding two aspects: (1) the size of the active area as well as (2) its fuel cell materials. The following major findings were obtained in these studies:
4.8 Summary of chapter 4

4.8.1 Impact of the size of active area

For the first time, the influence of the active area on the freezing mechanism was investigated systematically in section 4.6. Two different cell setups having different sizes of the active areas (1, 50 cm$^2$) were studied experimentally under subfreezing conditions. Furthermore, a Monte-Carlo simulation was performed based on the experimental data obtained from the 1 cm$^2$ cell, in order to extrapolate the freezing behavior to larger active areas. The following new key findings were gained in this section:

- The probability of freezing increases with the cell area, resulting in long and stochastic operating times for small cells and short and reproducible operating times for large cells. Consequently, conclusions from most publications performed on small scale PEFCs cannot be directly extrapolated to automotive cells in the order of several hundreds of cm$^2$.

- Cell-to-cell variations have a significant influence on the cold start capability of small scale fuel cells. Although the impact of the sample variability is, according to our simulation, limited to cell sizes up to 10 cm$^2$, optimized materials might further reduce the probability of freezing and improve the cold start capability of larger cells.

- Despite the large cell-to-cell and experiment-to-experiment variations for small cells, the minimal operating times converge to a value consistent with the operating time of large cells, which can be explained by the quantity of water uptake by the membrane and catalyst layer until the latter is blocked.

4.8.2 Impact of different GDL materials

In section 4.7, a statistical analysis of the freezing behaviour was performed on small-scale fuel cells combined with high resolution neutron radiography in order to study the influence of different hydrophobic coating loads and the existence of an MPL. The following key findings were obtained:

- Cell-to-cell variations are more dominant than influences of the materials variations at low coating loads: In the statistical analysis, a higher coating load reduces the cell-to-cell variations. This effect can be explained by the microstructure of the GDL and MPL materials which varies strongly within a material and acts as a seed for ice nucleation. With high coating loads, the seeds are covered by the hydrophobic coating. However, no significant differences were identified between the materials with low coating loads.

- Failures of cold start mainly occur during the first 10 minutes of operations: This effect can be explained by the creation of water pathways from the CL to the flowfield. After
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having created these water pathways, water is mainly transported along these preferential pathways, resulting in a highly reduced probability of facing a new seed for nucleation.

- Cells without MPL decrease the cell failure during the first 10 minutes of operation: The statistical analysis of the cold start has identified that no cell failure occurs in the first 7.5 minutes of operation with cells without MPL, whereas cells with MPL fail with a higher probability.

- Latent heat of freezing can be identified by voltage peaks: In the experiments, voltage peaks of several mV were measured shortly before cell failure. This effect has been attributed to an increase of the temperature induced by the latent heat of freezing.

- For technical applications GDLs without MPL and high coating loads might be optimized materials for improved cold start capability. However, numerical results of a Monte-Carlo simulation have shown limited impact above a cell size of 10 cm².

4.9 Outlook

For fuel cells of technical size, the first study has clearly shown that cells above 10 cm² cannot be operated for longer than the minimal operating time (e.g. with our materials 5 minutes at -7.5°C) defined by the water uptake of the polymer membrane and the pore space of the CL. However, we have also shown that small scale fuel cells are able to be operated for more than 2 h under subfreezing conditions. Hence, this study can serve as a fundamental basis for a innovative cell design with increased cold start capability. This concept might be realized by a segmented active area with independent segments below 10 cm². Based on this modification, significantly improved operating times are expected under subfreezing conditions.

Regarding the variations of the GDL materials, these experimental findings can serve to optimize GDL with an improved cold start capability. It is observed that GDLs with high coating load significantly improve the cold start capability as the seeds are covered with a hydrophobic coating. Unfortunately, these materials have shown a poor performance under technical operation conditions, which will be presented in chapter 5. However, modifications of the materials by confining optimized water pathways inside the GDL [114, 204, 205] have shown a significant improvement of the performance under technical operating conditions. Furthermore, the probability of freezing is expected to be significantly reduced, as the number of water pathways and thus the number of nucleation sides is reduced. Especially the GDL used in the concept of Forner et al. [205] are highly hydrophobized (30 wt% FEP), which strongly reduces the probability of failure. Hence, with these GDL materials, the best trade-off between cold start capability and performance under technical operating conditions is expected.
Operation at technical operating conditions: Effect of hydrophobic coatings of GDLs

In the previous two chapter chapter 3 and 4, fuel cell operation was investigated at subfreezing temperatures. In present chapter, the water transport will be studied at technical operating conditions, mainly focusing on the mass transport losses arising at different hydrophobic coating loads of the GDL. In the first section (see section 5.1), a motivation is given why hydrophobic coatings are required for GDLs, followed by a literature review in section 5.2. Subsequently, the materials and experimental protocols used during the experiments are described in section 5.3. In section 5.4 the experimental results are given and will be discussed in section 5.5. The chapter is summarized with a conclusion in section 5.6.

5.1 Motivation

As has been explained in section 1.5, the water transport inside a GDL is rather complex: Liquid water propagates under the effect of capillary forces from the catalyst layer (CL) to the flow channel [25]. In opposite direction, a sufficient diffusivity of the reactant gases is necessary to sustain the electrochemical reaction with limited mass transport losses (MTL). This concurrent two-phase flow can be adjusted by the material properties of the GDL such as porosity, tortuosity or hydrophobicity. As the porosity and tortuosity are mainly given by the manufacturing process of the GDL, these two parameter are not easily adjustable. However,

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the application of a hydrophobic coating can be simply implemented. A hydrophobic coating
affects the diffusion media in different ways: (i) by increasing the water contact angle and thus
the capillary pressure, (ii) by modifying the diffusion structure of the dry material, and (iii) by
affecting some characteristics such as the thermal conductivity.

In literature, various studies about the influence of hydrophobic coatings have been published
(see section 5.2). However, no study on the impact of GDL coatings includes a precise analysis
of the mass transport losses distinguishing between bulk (ternary diffusion in GDL) and non-
bulk losses (Knudsen and thin film diffusion in the CL). Moreover, all conducted studies were
performed on cells operated with technical stoichiometries below 5. Although the choice of
technical stoichiometries may seem straightforward, it implies important inhomogeneities along
the flow channels [182]. Under these conditions, and in the absence of local electrochemical
data, unravelling the impact of water on mass transport losses is impossible. Therefore, new
experimental insights about the water distribution and performance of PEFCs on the local scale
using differential cells will be presented in this chapter. By combining the pulsed gas analysis
(see section 2.3) and limiting current density measurements (see section 2.2) with high resolution
neutron radiography, an unprecedented insight of the impact of hydrophobic coating on both
water distribution and mass transport losses can be obtained.

5.2 Literature overview

The influence of hydrophobic coatings was investigated by various researchers with ex-situ and
in-situ techniques. Ex-situ studies performed with Scanning Electron Microscopy (SEM) have
shown an important impact of the coating on the pore structure of the GDLs [206]. Lim et
al. [25] reported that the coating preferentially accumulates at multiple intersecting graphite
fibers during the application process, which may lead to a blockage of the pores under certain
conditions. This finding is supported by the coating distributions published by Prasanna et
al. [207], who reported that high coating loads (up to 40 wt% PTFE) lead to almost complete
clogging of the GDL. A more detailed characterization of the change in the pore size distribution
was performed by Park and Popov [208] with mercury intrusion measurements. They have shown
that the pores affected by the coating are mainly in the range between 3 and 50 µm.

Measurements of the surface contact angle give very limited knowledge about the impact of
the coating, as the complex heterogeneous surface (carbon fibers and polymer coating) combined
to the porous nature of the material strongly affect the measurements. A good example of this
limitation is given in the literature overview in ref [208], where contact angles between 30-180°
are reported with similar materials. More advanced measurements of contact angle for porous
GDLs can be obtained by determining the internal contact angle (Washburn method) [209, 210].
In this method, the contact angle is measured on the basis of the dynamics of water uptake and
uptake of other liquids in the porous structure. However, the resulting internal contact angle
strongly depends on the model applied to the data. Ex-situ permeation measurements with
air [207, 211–213] or water [214] give information about the impact of coating on the material
permeability. Prasanna et al. [207] measured a highly decreased air permeability of the dry
GDL with higher coating load. Water permeation measurements have also shown that a higher
coating load results in an increased capillary pressure threshold [214]. Ismail et al. [215] assumed
that a reduction in the average pore size may not only decrease the permeability but may also
increase the permeability and tortuosity under certain conditions. LaManna and Kandlikar
[213] found out that a higher coating load causes a higher tortuosity, resulting in increased
three-dimensional diffusion pathways for water vapour. Capillary pressure measurements were
performed by Gostick et al. [216] with different liquids (e.g mercury, water, octane). Based on
these measurements it is assumed that an excessive amount of PTFE leads to a thicker layer of
coating but not necessarily to an increase of the carbon fraction covered by the coating [217].
Based on SEM measurements, Lobato et al. [218] concluded that a coating of 10 wt% PTFE
already leads to a coating coverage of 97.3 % of the graphite fibres. This finding is consistent
to measurements of Lim et al. [25]. More advanced investigations about local compression and
changes in the porosity were performed with X-ray tomography [219]. However, only Toray
carbon papers were investigated and no such information is available for other state of the art
GDL materials.

