INTERFACIAL MORPHOLOGY AND CONTACT RESISTANCE BETWEEN THE CATALYST AND MICRO POROUS LAYERS IN PROTON EXCHANGE MEMBRANE FUEL CELLS

by

Sebastian Prass
B.Sc. Fachhochschule (University of Applied Science) Bingen am Rhein, 2013

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

The Faculty of Graduate and Postdoctoral Studies
(Mechanical Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

April 2016

© Sebastian Prass, 2016
Abstract

The interface between the catalyst layer (CL) and the micro porous layer (MPL) in proton exchange membrane fuel cells (PEMFCs) has been studied in ex-situ experiments. The interfacial morphology, specifically the area, origin and dimensions of interfacial gaps in between compressed CLs and MPLs were investigated with high-resolution X-ray micro computed tomography. In a separate experiment, the electric contact resistance (CR) was evaluated using a custom four-point-probe setup for CLs with different compositions as a function of compression pressure and relative humidity (RH).

The interfacial gap area (fraction of the interface separated by gaps) was higher for gas diffusion layers (GDL, with MPL) – catalyst coated membrane (CCM) assemblies with large differences in the surface roughness of the CL and MPL. The interfacial gap area decreased with increasing compression and with increased similarity in roughness. Relatively large continuous gaps were found in proximity of specific cracks in the MPL. These are hypothesized to form due to the presence of large pores on the surface of the GDL, in which the MPL sags and cracks. Relatively small gaps form by means of the regular surface roughness features throughout the CL-MPL interface. Smaller pores on the GDL surface serving as substrate for the MPL could reduce the number of MPL crack-induced gaps. Moreover, adjusting the CL and MPL surface roughness parameters to achieve similar orders of roughness can result in fewer enclosed gaps, and therefore, enhance the mating characteristics.

The electric CR followed a similar trend for all the CL compositions, featuring a non-linear decrease in resistance with the increase in the compression pressure. Moreover, the CR was also found to increase with the ionomer content in the CL and with the increase in RH. Physical characterization of the CL surfaces revealed that this increase in the ionomer content enhances the surface roughness features and the surface coverage by the ionomer, both of which affecting the electrical CR towards the MPL. With increasing RH, the CR values doubled for all CL compositions as a result of humidity induced ionomer swelling with the uptake of water.
Preface

This thesis contains materials that have been published or are in press.

Section 2.1 to 2.3 and 3.1 to 3.3 are excerpts of a paper accepted for publication by the *Journal of Power Sources* in 2016. The author of this thesis was the principle author of all text in the aforementioned section, with minor editing by other authors of the published work namely Dr. Pradeep Kumar Sow, Dr. Walter Mérida and Dr. André Phillion. The author fabricated the samples, processed the data and prepared the manuscript, while Sadegh Hasanpour operated the computed tomography apparatus.

Section 2.1, 2.4, 3.4 and 3.5 are excerpts of a paper submitted to a Journal, which is to be published in 2016. The author of this thesis was the principle author of all text in the aforementioned section, with minor editing by other authors of the published work namely Dr. Pradeep Kumar Sow and Dr. Walter Mérida.
# Table of contents

Abstract .............................................................................................................................................. ii

Preface ................................................................................................................................................ iii

Table of contents .............................................................................................................................. iv

List of tables ....................................................................................................................................... vi

List of figures ....................................................................................................................................... vii

Nomenclature ...................................................................................................................................... x

Acknowledgements ............................................................................................................................ xi

1. Introduction ................................................................................................................................... 1

1.1 PEMFC functionality and components .................................................................................. 1

1.2 PEMFC assembly ..................................................................................................................... 3

1.3 Effect of the CL-MPL interface on the PEMFC performance ............................................. 4

1.4 Literature review ...................................................................................................................... 6

1.4.1 Interface morphology between the CL and MPL of a compressed GDL-CCM assembly ..... 6

1.4.2 Electric contact resistance at the CL-MPL interface ......................................................... 6

1.5 Contribution of this work on the CL-MPL interface advancement ........................................ 7

2. Experimental methods ................................................................................................................ 9