Various researchers investigated the influence of PTFE coating in operating cells. However,
in most of the cases, GDLs without MPL [25, 208, 211, 214, 220, 221] and/or non state of
the art membranes [25, 208, 211, 214, 220, 222] were used. As a consequence, most reported
results are based on cells with very low performance hardly reaching 1 A cm\(^{-2}\) [25, 208, 211,
214, 220, 222] under reasonable operating conditions. Most investigations were performed
on 25-50 cm\(^2\) lab-scale fuel cells [25, 208, 211, 212, 214, 220, 224], while only two studies were
conducted with smaller cells (active areas < 10 cm\(^2\)). Lin et al. [225] used a 6 cm\(^2\) fuel cell with
technical stoichiometries (below 5) with interdigitated flow fields, which induces major changes
in the gas and water transport mechanisms. Mukundan et al. [182] performed in-plane neutron
radiography measurements on a 2.25 cm\(^2\) small-scale cell. In order to be able to compare these
results to a technical fuel cell with an active area of 50 A cm\(^{-2}\), a flow field with a single serpentine
was used in their experiments resulting in similar channel lengths and gas velocities. The authors
investigated the influence of the water distribution on the performance using commercial GDL
materials of SGL series 24 with 5 and 20 wt% PTFE. However, no precise analysis of the water
distribution was performed comparing these two materials. A more detailed analysis was carried
out on the microporous layer (MPL), where the amount of hydrophobic coating inside the MPL
was identified of being critical for an efficient water removal.
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For the characterization, several studies rely on IV curves only [208, 211, 212, 214, 220], sometimes complemented by impedance spectroscopy measurements [25, 207]. A few more studies use more specific methods such as pressure drop analysis [225], limiting current [221] measurements, oxygen gain analysis [207], and neutron radiography [182]. Various optimal coating levels of 5 wt% [221, 226], 10 wt% [25], 20-23 wt% [182, 207, 223] or even 30 wt% [223] are claimed in literature.

Although many publications find similar experimental results, different explanations are given. A good agreement can be found on the fact that uncoated GDLs tend to show a high risk of flooding inside the GDL [212, 227, 228] although there is no visualization data available showing which amount of water is to be considered as flooding. Tseng and Lo [212] explained this flooding by a quick removal of the water from the CL but accumulation inside the GDL which leads to significant performance drop. Shimpalee et al. [227] did a numerical analysis of GDL water flooding. They showed results on state of the art materials with large differences between uncoated and coated GDL. They explained the lower performance of the GDL without coating by a partial flooding of its pores.

In contrast, the explanation about the water transport inside highly PTFE coated GDLs is very different in literature. According to Park et al. [211], highly PTFE coated GDLs have a higher risk of flooding the CL which leads to a deactivation of the cell. These findings can be related to the fact that no MPL was used in these specific experiments. Furthermore, they assume that the total amount of water is higher inside highly coated GDLs, as capillary condensation takes place resulting from the smaller pore size. Lim et al. [25] explained the poor performance at high coating loads by the fact that their coating process results in a thin film on the surface of the GDL which leads to a substantial diffusion resistance of the reactant gases. Prasanna et al. [207] reported about a better water removal at low coating loads of 10 wt% PTFE.

Regarding the resulting ohmic losses, contradictory findings are published in literature. Several studies [207, 212, 215, 229] reported about increasing ohmic losses with higher coating levels due to the additional unconductive coating. In contrast to this, Chang et al. [221] identified constant ohmic losses between coating loads of 5 and 20 wt% PTFE.

5.3 Experimental

Cell materials

The following experiments were performed with the Multicell setup presented in section 2.5. A catalyst coated membrane (CCM) (Primea 5710, W.L. Gore & Associates, Inc., USA) was used as presented in subsection 2.5.4. Commercial GDLs were used from the SGL Carbon Group
5.3 Experimental

Series 24 [116] with a MPL containing 23 wt% PTFE [230]. Table 5.1 depicts the four different configurations of GDLs used. The amount of PTFE was varied on the anode between 0 and 5 wt% and 0, 5, and 20 wt% PTFE on the cathode side, respectively. Three identical cells of the basecase were operated, which served to calculate error bars in subsequent figures with 2.57 times standard deviation.

<table>
<thead>
<tr>
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<th>2</th>
<th>3</th>
<th>4</th>
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<tr>
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<td>SGL 24 BC</td>
<td>SGL 24 AC</td>
<td>SGL 24 BC</td>
</tr>
<tr>
<td></td>
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<td>(5 wt% PTFE)</td>
<td>(0 wt% PTFE)</td>
<td>(5 wt% PTFE)</td>
</tr>
<tr>
<td>Cathode GDL</td>
<td>SGL 24 BC</td>
<td>SGL 24 AC</td>
<td>SGL 24 AC</td>
<td>SGL 24 DC</td>
</tr>
<tr>
<td></td>
<td>(5 wt% PTFE)</td>
<td>(0 wt% PTFE)</td>
<td>(5 wt% PTFE)</td>
<td>(20 wt% PTFE)</td>
</tr>
</tbody>
</table>

Table 5.1: Fuel cell configurations analyzed during the experiments.

Figure 5.1: Scanning electron microscopy images of (a) SGL 24AC (0 wt % PTFE), (b) SGL 24BC (5 wt% PTFE), (c) SGL 24DC (20 wt% PTFE). Images were taken with a magnification of 500; the voltage was set to 3kV at a working distance of 6.6 mm. Reprinted from Biesdorf et al. [105] with permission of the Electrochemical Society. Copyright 2014 Electrochemical Society.

In Figure 5.1, SEM images of the structure of the three different GDLs are visualized. The base material of the GDL without PTFE shows its pure carbon fibre structure with carbon binder (flake structure). With increasing coating load (5 wt% PTFE), the mesopores of the porous binder are partly covered with PTFE, while the macropores (> 50 µm) [231] are not affected. This finding is in good agreement with results presented by Lim et al. [25]. At higher coating loads (20 wt% PTFE), some of the macropores are blocked by the PTFE as well. These findings can be confirmed by the pore size distribution published in ref [26].

The preferential location of the coating can be understood by considering its application procedure. Although the exact coating procedure applied for the commercial material is not known, the usual method is to apply an emulsion of PTFE particles (range of 200 nm) in water to the carbon paper. The surfactant present in the emulsion helps for a complete wetting of the carbon fibers. Intersections of several fibers are favourable locations for meniscus formations. Consequently, small pores can be completely blocked by the surface treatment, whereas big
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pores remain unchanged. Besides the changes in the pore morphology, thermal conductivity measurements on GDLs with different coating loads were reported to reduce conductivity of SGL GDLs by a factor of two by applying a coating of 20 wt% PTFE compared to the material with 5 wt% PTFE [232].

Imaging setup

The neutron experiments were performed at the ICON beamline [89] of the Swiss Spallation Neutron Source (SINQ) at the Paul Scherrer Institute. The cells were imaged with the membrane parallel to the beam axis (in-plane configuration) with a tilted imaging setup [7, 85, 115, 125]. A pixel size of 5 x 66 µm/pixel with an effective resolution (FWHM) of approx. 30 µm across and 198 µm along the membrane was obtained. A good trade-off between spatial and time resolution is obtained with an exposure time of 15s with this imaging setup [53]. The camera was an Andor NEO with 2592 x 2160 pixels. The image processing was performed according to subsection 2.1.6 and calibrated by a factor 1.53 according to the experimental procedure presented in subsection 2.1.7.

Experimental protocol

The results hereafter are based on four experiments (see Table 5.2): (1) current-voltage curve, (2) continuous operation, (3) RH-map and (4) limiting current measurements. The current-voltage (IV) curve experiment consisted of 11 steps of current variations, maintained during 20 minutes. The second experiment investigated the stability of the PEFC performance during 2h of continuous operation at 1 Acm$^{-2}$ under full humidification. The third experiment consisted of asymmetric variations of the anode and cathode humidification, which will be called RH-map in the following [233]. As the water balance equilibrates already after 3 minutes in these differential cells, every operation point was held only for 15min.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>UI-Curve</th>
<th>Cont. operation</th>
<th>RH-Map</th>
<th>Lim. current</th>
</tr>
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<td>2</td>
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</tr>
<tr>
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<td>120</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 5.2: Operating conditions during the four different experiments.
The limiting current density measurements were carried out at two cell voltages of 0.3 V and 0.2 V, respectively, at 70°C under dry and fully humidified conditions. The concentrations were chosen at 0.25, 0.5, 1.0, 2.0% O₂ in N₂. In order to investigate the differences in diffusivity of oxygen in helium, limiting current density measurements with 0.125, 0.25, 0.5, 1.0% O₂ in He were also performed. A first measurement was done using relatively dry gases (Anode: 30%RH / Cathode: 30%RH) to obtain the limiting current density without water in the GDL. Then, the cell was operated at 1 A cm⁻² and full humidity for 1 h, before making a second measurement of the limiting current density with fully humidified gases, keeping the water previously accumulated in the GDLs. If not specified elsewhere, all other experiments were performed at a constant current density of 1 A cm⁻². The cell temperature was maintained at 70°C at a pressure of 2 bar abs on both sides. The gas flows were 0.4 NL/min on the anode and 1 NL/min on the cathode side, translating into stoichiometries of approximately 60 on both sides.

5.4 Results

In this section, the experimental results of the four experiments described in Table 5.2 are presented.

UI-Curve

As has been reported in several publications [25, 182, 207, 208, 211, 212, 214, 220, 225], the PTFE-loading has a crucial influence on the overall cell performance especially at high current densities. Figure 5.2 (a) depicts the current-voltage curves of the four different cell configurations under full humidification. As expected, the main differences between the four cell configurations can be clearly identified in the high current density region where mass transport losses become important. The cell with the GDL without PTFE on the anode side shows no significant differences compared to the base case with 5 wt% PTFE on both sides. On the contrary, any change of the PTFE concentration on the cathode side leads to significant performance losses at current densities above 0.3 A cm⁻². These measurements are significantly different to ref [182] where best performances was obtained with 20 wt% PTFE with similar materials but with a different cell setup (active area of 50 cm²).

An indicator of activation losses is calculated based on the difference of the oxygen pulse voltage (corrected for its ohmic loss) with its thermodynamical equilibrium potential. The activation losses indicate no significant deviations between the four cell configurations, as the same catalyst-coated-membrane (CCM) was used. Nevertheless, in the region of high current densities, the cells with the poorest performance (0 wt% and 20 wt% PTFE) show the lowest
Figure 5.2: Cell voltage and indicator of performance losses during a current-voltage curve under full humidification, (a) overall cell performance, Indicator of (b) activation losses, (c) ohmic losses, (d) bulk mass transport losses, and (e) non-bulk mass transport losses. Reprinted from Biesdorf et al. [98] under the terms of the Creative Commons Attribution 4.0 License (CC BY).
activation losses (Figure 5.2 (b)). This fact can be explained by the lower overall cell potential, which leads to a lower oxide coverage of the platinum catalyst, resulting in a higher number of active sites of the catalyst [111, 112].

In between the four configurations, no significant differences of ohmic losses can be observed. This is in contrast to some findings in literature, where increased electrical resistances were measured [226, 229, 234]. However, as the coating is just applied on the surface of the GDL, the electrical bulk conductivity is not expected to decrease. In contrast, the contact resistance between GDL and lands of the flow field might be increased. As the experiments reported in ref [226, 229, 234] were performed with GDLs of different manufactures, the comparability with these measurements is limited.

The pulsed gas analysis (PGA) enables the differentiation between bulk and non-bulk mass transport losses (MTL) (see Figure 5.2 (d-e)). The figures reveal that the difference of the overall performance between the four cell configurations mainly results from differences in bulk losses. The configurations without and with excessive PTFE on the cathode side show a strong increase of losses at current densities larger than 0.3 Acm$^{-2}$. This increase might be either a result of water flooding or changes of the morphology of water in the GDL resulting from the supplementary coating and will be analysed with neutron radiography subsequently. The cell without PTFE on the anode side do not show any dependency induced by the coating process. Consequently, the overall mass transport is only limited by the cathode side. This is not surprising as the transport on the cathode side relies on oxygen diffusion in nitrogen and water vapor, while the transport on the anode side with pure hydrogen depends mostly on convection - it is however worth mentioning here that the situation may be different when using an anode recirculation loop where nitrogen can accumulate over time. Non-bulk losses on the cathode are not varying between the four configurations and their magnitude is in good agreement with our previous results [104]. This indicates that different PTFE loadings in the GDL do not impact the flooding of the CL [225].

**Continuous operation**

The overall cell voltage (a) and the indicators of bulk (b), non-bulk (c) and ohmic (d) losses during continuous operation at full humidification are shown in Figure 5.3.

At $t < 0$ min the cells are operated under full humidification on the anode and dry air on the cathode. The cells show a similar voltage (a little less than 700 mV) at 1 Acm$^{-2}$. However, a slightly lower cell voltage can be found at the cell with 20 wt% PTFE on the cathode which arises from increased bulk losses (Figure 5.3 (b)). At full humidification on both sides ($t > 0$ min), the PTFE loading has a much larger impact. All cells with 5 wt% PTFE on the cathode side (regardless of their PTFE loading on the anode side) are only slightly influenced by the increased
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humidification. The cell with 20 wt% PTFE on the cathode side shows a substantial but stable decrease of voltage of approx. 75 mV. The voltage of the cell without PTFE on the cathode decreases stepwise without stabilizing during the 2 hours of the experiment. Figure 5.3 (b) highlights that the main differences between the four cell configurations can be explained by the bulk diffusion losses. Both configurations with 5 wt% PTFE on the cathode side show only minor influence (≈ 25 mV) of the change in the operating condition. In contrast, the cell with 20 wt% of PTFE undergoes a significant increase of bulk losses, which results in a voltage drop of 75 mV of the overall cell voltage. The configuration without PTFE on the cathode side shows strongly rising bulk losses and does not reach any stable point until the end of the experiment. Unfortunately, the temporal resolution of the PGA is limited (helox pulses and O$_2$ pulses are switched each 5 minutes), and the stepwise decrease of the overall voltage is not apparent in the bulk losses. However, the absolute value of the bulk diffusion losses matches well the decrease of the overall voltage. An explanation will be given subsequently in the discussion part in section 5.5.

Consistent with the previous experiment, the non-bulk and ohmic losses show negligible deviations in between the four configurations and is an indication that the absence of excess of PTFE in the GDL has little influence on CL flooding.

High resolution neutron radiographs enable the correlation of water distributions with mass transport losses. At the beginning of the experiment (see Figure 5.4 (a)) similar water distributions can be found between the first three configurations. The configuration with 20 wt% PTFE shows slightly less water in the GDL. A strong gradient can be observed between water accumulation under the rib and channel which is consistent with literature [235, 236]. At the end of the experiment (see Figure 5.4 (b)), similar water distributions as in the beginning are obtained for most of the cells. However, the cell without PTFE on the cathode side has more water accumulation under the channel at the end of the experiment, resulting in an almost even distribution of water between the region under the ribs and under the channels. A detailed observation also shows that there is a preferential accumulation for water at the channel edges near the GDL. In summary, the large increase of mass transport losses observed for the cell without PTFE on the cathode side does not correspond to a massive flooding of the GDL, but to a redistribution of the water to specific locations which are particularly detrimental for mass transport. Interestingly, the blockage of the second channel of the cell configuration without PTFE on the anode side, does not translate into any decrease of performance of the cell configuration. The findings above explain the tendencies observed in ref [212, 227, 228] where high mass transport losses are measured with cells without coating. In summary, we point out that it is not a flooding of the entire GDL, but a redistribution of water to certain detrimental regions of the GDL, which significantly affect the performance.

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Figure 5.3: Indicators of performance losses during 2 h of operation under full humidification (a) cell voltage, (b) bulk mass transport losses, (c) non-bulk mass transport losses, and (d) ohmic losses. Cells operated at 1 Acm\(^{-2}\). Reprinted from Biesdorf et al. [98] under the terms of the Creative Commons Attribution 4.0 License (CC BY).
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<table>
<thead>
<tr>
<th>An: 5wt% PTFE</th>
<th>5wt% PTFE</th>
<th>0wt% PTFE</th>
<th>5wt% PTFE</th>
<th>20wt% PTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca: 5wt% PTFE</td>
<td>0wt% PTFE</td>
<td>5wt% PTFE</td>
<td>0wt% PTFE</td>
<td>5wt% PTFE</td>
</tr>
</tbody>
</table>

(a) $t \sim 0-30\text{min}$

(b) $t \sim 1.5-2\text{h}$

**Figure 5.4:** In-plane water distribution averaged during the (a) first and (b) last 30 minutes for the four configurations during continuous operation at full humidification. The dotted line in the middle depicts the membrane, with its anode on the left and cathode on its right. The five fringes depict the gas channels of the flow field. The gas diffusion layer is situated between the dotted line (membrane) and the bottom of the flow fields. The amount of water is represented in false color code (yellow = dry, blue = wet) which corresponds to 0 and 1.7 mm water. As the effective resolution is improved in direction perpendicular to the membrane, the images are magnified by a factor of approx. 6 in x-direction. Reprinted from Biesdorf et al. [98] under the terms of the Creative Commons Attribution 4.0 License (CC BY).
5.4 Results

RH-Map

The operation of the cells under asymmetric variations of the humidification on anode and cathode (RH-map) [233] provide detailed information about the influence of the local humidity on cell performance. The indicators of bulk, non-bulk and ohmic loss are depicted in Figure 5.5 (b-d) as a function of the humidification (see Figure 5.5 (e)). Similarly to previous findings of our group [233], there is an optimal operation point with a fully humidified anode and a dry cathode, where losses are minimized. The same trends are observed concerning the influence of anode and cathode relative humidity, but with different quantitative values. The cell with 20 wt% PTFE on the cathode side shows the strongest dependence of the bulk losses on humidification level, consistently with the previous experiment. A point worth noting is the increase of bulk losses in very dry conditions compared to the optimal case. Such an increase can hardly be attributed to water accumulation and was explained in a previous publication showing similar results [104] by the fact that, with increased membrane resistance, the cells increasingly rely on current production under the ribs. This effect is visible on all cells, but particularly affects the cell with a high PTFE loading, which suggests that the diffusivity of the dry structure is significantly affected in this case.

Although the losses of the cell without PTFE on the cathode are smaller than those of the cell with 20 wt% PTFE, we have to remind that every operating condition has only been maintained during 20 minutes. According to previous experiments, most cells stabilize within this time with the exception of the cell without PTFE on the cathode side. We would thus expect the losses of this cell to raise higher in Figure 5.5 (b) if the operating conditions would be maintained for a longer time.