2.1 Materials and sample preparation ........................................................................................... 9

2.2 Surface profilometry, SEM imaging and EDX analysis .......................................................... 11

2.2.1 Scanning electron microscopy – energy dispersive X-ray analysis .................................... 11

2.2.2 Optical profilometry ......................................................................................................... 11

2.2.3 X-ray micro-computed tomography .................................................................................. 12

2.3 X-μCT investigation of interfacial morphology .................................................................... 12

2.3.1 GDL-CCM assembly preparation ....................................................................................... 12

2.3.2 X-μCT scanning procedure ............................................................................................... 13

2.3.3 Image processing and analysis ............................................................................................ 15
2.4 Electric contact resistance at the CL-MPL interface ............................................. 17

3. Results and discussion .............................................................................................. 20
   3.1 Surface roughness and structure of the MPL and CL samples............................... 20
   3.2 X-µCT investigation of interfacial morphology ...................................................... 23
      3.2.1 Origin and area of interfacial gaps ................................................................. 23
      3.2.2 Roundup ........................................................................................................ 26
   3.3 Electric contact resistance ...................................................................................... 28
      3.3.1 Effect of compression pressure and CL composition ...................................... 28
      3.3.2 Effect of relative humidity and CL composition ............................................. 32
      3.3.3 Roundup ........................................................................................................ 35

4. Conclusions ................................................................................................................. 36
   4.1 Future work ........................................................................................................... 37

References ...................................................................................................................... 39
List of tables

Table 1-1: Experimental and modelling studies on the electric CL-MPL CR .................................................. 6

Table 3-1: Average surface roughness $R_a$ of the CLs and the MPL of the GDL ........................................... 22

Table 3-2: Fluorine content of the CL surface asperities obtained by SEM-EDX ............................................. 30
List of figures

Figure 1-1 Illustration of the PEMFC components and function ............................................................... 2

Figure 1-2: Fabrication and assembly of the components (CCM and GDLs with MPLs) to the 5-layer membrane electrode assembly (MEA) .................................................................................................................. 3

Figure 1-3: Cross-sectional image of the 5-layer MEA taken by scanning electron microscope (SEM) in back-scattered electron (BSE) mode (the GDL and MPL are usually referred to as GDL) ....................... 4

Figure 1-4: Illustration of the CL-MPL interface at increasing magnification ........................................... 4

Figure 1-5: Thesis structure overview ...................................................................................................... 8

Figure 2-1: CL fabrication onto a) different substrates via b) spray coating of the CL inks on the substrates, c) finished CLs on Nafion PEM and GCC disk ..................................................................................... 9

Figure 2-2: Schematic of a surface profile, the arithmetic roughness is the average height variation of \( y_i \) per sample interval \( l \) .................................................................................................................. 12

Figure 2-3: Schematic of X-\( \mu \)CT technology, the detector measures the attenuation of X-rays penetrating through the sample to generate cross-sectional images .................................................................. 12

Figure 2-4: Illustration of the clamping setup compressing the GDL-CCM assembly ............................... 13

Figure 2-5: Pore size distributions of the CL, MPL, GDL and the interfacial gaps \( ^{26,32,46} \) ........................... 14

Figure 2-6: Processing steps of the cross-sectional images showing the GDL-CCM assembly in the clamping setup with a) the original image, b) cropped to the CL-MPL-interfacial region showing the CL, a part of the MPL and membrane after enhancing the contrast, c) after application of the 3D-median filter and the threshold function, d) reconstructed 3D dataset ........................................................................ 15

Figure 2-7: Image analysis starting from a) section of a segmented 3D dataset, b) its projection in through-plane direction, c) binarized projection (for \( A_{\text{void}} \)) and d) cross-section of the MPL showing only cracks (for \( A_{\text{crack}} \)) ........................................................................................................................................ 16
Figure 2-8: a) the 4PP setup in a climate chamber, b) an illustration of the main components, the four sensing probes are placed at each of the planes (A, B, C, D), c) the current forcing electrode with the circular micro sensing probe in the center ................................................................. 17