The indicator of non-bulk losses shows no major differences between the four configurations. A slight decrease with increasing humidification is observed, which can be explained by a better ionic conductivity of the ionomeric phase inside the CL [85]. This is contradictory to some claims in literature [211] where increased losses with high coating loads of the GDL are attributed to flooding the CL. However, we are currently not aware of any publication demonstrating this claim.

Figure 5.5 (e) shows that the ohmic losses are strongly decreasing with increasing humidification. Consistent with previous findings [233], the ohmic losses are mainly determined by the anode humidification. This effect is specific to differential cells, where the quantity of water vapor which can be taken up by the gas flow is not limiting [233]. In technical PEFCs, the membrane humidification is mainly affected by the humidity of the cathode gas flow which is much bigger than the anode flow [233]. As has already been shown in the two previous experiments, no significant deviations can be found at high humidity between the ohmic losses of the four
different cell configurations. All cells tend to dry out with low humidity, but no clear trend can be extracted from these differences.

Figure 5.6 illustrates the spatial water distribution at selected humidification conditions. At low humidification conditions on both sides (Figure 5.6 (a)), almost no water can be found inside the GDL and flow fields. The increased mass transport losses, in particular those of the cell with the highest amount of PTFE, can therefore not be explained by the quantity of water accumulated. This apparent discrepancy will be further commented in the discussion section. Under full humidification on the cathode and dry gases on the anode (Figure 5.6 (b)), low saturation levels are observed in the cathode GDLs. Despite this, the bulk losses are still higher
### Figure 5.6:
In-plane water distributions at various humidification conditions: (a) 40/40, (b) 0/100, (c) 100/0, and (d) 100/100 %RH on anode and cathode, respectively. Reprinted from Biesdorf et al. [98] under the terms of the Creative Commons Attribution 4.0 License (CC BY).
than in the optimal case. As the membrane is not yet well humidified under this condition (high ohmic losses), the same explanation as for dry condition holds. As can be clearly seen from the neutron radiographs, water condenses inside the manifolds of the flow channels of the cathode (bottom of flow channels) indicating that the cathode flow is actually slightly over-humidified, but the dry anode flow is sufficient to avoid condensation in the GDL, even on the cathode side.

Figure 5.6 (c) shows the water distribution under optimal operating conditions (full humidification on the anode and dry cathode). It can be observed that water condenses inside the cathode GDL under the ribs of the flow channels. However, as can be seen from the performance data (Figure 5.5), water accumulation under the ribs of the flow channels does not affect the bulk mass transport losses significantly: the bulk losses are lower than in the previous condition with no water in the GDL. Similar to previous measurements, water appears in the manifolds of the flow channels, indicating a slight over-humidification. Interestingly, the cell with the highest amount of PTFE shows an increased water accumulation in the anode GDL and the ribs of the anode flow field.

Under full humidification (Figure 5.6 (d)) water accumulates in all layers of the PEFC including in the GDL under the flow channels. This directly translates into increased bulk mass transport losses.

The average amount of water inside the GDL of the anode and cathode is depicted in Figure 5.7. On the anode side, most cells show similar water saturation levels. Merely, the cell with 20 wt% PTFE on the cathode side shows higher water accumulations at anode humidifications above 60 %RH. Furthermore, the cell without PTFE on the anode shows a slightly higher amount of water at full humidification, which may be a result of the interaction with flooded channels (see Figure 5.6).

On the cathode side, very similar values for all cells are obtained for anode humidifications below 80 %RH. Above this value, the cells with 0 wt% and 5 wt% PTFE have similar saturation levels. However, the cell with 20 wt% PTFE shows significantly less water. As this cell is the one with the largest mass transport losses, this figure clearly shows that diffusion limitations are not only a function of the integral water saturation level of the GDL. More likely, the form of the water accumulation has an even major influence and has to be taken into account.

Analogous to the GDL, the water saturation levels inside the MPL are plotted in Figure 5.8. As can be seen, no clear differences can be measured between the cells. This can be explained by the fact that the same MPL material was used for all cells, but also indicates that the PTFE content of the GDL has a limited effect on water in the MPL.
5.4 Results

Limiting current density

Figure 5.9 depicts the results of the limiting current density measurements of oxygen in (a) nitrogen and (b) helium as a function of its oxygen concentration. Under dry conditions all cells, except the cell with the highest PTFE loading, show similar limiting current densities in nitrogen. However, the cell with 20 wt% of PTFE shows a significantly lower performance in the dry state, which correlates to the increase of bulk mass transport losses observed with the PGA. Under full humidification, the limiting currents are strongly decreased due to the condensation of liquid water inside the PEFC. The cells with 5 wt% PTFE on the cathode show a decrease of approximately 25% of their limiting current compared to the dry state. Consistently with the previous measurements with PGA, the cell without PTFE on the cathode side is strongly influenced by the accumulation of water, with a limiting current approximately 3 times lower than its value for a dry GDL (see Table 5.3). If the limiting current values are linearly extrapolated to an oxygen concentration of 21%, a limiting current density close to 1 Acm$^{-2}$ is obtained which is similar to the values obtained in the IV curve in Figure 5.2. The

![Figure 5.7: Integral amount of water inside the GDL in the anode and cathode side at various humidification conditions. Reprinted from Biesdorf et al. [98] under the terms of the Creative Commons Attribution 4.0 License (CC BY).](image)
effect of water accumulation on the cell with 20 wt% PTFE is a reduction of 35% of the limiting current density, which is also a stronger reduction than in the case with 5 wt% PTFE.

Under mixtures with helium (see Figure 5.9 (b)), increased limiting currents are reached compared to operations under nitrogen, which result from the increased diffusivity of oxygen in helium. According to Kocha et al. [107], the enhancement of diffusivity is of approximately 2 for a case where the water vapor represents an important molar fraction. In our case (70°C, 2 bar\textsubscript{abs}), the water molar fraction is at most 0.16 and the enhancement of diffusivity should be near to the value of 3.5 corresponding to dry gases. In order to evaluate this improvement, an improvement factor of the slope (IFS) is introduced as the ratio of the slope under air and helox. As shown in table 3, the increase of the IFS value when using helium based mixtures is lower than this and ranges from 1.8 to 2.1. A likely explanation to this apparent discrepancy is the limitation introduced by the non-bulk diffusion terms (e.g. diffusion through the ionomer in the catalyst layer), which are not affected by the introduction of helium. Consistently with this explanation, the effect of using helium is generally higher in cases with lower current densities, attributed to high bulk diffusion losses.
5.4 Results

Figure 5.9: Limiting current density as a function of the concentration of oxygen in (a) nitrogen and (b) helium. Reprinted from Biesdorf et al. [98] under the terms of the Creative Commons Attribution 4.0 License (CC BY).

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Table 5.3: Ratio of the increase of the limiting current under mixtures of helium and nitrogen at two different humidification conditions.
Figure 5.10: In-plane water distribution of PEFC during (a) limiting current measurements and (b) continuous operation at full humidification. Reprinted from Biesdorf et al. [98] under the terms of the Creative Commons Attribution 4.0 License (CC BY).

Figure 5.10 shows the water distribution during (a) the limiting current experiment after water accumulation and (b) the continuous operation. At first glance, significant differences can be observed between the two sets of images. During the measurements of limiting current density, water tends to accumulate under the flow channel inside the cathode GDL. As has been identified during our previous experiments, these regions are critical with respect to bulk mass transport losses. These differences in the water distribution might be related to differences in the local current density distribution between channel and rib, which results from the highly diluted oxygen inside the carrier gas, and also to the lower average current density ($<0.3\, \text{Acm}^{-2}$). To this last point, it must be noted that experiments conducted with large current densities and higher concentrations [82] also likely result in a modified water distribution due to the important heat production at the voltages used for limiting current measurements. Consequently, the significance of limiting current measurements for real cell operation may be
5.5 Discussion

Influence of the coating on water accumulation

For pore networks with certain wettability, the capillary pressure $p_c$ can be calculated according to the Young-Laplace equation (see Equation 1.22). Consequently, a hydrophobic coating affects the capillary pressure in two ways: First, due to the increase of contact angle of the carbon fibres, the capillary pressure rises. Second, as the coating reduces the average pore diameter, the capillary pressure is further increased [216, 237]. While it seems logical that high loads of hydrophobic coating will result in increased capillary pressures, the way this impacts the water accumulation is not straightforward. At a first glance, we could deduce from the water amounts measured in Figure 5.7 (reduced water content in the cathode and increased water content in the anode) that the increase of PTFE loading to 20 wt% on the cathode results in an enhancement of back diffusion/permeation due to the increase of capillary pressure.

However, the double dead-end experiment performed originally for calibration purposes (see subsection 2.1.7) gives a further insight: in this experiment, no water removal by the gas flow occurs, which allows to observe directly the amount of water transported to the anode and cathode. The result of this experiment was that, out of 8 mg of water produced during 1 minute with a current density of 1.4 Acm$^{-2}$, 6.5 mg was transported to the cathode and 1 mg to the anode (the remaining quantity staying in the membrane area), with a negligible impact of the PTFE coating. This finding is contradictory to publications found in literature [238], where a hydrophilic coating of the anode GDL reduces the mass transport losses of a PEFC. A more likely explanation of the reduced amount of water for the GDL with 20 wt% of PTFE is given by taking into account the fact that the internal surfaces of a GDL have mixed wettability [239]. The fraction of hydrophilic pores, which will naturally tend to fill with water, will be reduced when using a large amount of coating, which will logically result in lower water content. Beside the mixed wettability, Reshetenko et al. [224] have shown by XPS measurements that even the local surface composition of $C_xF_y$ species change significantly with different coating...
5. OPERATION AT TECHNICAL OPERATING CONDITIONS

loads, resulting in an impact on water distribution and performance. Another explanation can be given by the different morphology of the water accumulation. Water accumulates as a film onto a hydrophilic surface, whereas as a droplet onto a hydrophobic surface (see Figure 5.11). As the water-air interface area is highly increased as a droplet, water uptake by evaporation and shear force is increased, resulting in a better water removal. Besides the surficial properties, the thermal characteristics change by applying a hydrophobic coating. It has been reported (38) that the thermal conductivity of the materials used during these measurements is strongly decreasing with increasing coating loads of PTFE. As has been reported by Owejan et al. [84], a GDL with a higher thermal conductivity induce smaller temperature gradients across the GDL. According to various studies [71, 240–242], temperature gradients lead to a phase-change-induced flow (heat-pipe effect) inside the GDL from CL towards the land of the flow field. This effect can be observed in the through-plane water distribution inside GDLs with a high temperature gradient (low thermal conductivity/high PTFE coating) where the water tends to accumulate closer to the flow channels compared to the cases of the uncoated GDLs.

![Figure 5.11: Schematics of the water accumulation inside a hydrophilic pore (left) and hydrophobic pore (right). Reprinted from Biesdorf et al. [98] under the terms of the Creative Commons Attribution 4.0 License (CC BY).](image)

Local water accumulations inside GDL without coating

The cell without PTFE in the cathode suffers from a strong increase of mass transport losses during the 2 hours of operation. Although the average amount of water in the cathode GDL is not increasing over time, a redistribution of water is observed, with preferential accumulations under the channels and at the edges formed by the channel walls and the GDL. This redistribution can be once again explained by the different water accumulation onto the graphite fibers of the GDLs. With a low PTFE coating load, water accumulates in form of a water film onto the fibers.
5.5 Discussion

whereas water accumulates in form of droplets in more hydrophobic GDLs (see Figure 5.11). Consequently, the surface of water is highly increased in the case of a hydrophobic GDL, resulting in a better water uptake by evaporation or drag force of the passing gas. As analyzed and explained previously [104], the regions under the channel and at the GDL/rib/channel edge are more critical with regard to mass transport, because they concentrate a higher flux of diffusive oxygen transport, which explains the massive losses observed with this cell.

In order to understand the stepwise decrease of the voltage (blue) in more detail, Figure 5.12 depicts the temporal evolution of the cell voltage correlated with its amount of water under the flow channels inside the GDL (orange) and bottom of the flow channel (green and red). The cell voltage can be clearly correlated to recurrent minima of the water thickness inside the flow channel. Although the amount of water inside this region rises up again to approximately 1.5 mm of liquid water, the cell voltage remains reduced. Regarding the water distribution inside the GDL, no correlation can be identified to the stepwise decrease. A possible explanation of the ongoing process might be the following: At the beginning of the experiment, water is accumulating as droplets on top of the GDL (see Figure 5.12). After reaching a critical cluster size, water is kept at the GDL/channel/rib interface. With our imaging configuration, this would translate in high thickness of water in direction of the beam on a very small pixel area, and in the vicinity of the gold coating of the channels. With the imaging configuration used, it is probable that such accumulations in a very concentrated image region would not be visible, which explains that the hypothesis illustrated in Figure 5.12 is only visible as droplets disappearing from the GDL/channel interface.

Influence of high levels of coating on diffusivity

Compared to water, the reactant gases (H\textsubscript{2}, Air) are transported in the opposite direction through the GDL. On the cathode side, the transport of oxygen mostly relies on diffusion in nitrogen.

According to Equation 1.20, the diffusivity is dependent on the GDL structure and saturation level of liquid water inside the gas diffusion layer and is described based on an effective diffusivity \(D_{\text{eff}}\). As has been reported in Figure 5.1, the porosity is decreased and the tortuosity is increased by the addition of a hydrophobic coating. According to a simple mass balance, the initial porosity of the GDL without coating decreases by 1.24% in the case of 5 wt% PTFE and 4.97% with 20 wt% PTFE. Although these values seem to be rather small, Hwang and Weber [243] reported that even small changes of porosity can result in a strong reduction of effective diffusivity. This influence has been clearly identified in our experiment at low humidifications, where an essential offset was measured with the cell of 20 wt% PTFE.
5. OPERATION AT TECHNICAL OPERATING CONDITIONS

Beside the change of the values for unsaturated media, the effect of water on porosity and tortuosity can depend on the coating load of the fibers (cf. illustration in Figure 5.11). As has been shown by Ziegler et al. [203], water accumulates as a film of water onto hydrophilic carbon fibers, whereas in form of droplets onto hydrophobic fibers (see schematic Figure 5.11 (a)). Consequently, identical saturation levels (identical effective porosity) may lead to significant differences of the tortuosity. As the effective diffusivity is a function of both parameters (see eq. 4), a higher sensitivity to water can be expected for highly coated GDLs. This characteristic was clearly observed in Figure 5.5, where the configuration with 20 wt% PTFE has shown the highest sensitivity to water according to the PGA analysis. Similar results were published by Lim et al. [25] who identified a higher sensitivity of the cell performance with high coating load on the stoichiometry in undersaturated operating conditions on the cathode side. The results obtained using limiting current density measurements give a complementary insight to the PGA method. The impact of PTFE loading on the diffusivity of the dry GDL is clearly shown by the reduction of limiting current between the cases with 5 wt% and 20 wt% PTFE on the cathode side. If we would assume that the water impacts the diffusivity of both materials in the same way in relative terms (which corresponds to the use of a modified Bruggeman relation [82] with the same exponent), the higher sensitivity to water of the cell with 20 wt% PTFE could be explained by the non-linearity of the overpotential as a function of oxygen concentration. Due to this non-linearity, a given relative reduction of the diffusivity has a larger impact in terms of voltage loss.

**Figure 5.12:** Temporal evolution of the cell voltage and water thickness inside the uncoated GDL. Reprinted from Biesdorf et al. [98] under the terms of the Creative Commons Attribution 4.0 License (CC BY).
if the GDL has a lower initial diffusivity. However, the relation between water accumulation and limiting current density contradicts this explanation: Although the quantity of water is smaller in the cell with 20 wt% PTFE (in particular during the limiting current measurements), the limiting current density is reduced in a larger extent for this cell. In consequence, at least a part of the increased sensitivity to water of the cell with high PTFE loading has to be attributed to a different morphology of water (cf. illustration in Figure 5.11).

**Effect of coating on CL/MPL flooding**

According to the literature [104, 107], non-bulk losses originate from diffusive transport inside small pores (Knudsen diffusion) and through the ionomer in the catalyst layer (thin film diffusion). Consequently, CL flooding is expected to be visible as an increase of the indicator of non-bulk losses, as observed for example in the case of cells without MPL on the cathode side [83]. During the experiments (see Figure 5.3 and Figure 5.6), no differences between the four cell configurations were identified. Consequently, the PTFE loading of the GDL seem to have no considerable influence on CL flooding. This has not been anticipated, as the capillary pressure of water increases with increasing coating, leading to reduced water permeation and increased accumulation at its interface. However, if we calculate the integral amount of water during the RH-Map inside the MPL (see Figure 5.8), no differences can be found between the four cell configurations. As the cells have the same MPLs with a high PTFE concentration (23 wt% PTFE) [244] and much smaller pore sizes (<100 nm) than the GDL, the capillary pressure of liquid water is expected to be much higher than inside the GDL (see Equation 1.22). Consequently, CL flooding is determined by the composition and the surface properties (e.g. cracks) of the MPL and not by the PTFE concentration of the GDL. This finding is in good agreement with ref [225] where a higher risk of CL flooding was correlated to higher coating levels of GDLs without MPL.

**Effects of coating on contact resistance**

During the experiments no significant differences of the electric resistance were identified between the four configurations. This is surprising, as the supplementary unconductive PTFE-coating should increase the contact resistance between flowfield and GDL. However, the bulk resistance of the GDL should not be increased, as the coating has been applied subsequently onto the pure carbon fibers. According to Mathias et al. [226], the contact and bulk resistance of the GDL increases by adding a hydrophobic coating. During our measurements, the ohmic losses measured include conductivity losses originating from the PFSA membrane as well as electrical bulk and contact resistance of the GDL. As the conductivity of the membrane is significantly lower compared to the values from the GDL, changes of the ohmic losses account for only a small
portion and may be hidden behind the dominating variations of the PFSA membrane. Besides this effect, the measurements in literature [207, 212, 226] were performed with Toray where this effect can be significant. SGL features a highly porous carbon binder which strongly increases the contact surface, leading to significantly lower bulk and contact resistances as compared to materials of Toray.