Figure 3-1: SEM images of the CL surfaces at magnifications of 200x and 2000x and the MPL surface at 100x and 1000x .................................................................................................................. 20

Figure 3-2: Images and statistical data of the CL and MPL surfaces obtained by optical profilometry ..... 21

Figure 3-3: SEM images of the surface irregularities as a) fine cracks and b) dents and holes in the MPL22

Figure 3-4: In-plane cross-sections of the reconstructed 3D dataset through a) the transition region from fibrous GDL to the MPL and b) the MPL with cracks and gaps at the CL-MPL interface in dark grey tones.

Part c) shows the interfacial gaps induced by cracks in the MPL (1), cracks in the MPL without surrounding gaps (2) and gaps induced by the surface roughness of the layers (3) ......................... 23

Figure 3-5: Interfacial gap (1) induced by a crack in the MPL (2) with the underlying CL (3) shown in light grey tones, a) top- and b) side-view, c) the 3D volume ........................................................................................................... 24

Figure 3-6: Surface roughness induced interfacial gap (1) on the CL (2) in light grey tones, a) top- and b) side-view, c) the 3D volume .................................................................................................................. 25

Figure 3-7: Interfacial gap area $A_{\text{gap}}$ and areal crack density $A_{\text{crack}}$ at both compressions of 30% and 50% and the relative difference between the roughness parameters $R_s$ of CL and MPL per CL composition, the insets illustrate the effect of increasing similarity between the roughness of CL and MPL ......................... 25

Figure 3-8: $R_{\text{C(CL-MPL)}}$ as a function of the compression pressure for the three CL compositions (I/C = 0.3, 0.6 and 0.9) at 20% RH ..................................................................................................................................... 29

Figure 3-9: SEM images showing the CL surface morphologies with varying ionomer content. Spot A and Spot B in the images correspond to the peaks and valleys on the CL surfaces used for EDX mapping ..... 30
Figure 3-10: CR between CL 1 and the MPL (RH = 50%) at increasing compression, and the interfacial gap area at 1.7 and 4.1 N·mm⁻². The insets show the projections of the 3D datasets at the particular pressure, from which the gap area was calculated. .............................................................................................................................................. 31

Figure 3-11: Experimental results for the effect of RH on \( R_{C(CL-MPL)} \) for a) CL 1 and b) \( R_{C(CL-MPL)} \) at a compression pressure of 1 N·mm⁻² for the three CL at varying RH from 20 to 80% ........................................... 33

Figure 3-12: Comparison of \( R_{C(CL-MPL)} \) to experimental studies on the CR between the CL and diffusion media reported in the literature⁷¹,³⁷ .............................................................................................................................................. 34
## Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_a$</td>
<td>Average roughness parameter</td>
<td>μm</td>
</tr>
<tr>
<td>$R_{a,CL}$</td>
<td>Average roughness parameter of catalyst layer</td>
<td>μm</td>
</tr>
<tr>
<td>$R_{a,MPL}$</td>
<td>Average roughness parameter of micro porous layer</td>
<td>μm</td>
</tr>
<tr>
<td>$\Delta R_a$</td>
<td>Difference between roughness parameters</td>
<td>μm</td>
</tr>
<tr>
<td>$A_{void}$</td>
<td>Void area (gaps and cracks) per interfacial area</td>
<td>%</td>
</tr>
<tr>
<td>$A_{gap}$</td>
<td>Gap area per interfacial area</td>
<td>%</td>
</tr>
<tr>
<td>$A_{crack}$</td>
<td>Crack area per interfacial area</td>
<td>%</td>
</tr>
<tr>
<td>$R_{GDL/MPL-CL/GCC}$</td>
<td>Area specific resistance of gas diffusion layer – catalyst coated</td>
<td>mΩ·cm²</td>
</tr>
<tr>
<td>$R_{GDL/MPL}$</td>
<td>Area specific resistance of gas diffusion layer including micro porous layer</td>
<td>mΩ·cm²</td>
</tr>
<tr>
<td>$R_{CL/GCC}$</td>
<td>Area specific resistance of catalyst layer on gold-coated copper disk</td>
<td>mΩ·cm²</td>
</tr>
<tr>
<td>$R_{C(CL-MPL)}$</td>
<td>Contact resistance between catalyst and micro porous layer</td>
<td>mΩ·cm²</td>
</tr>
</tbody>
</table>