5.6 Summary of chapter 5

For the first time, the impact of different amounts of PTFE coatings inside the GDLs of polymer electrolyte fuel cells in terms of mass transport losses was precisely quantified using differential cells. Based on the combination of three complementary characterization techniques (neutron radiography, limiting current density, pulsed gas analysis), a detailed characterization of the local mechanisms was elaborated on state of the art materials. The combination of these three analytic methods allows the correlation of the water distributions obtained with high resolution in-plane neutron radiography to effects of bulk and non-bulk mass transport losses inside the GDL and CL. Based on the study of the polarization curves, continuous operation during 2h and asymmetric variations of the feed gas stream, the following new key findings were obtained:

- High mass transport losses do not always correlate with higher amount of water: The cell with the highest amount of PTFE has shown the lowest amount of water, although increased mass transport losses are observed. In this chapter, these losses are explained with a different morphology (film, droplet) of water accumulation.

- Mass transport losses do primarily correlate with the location of water accumulation: The amount of water inside the cathode GDL without hydrophobic coating is not increased. However, water redistributes over time inside the GDL towards the regions under the flow channel, resulting in massive mass transport losses.

- The amount of PTFE in the GDL has a minimal impact on the flooding of the MPL and of the CL.

- Operation under limiting current densities lead to significant changes of the water distribution: The neutron radiographs have identified substantial differences between the water distribution during operation under limiting current and normal operation. Nevertheless, these measurements give a very complementary insight to the pulsed gas analysis method.
Conclusions and outlook

In the present chapter, a final conclusion and outlook of the thesis is given which is structured in three parts: First, a brief overview regarding the utilization of energy selective neutron radiography to distinguish water and ice is given in section 6.1, followed by general remarks about the in-situ experiments performed at subfreezing and at technical operating conditions in section 6.2. Subsequently, the chapter is concluded with a specific outlook regarding the presented results in this PhD thesis (see section 6.3).

6.1 Summary of energy selective neutron radiography

In chapter 3, a new approach to distinguish liquid water and ice in fuel cells was presented. The distinction is based on arising differences between the neutron cross section of water and ice in the cold energy range. As a significant portion of the energy spectrum at the neutron beam lines at the Paul Scherrer Institute is in the thermal energy range, no differences can be observed with the full beam. Therefore the analysis was based on the comparison of exposures at low and high neutron energies. According to the acquisition in an interleaved fashion, a new parameter was calculated which is independent on the water thickness and molar density but relies exclusively on the aggregate state.

This new measurement concept was studied with three different energy selective neutron radiography techniques: (1) neutron filter methodology (see section 3.5), (2) time of flight technique (see section 3.6), and (3) velocity selector methodology (see section 3.7). The experiments with the neutron filter were carried out with polycrystalline beryllium as filter material. By introducing the filter inside the beam axis, neutrons above its cutoff energy are filtered out and the cold energy region is emphasized. Finally, a contrast of about 1.6% between liquid water and ice was obtained with our imaging setup. Based on the proposed measurement concept, the temporal evolution of the aggregate state of water can be investigated without any
prior knowledge of its thickness. Using this technique, the existence of supercooled water was unambiguously proven inside fuel cells with a direct measurement method for the first time.

The velocity selector filters neutrons according to their propagation speed in a narrow energy band. This technique has two major drawbacks for fuel cell applications: First the neutron flux is highly reduced compared to the neutron filter, which strongly limits its application for dynamic measurements. Second, the iteration between different neutron energies is rather slow which prohibits the measurement concept for time resolved measurements. Hence for highly dynamic studies like the water transport inside fuel cells, this technique is not suitable.

As last energy selective imaging technique, the differentiation of water and ice was investigated with the time of flight methodology. Similar to the previous technique, the neutron flux is strongly decreased, as the continuously provided neutrons are pulsed and investigations of dynamic systems are very limited. However, as a high selectivity between different neutron energies is obtained with this technique, a substantial contrast of more than 5% between water and ice was measured. However, further improvements regarding the neutron flux would make this technique highly suitable for fuel cell applications (see section 6.3).

With the current experimental setups, the best trade-off between temporal, spatial and energy resolution was obtained with the motorized neutron filter. However, with further improvements regarding the neutron flux of the time of flight technique (see section 6.3), promising results can be expected for time resolved measurements.

6.2 Summary of in situ experiments

Based on the prior knowledge of producing supercooled water at subfreezing temperatures, optimal GDL properties need to be identified (e.g. hydrophobic coating load, existence of MPL) to stabilize the supercooled aggregate state without reducing the cell performance at technical operating temperatures.

In the first step, the cold start capability was investigated on base materials with fuel cells of different size of the active area, including a large count of experiments (>200) on the 1 cm$^2$ cells to perform a statistical analysis of aggregate state transition from supercooled to frozen water. As outcome of this study, a strongly reduced cold start capability was identified with increasing size of the active area and the operating times change from stochastic values for small cells to reproducible values for large cells. Both effects were explained by a higher probability of the aggregate state transition from supercooled water to ice in large cells. Based on these experimental data, a Monte Carlo simulation was performed in order to extrapolate the experimental results obtained with the small scale fuel cell to technical systems. It turned out that fuel cells with an active area above 10 cm$^2$ cannot be run for longer than a few minutes. This
study clearly highlights that material investigations for cold starts have to be studied on small scale fuel cells.

Consequently, the effect of different GDL properties (variations of coating load and existence of MPL) at subfreezing temperatures was studied as a statistical analysis of 1200 cold starts on small scale fuel cells. It has been shown that especially at low coating loads cell-to-cell variations were more dominant than materials variations. However at high coating loads, a significant reduction of the freezing probability was observed, which was explained with a coverage of the nucleation seeds by the hydrophobic coating. In order to estimate its impact on technical systems, the dependency of the active area of fuel cells on the cold start capability was judged based on previous study and only a minor impact was observed for cells above 10 cm².

In order to judge if the GDL with high coating loads are also suitable for operation under technical operating conditions, four different combinations of PTFE-loadings on both anode and cathode were studied at 70°C. The measurements were also performed on differential PEFCs which were characterized with high resolution neutron radiography combined with two electrochemical methods: pulsed gas analysis and limiting current density measurements. Using the combination of the neutron radiographs with these two electrochemical measurements, a new insight on the impact of water on mass transport losses was obtained. Under high humidification conditions, GDLs without hydrophobic coating do not accumulate more water than coated GDLs, but the water distributes differently and accumulates in the region under the channel of the flow field. Cells with high PTFE coating show higher mass transport losses despite the relatively small quantity of water, which was explained by a different morphology of water accumulation. Hence, even if the cold start capability is slightly improved with the highly coated GDLs, a significantly reduced performance is obtained at technical operating conditions.

6.3 Outlook

In this thesis, a new imaging technique was developed to distinguish water from ice. During these measurements, the best applicability for fuel cells was obtained with the motorized neutron filter. However, several improvements can be performed to enhance the spatial and temporal resolution as well as the contrast between water and ice.

The highest potential for improvements was identified for the time of flight technique, where full energy spectra were recorded at the expense of the neutron flux. Furthermore with the current detector setup, spatial resolutions in the orders of mm were obtained which are not suitable for investigations of fuel cells (see section 3.6). Regarding the energy resolution of the TOF technique, the present precision is not required for the dual spectrum technique and could be reduced to increase the time resolution. The actual setup at the BOA beamline of PSI consists of a rotating disk with a narrow slit angle of 17° rotating with a frequency of
6. CONCLUSIONS AND OUTLOOK

20 Hz. Consequently, a redesign (e.g. with an increased number or width of the slits) can highly improve the neutron flux and thus its application for fuel cell investigations. Another possibility is to measure at a pulsed neutron source like e.g. ISIS in Oxfordshire (UK). Besides that, the spatial resolution is increased at this beamline using a new detector technology developed e.g. by Tremsin et al. [149] with pixel sizes down to 55 µm.

Regarding the neutron filter, the experimental contrast can be improved by a factor of more than 3.5 based on two modifications: First, by fully understanding the differences between the theoretical and experimental contrast with the utilized neutron filter (e.g. beam hardening, background correction, sample scattering, interference with enclosing materials), an improvement by a factor of around 2 can be reached. Second, the neutron filter can be tuned (e.g. by cooling down the filter) and another maximal improvement by a factor of 1.5 can be obtained (calculated with 0% transmission at high energies and 100% transmission at low energies).

Furthermore, several improvements can be performed regarding the limiting current density technique. As has been highlighted in this thesis, the limiting current density technique gives limited information about mass transport losses due to significant changes of the water accumulation. Hence, this methodology can be improved by adapting this concept to a pulsed limiting current technique similarly to the concept of the pulsed gas analysis. To this end, the fuel cells need to be operated in continuous potentiostatic operation. Based on short gas pulses of depleted oxygen, limiting currents can be reached depending on its oxygen concentration. Analogue to the pulsed gas analysis, the gas switch needs to be performed as pulses of 1 s in order to keep similar operating conditions (e.g. water distribution). However, this setup requires a significant modification of the current testbench infrastructure.

Regarding the in-situ experiments, various experiments are of great interest by combining the Multicell setup with neutron radiography and the pulsed gas analysis. In this thesis, experiments were exclusively performed on commercial gas-diffusion layers. However, in further experiments modified GDLs (e.g. from Forner et al. [205]) should be investigated to get a more fundamental understanding about the ongoing mechanisms during real operation. Based on these results, a redesign of the GDLs can be implemented to make these materials suitable for technical systems. Furthermore, these materials can be used at subfreezing temperatures as they can be specially adapted for stability of supercooled water which is particularly important for technical systems. Besides that, several parameters of the layers used need to be clearly understood, like e.g. the number of cracks, material composition and PTFE content.
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## Symbols, Indices and Abbreviations

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<th>Description</th>
<th>Unit</th>
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<tr>
<td>$\Delta G$</td>
<td>Gibbs free enthalpy</td>
<td>$[J \cdot mol^{-1}]$</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>Reaction enthalpy</td>
<td>$[J \cdot mol^{-1}]$</td>
</tr>
<tr>
<td>$\Delta S$</td>
<td>Reaction enthalpy</td>
<td>$[J \cdot mol^{-1} K^{-1}]$</td>
</tr>
<tr>
<td>$c$</td>
<td>Concentration</td>
<td>$[mol \cdot cm^{-3}]$</td>
</tr>
<tr>
<td>$c_p$</td>
<td>Heat capacity</td>
<td>$[JK^{-1}]$</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusivity</td>
<td>$[cm^2 \cdot s^{-1}]$</td>
</tr>
<tr>
<td>$d$</td>
<td>Pore diameter</td>
<td>$[mm], [nm]$</td>
</tr>
<tr>
<td>$d_{hkl}$</td>
<td>Lattice distance</td>
<td>$[pm]$</td>
</tr>
<tr>
<td>$e$</td>
<td>Electron</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$E$</td>
<td>Energy</td>
<td>$[J]$</td>
</tr>
<tr>
<td>$e$</td>
<td>Slit width of beam limiters</td>
<td>$[mm]$</td>
</tr>
<tr>
<td>$f$</td>
<td>Liquid fraction parameter</td>
<td>$[-]$</td>
</tr>
<tr>
<td>$I$</td>
<td>Beam intensity</td>
<td>$[a.u.]$</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
<td>$[A]$</td>
</tr>
<tr>
<td>$i$</td>
<td>Current density</td>
<td>$[A cm^{-2}]$</td>
</tr>
<tr>
<td>$i_{lim}$</td>
<td>Limiting current density</td>
<td>$[A cm^{-2}]$</td>
</tr>
<tr>
<td>$L$</td>
<td>Distance between source and sample</td>
<td>$[m]$</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass</td>
<td>$[kg]$</td>
</tr>
<tr>
<td>$\dot{m}$</td>
<td>mass flow</td>
<td>$[kg \cdot s^{-1}]$</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar mass</td>
<td>$[g \cdot mol^{-1}]$</td>
</tr>
<tr>
<td>$n$</td>
<td>Number</td>
<td>$[-]$</td>
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## SYMBOLS, INDICES AND ABBREVIATIONS

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<td>$N$</td>
<td>Molar density</td>
<td>$[\text{mol m}^{-3}]$</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure</td>
<td>$[\text{bar}]$</td>
</tr>
<tr>
<td>$P$</td>
<td>Power</td>
<td>$[\text{W}]$</td>
</tr>
<tr>
<td>$Q$</td>
<td>Charge produced</td>
<td>$[\text{C}]$</td>
</tr>
<tr>
<td>$q$</td>
<td>Heat flux</td>
<td>$[\text{W} \cdot \text{cm}^{-2}]$</td>
</tr>
<tr>
<td>$q_c$</td>
<td>Accumulated charge</td>
<td>$[\text{C}]$</td>
</tr>
<tr>
<td>$r$</td>
<td>Geometric blurring</td>
<td>$[\text{mm}]$</td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance</td>
<td>$[\Omega]$</td>
</tr>
<tr>
<td>$r$</td>
<td>Resistivity</td>
<td>$[\Omega \cdot \text{cm}^2]$</td>
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<tr>
<td>$RH$</td>
<td>Relative humidity</td>
<td>$[% \text{RH}]$</td>
</tr>
<tr>
<td>$s$</td>
<td>Saturation level</td>
<td>$[%]$</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>$[\text{K}, \circ \text{C}]$</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>$[\text{s}, \text{min}, \text{h}]$</td>
</tr>
<tr>
<td>$U$</td>
<td>Voltage</td>
<td>$[\text{V}]$</td>
</tr>
<tr>
<td>$v$</td>
<td>velocity</td>
<td>$[\text{m s}^{-1}]$</td>
</tr>
<tr>
<td>$\text{wt%}$</td>
<td>Weight percent</td>
<td>$[%]$</td>
</tr>
<tr>
<td>$z$</td>
<td>Number of electrons</td>
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<td>$\alpha$</td>
<td>Charge transfer coefficient</td>
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<tr>
<td>$\beta$</td>
<td>Phase angle of velocity selector</td>
<td>[°]</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Material thickness</td>
<td>[mm]</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Optical density</td>
<td>[-]</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Porosity</td>
<td>[%]</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Overpotential</td>
<td>[\text{V}]</td>
</tr>
<tr>
<td>$\eta_{\text{scint}}$</td>
<td>Conversion efficiency of scintilator</td>
<td>[-]</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelengths</td>
<td>[\text{A}]</td>
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<tr>
<td>$\lambda_{\text{hydra}}$</td>
<td>Membrane hydration</td>
<td>$[n(H_2O)/n(SO_3H)]$</td>
</tr>
<tr>
<td>$\lambda_{\text{stoeic}}$</td>
<td>Stoichiometry</td>
<td>[-]</td>
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<tr>
<td>$\lambda_{\text{surface}}$</td>
<td>Surface tension</td>
<td>$[\text{Nm}^{-1}]$</td>
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<tr>
<td>$\lambda_c$</td>
<td>Cutoff wavelengths</td>
<td>[\text{A}]</td>
</tr>
<tr>
<td>$\Sigma$</td>
<td>Macroscopic cross section</td>
<td>$[\text{mm}^{-1}]$</td>
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<tr>
<td>$\sigma$</td>
<td>Microscopic cross section</td>
<td>[barn]</td>
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<tr>
<td>$\sigma_{\text{Mem}}$</td>
<td>Membrane conductivity</td>
<td>[S m$^{-1}$]</td>
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<tr>
<td>$\tau$</td>
<td>Tortuosity</td>
<td>[%]</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Contact angle</td>
<td>[°]</td>
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<td>$\theta$</td>
<td>Grain orientation</td>
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<td>$\Omega$</td>
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<tr>
<td>$\omega$</td>
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### Constants

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<td>$F$</td>
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<td>$R$</td>
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<tr>
<td>(-)</td>
<td>Negatively charged</td>
</tr>
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<td>(+)</td>
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<tr>
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<td>Standard conditions (T=298.15K, p=1 atm)</td>
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<td>Charge Transfer</td>
</tr>
<tr>
<td>$DC$</td>
<td>Dark current</td>
</tr>
<tr>
<td>$DCOB$</td>
<td>Dark current and open beam corrected image</td>
</tr>
<tr>
<td>$DNCA$</td>
<td>Dark non-changing area</td>
</tr>
<tr>
<td>$eff$</td>
<td>Effective</td>
</tr>
<tr>
<td>$el$</td>
<td>Elastic</td>
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<td>$elec$</td>
<td>Electric</td>
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<td>$eq$</td>
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<td>$filter$</td>
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<td>$H_2O$</td>
<td>Water</td>
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<tr>
<td>$HOR$</td>
<td>Hydrogen Oxidation reaction</td>
</tr>
<tr>
<td>$ic$</td>
<td>Incoherent</td>
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<td>$ice$</td>
<td>Ice</td>
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<td>$Int$</td>
<td>Intensity corrected</td>
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<td>$ion$</td>
<td>Ionic</td>
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<tr>
<td>$Kn$</td>
<td>Knudsen diffusion</td>
</tr>
<tr>
<td>$lattent$</td>
<td>Heat release from Lattent heat</td>
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<tr>
<td>$LQ$</td>
<td>Liquid</td>
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<tr>
<td>$MTL$</td>
<td>Mass transport losses</td>
</tr>
<tr>
<td>$NCA$</td>
<td>Non-changing area</td>
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<tr>
<td>$nofilter$</td>
<td>No filter</td>
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### Symbol Description

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<tr>
<td>$\cdot_{\text{Noise}}$</td>
<td>Noise</td>
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<tr>
<td>$\cdot_{\text{non-bulk}}$</td>
<td>Non-bulk</td>
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<tr>
<td>$\cdot_{\text{nw}}$</td>
<td>Non-wetting</td>
</tr>
<tr>
<td>$\cdot_{\text{Ohm}}$</td>
<td>Ohmic</td>
</tr>
<tr>
<td>$\cdot_{\text{ORR}}$</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>$\cdot_{\text{out}}$</td>
<td>Outlet</td>
</tr>
<tr>
<td>$\cdot_{\text{oxygen}}$</td>
<td>Oxygen</td>
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<tr>
<td>$\cdot_{\text{pore}}$</td>
<td>Pore</td>
</tr>
<tr>
<td>$\cdot_{\text{r}}$</td>
<td>Reaction</td>
</tr>
<tr>
<td>$\cdot_{\text{ref}}$</td>
<td>Reference</td>
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<td>$\cdot_{\text{ref}}$</td>
<td>Reference image</td>
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<tr>
<td>$\cdot_{\text{refd}}$</td>
<td>Referenced image</td>
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<tr>
<td>$\cdot_{\text{rel}}$</td>
<td>Relative</td>
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<tr>
<td>$\cdot_{\text{rev}}$</td>
<td>Reversible</td>
</tr>
<tr>
<td>$\cdot_{\text{sbkg}}$</td>
<td>Corrected for scattered background</td>
</tr>
<tr>
<td>$\cdot_{\text{SBKG}}$</td>
<td>Scattered background</td>
</tr>
<tr>
<td>$\cdot_{\text{suc}}$</td>
<td>Suction</td>
</tr>
<tr>
<td>$\cdot_{\text{th}}$</td>
<td>Thermodynamic</td>
</tr>
<tr>
<td>$\cdot_{\text{w}}$</td>
<td>Wetting</td>
</tr>
<tr>
<td>$\cdot_{\text{water}}$</td>
<td>Water</td>
</tr>
<tr>
<td>$\cdot_{\text{wrk}}$</td>
<td>Working image</td>
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### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>1D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>BOA</td>
<td>Beamline for Neutron Optics and other Approaches</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
</tr>
<tr>
<td>CCM</td>
<td>Catalyst Coated Membrane</td>
</tr>
<tr>
<td>CL</td>
<td>Catalyst Layer</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>FF</td>
<td>Flowfield</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
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<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>HE</td>
<td>High energy</td>
</tr>
<tr>
<td>HFR</td>
<td>High frequency area resistance</td>
</tr>
<tr>
<td>HMI</td>
<td>Hahn-Meitner Institute</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen oxidation reaction</td>
</tr>
<tr>
<td>ICON</td>
<td>Imaging with Cold Neutrons</td>
</tr>
<tr>
<td>IMAT</td>
<td>Imaging and Materials Science and Engineering</td>
</tr>
<tr>
<td>ISIS</td>
<td>ISIS neutron source</td>
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<tr>
<td>JAERI</td>
<td>Japan Atomic Energy Research Institute</td>
</tr>
<tr>
<td>J-Parc</td>
<td>Japan Proton Accelerator Research Complex</td>
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<tr>
<td>KAERI</td>
<td>Korea Atomic Energy Research Institute</td>
</tr>
<tr>
<td>KURRI</td>
<td>Kyoto University Research Reactor Institute</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid-crystal display</td>
</tr>
<tr>
<td>LE</td>
<td>Low energy</td>
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<tr>
<td>LSF</td>
<td>Line spread function</td>
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<td>MFC</td>
<td>Mass flow controller</td>
</tr>
<tr>
<td>MPL</td>
<td>Micro porous layer</td>
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<tr>
<td>MRI</td>
<td>Magnetic Resonance Imaging</td>
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<tr>
<td>MTL</td>
<td>Mass transport losses</td>
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<tr>
<td>NF</td>
<td>Neutron filter</td>
</tr>
<tr>
<td>NIAG</td>
<td>Neutron Imaging and Activation Group</td>
</tr>
<tr>
<td>NIST</td>
<td>National Institute of Standards and Technology</td>
</tr>
<tr>
<td>NR</td>
<td>Neutron radiography</td>
</tr>
<tr>
<td>OB</td>
<td>Open beam</td>
</tr>
<tr>
<td>OCV</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>PC</td>
<td>Pressure controller</td>
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<tr>
<td>PEFC</td>
<td>Polymer Electrolyte Fuel Cell</td>
</tr>
<tr>
<td>PFSA</td>
<td>Perfluorosulfonic acid</td>
</tr>
<tr>
<td>PGA</td>
<td>Pulsed gas analysis</td>
</tr>
<tr>
<td>PSI</td>
<td>Paul Scherrer Institut</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
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<tr>
<td>PSU</td>
<td>Pennsylvania State University</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluorethylene</td>
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<tr>
<td>SINQ</td>
<td>Swiss Spallation Neutron Source</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal-to-noise ratio</td>
</tr>
<tr>
<td>SNS</td>
<td>Spallation Neutron Source</td>
</tr>
<tr>
<td>TOF</td>
<td>Time of flight</td>
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<tr>
<td>UC</td>
<td>University of California</td>
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<tr>
<td>VS</td>
<td>Velocity selector</td>
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</table>
Publication list

Peer reviewed papers (as author or co-author)

2016


2015


PUBLICATION LIST


2014


Peer reviewed conference proceedings


Presentations

Talks


J. Biesdorf, P. Oberholzer, T. J. Schmidt, P. Boillat, Impact of PTFE content in GDLs on PEFC performance evaluated by neutron radiography combined with pulsed helox analysis, European Hydrogen Energy Conference 2014, Seville, Spain, March 12-14

J. Biesdorf, P. Oberholzer, F. Bernauer, A. Kaestner, P. Vontobel, E.H. Lehmann, T.J. Schmidt, P. Boillat. Distinction between liquid water and ice based on dual spectrum neutron imaging, 10th Modval, Bad Boll, Germany, March 19-20, 2013,

Poster

J. Biesdorf, P. Oberholzer, F. Bernauer, A. Kaestner, P. Vontobel, E.H. Lehmann, T.J. Schmidt, P. Boillat. Distinction between liquid water and ice based on dual spectrum neutron imaging, JUM@P’13: Third Joint Users’ Meeting@PSI, Villigen, Switzerland, September 18-20, 2013,
Declaration of Self-Citation

For better readability we resigned from indicating self-citations in italic or in quotations marks. Self-citations are indicated as footnotes in the respective chapters. For further clarifications, the self-citations are listed subsequently.

Part of the text of chapter 1 was published in [28]:


JB and PS performed the experiments, JB, PS and MS processed the data, PB and JB performed the simulation, JB prepared the manuscript. TJS and PB supervised the work, evaluated and edited the manuscript.

Part of the text in chapter 2 was published in [97], [98], [245] and [246]:

**Accuracy of water quantification in fuel cells by neutron imaging**, P. Boillat, J. Biesdorf, and P. Oberholzer, Annual report 2013, Laboratory of Electrochemistry, Paul Scherrer Institut, Switzerland, page 12; doi: 10.3929/ethz-a-007047464

PB, JB and PO performed the experiments, PB processed the data and prepared the manuscript.


JB and PB performed the experiments, JB wrote the manuscript, AFQ assisted in data interpretation and manuscript evaluation, PB and TJS supervised the work, evaluated and edited the manuscript.


JB and PB performed the experiments, JB wrote the manuscript, AFQ assisted in data interpretation and manuscript evaluation, PB and TJS supervised the work, evaluated and edited the manuscript.
DECLARATION OF SELF-CITATION

Reproducibility of performance and water distribution of small scale differential fuel cells,
J. Biesdorf, P. Oberholzer, T. J. Schmidt, P. Boillat, Annual report 2013, Laboratory of Electrochemistry, Paul Scherrer Institut, Switzerland, page 16-17; doi: 10.3929/ethz-a-007047464
JB and PB performed the experiments, JB wrote the manuscript, PO assisted in data interpretation and manuscript evaluation, PB and TJS supervised the work, evaluated and edited the manuscript.

Part of the text of chapter 3 was published in [42] and [123]:

Dual Spectrum Neutron Radiography: Identification of Phase Transitions between Frozen and Liquid Water,
JB, PO, PB performed the experiments. JB wrote the manuscript, JB performed image processing, FB motorized the neutron filter, all authors assisted in data interpretation, PB and TJS supervised the work, evaluated and edited the manuscript.

Distinction of Liquid Water and Ice Based on Dual Spectrum Neutron Imaging,
JB, PO, PB performed the experiments. JB and PB wrote the manuscript, JB performed image processing, FB motorized the neutron filter, all authors assisted in data interpretation, PB and TJS supervised the work, evaluated and edited the manuscript.

Part of Chapter 4 was published in [28] and parts were submitted to the Journal of Electrochemical Society:

When Size Matters: Active Area Dependence of PEFC Cold Start Capability,
JB and PS performed the experiments, JB, PS and MS processed the data, PB and JB performed the simulation, JB prepared the manuscript. TJS and PB supervised the work, evaluated and edited the manuscript.

Parametric study of diffusion layer properties on cold start capability of PEFCs,
JB and MS performed the experiments, JB and MS processed the data, AFC assisted in data interpretation and manuscript evaluation, JB prepared the manuscript. TJS and PB supervised the work, evaluated and edited the manuscript.
Part of chapter 5 was published in [98] and [105]:

**Impact of Hydrophobic Coating on Mass Transport Losses in PEFCs,**

JB and PB performed the experiments, JB wrote the manuscript, AFQ assisted in data interpretation and manuscript evaluation, PB and TJS supervised the work, evaluated and edited the manuscript.

**Influence of Hydrophobic Coating of Gas Diffusion Layers on the Performance and Water Transport inside PEFC,**

JB and PB performed the experiments, JB wrote the manuscript, PO assisted in data interpretation and manuscript evaluation, PB and TJS supervised the work, evaluated and edited the manuscript.
DECLARATION OF SELF-CITATION
Curriculum Vitae

Personal information

Name: Johannes Biesdorf  
Date of birth: May 29th 1988  
Place of birth: Trier (Germany)  
Nationality: German

Education

2012 - 2016 Swiss Federal Institute of Technology Zürich  
Doctoral Thesis  
Title of the thesis: Neutron radiography of Polymer Electrolyte Fuel cells: From conventional towards energy selective neutron imaging

2009 - 2012 École Nationale d’Ingénieurs de Metz (France)  
MSc in Mechanical Engineering

2007 - 2012 Technical University of Kaiserslautern (Germany)  
MSc in Mechanical Engineering  
Title of the master thesis: Influence of air contaminants on planar, self-breathing hydrogen PEM fuel cells in an outdoor environment

1998 - 2007 Humbold Gymnasium Trier (Germany)