### Acronym

- **4PP**: Four point probe
- **CCM**: Catalyst coated membrane
- **CL**: Catalyst layer
- **CR**: Contact resistance
- **EDX**: Energy dispersive X-ray
- **GCC**: Gold-coated copper
- **GDL**: Gas diffusion layer
- **I/C**: Ionomer/carbon
- **MEA**: Membrane electrode assembly
- **MPL**: Micro porous layer
- **PEMFC**: Proton exchange membrane fuel cell
- **PFSA**: Perfluorosulfonic acid
- **Pt**: Platinum
- **PTFE**: Polytetrafluorine
- **RH**: Relative humidity
- **SEM**: Scanning electron microscope
- **X-μCT**: X-ray micro-computed tomography
Acknowledgements

There are many people from whom I benefitted a great deal during my time at the UBC. I would like to take this opportunity to thank my supervisor Prof. Walter Mérida from the Department of Mechanical Engineering for his guidance in preparing certain sections into becoming manuscripts for journal articles, and his support throughout my MASc program.

My colleagues have always been very friendly and helpful, and I gained technical knowledge, workplace experience as well as friendships from all the guys. Dr. Pradeep Kumar Sow, with whom I had numerous very interesting and enlightening discussions, has put me on track and I benefited a lot from his knowledge.

Dr. André Phillion and Sadegh Hasanpour, assistant professor and MASc candidate at the School of Engineering, UBC Okanagan, were of immense value for taking the time to conduct the X-μCT measurements with samples I provided and for their help during the manuscript editing.

Finally, my study is backed unconditionally by my family in Germany, who pushed me forward when I lacked energy, almost without a single complaint of my lack of accompany. I am proud to receive their love and care and that what I have achieved can make them proud in return.
1. Introduction

This work presents the results of ex-situ experimental studies on the interface between two seminal layers in the proton exchange membrane fuel cell (PEMFC), namely the catalyst layer (CL) and the microporous layer (MPL). The research focussed on the formation of interfacial gaps and the electric contact resistance, and is motivated by the need to understand the interaction of these layers. A better understanding of the mating characteristics between CL and MPL can help to find possible ways to reduce the impact of the interface on the performance of the PEMFC and, hence, enable a more cost-efficient use of materials.

1.1 PEMFC functionality and components

Similar to William Grove’s gas battery, the first reference of a crude fuel cell in 1838, modern PEMFCs enable the conversion of chemical energy stored in Hydrogen and Oxygen into electric energy and water. A PEMFC consists of an electrolyte enclosed by a pair of electrodes, which are continuously supplied with Hydrogen and Oxygen reactants\(^1\). At the anodic electrode, Hydrogen is split into protons and electrons, which combine at the cathodic electrode with Oxygen to form water. The half-cell and overall reactions are as follows:

\[
\text{Anode: } \quad H_2 \rightarrow 2H^+ + 2e^- \quad (1.1)
\]

\[
\text{Cathode: } \quad O + 2H^+ + 2e^- \rightarrow H_2O \quad (1.2)
\]

\[
\text{Cell: } \quad 2H_2 + O_2 \rightarrow 2H_2O \quad (1.3)
\]

The electrolyte allows only protons to conduct from anode to cathode, whereas the electrons are conducted through an external load and thereby perform work as illustrated in Figure 1-1.
The reactions as well as the mass and energy transport occur in an assembly of components, where each component fulfils multiple functions\(^1\). The proton exchange membrane (PEM) acts as electrolyte conducting the protons between the thin CLs (~1 – 20 µm)\(^2\) and similarly separates the reactant gases. The porous CLs are deposited onto the PEM and thereby form the catalyst coated membrane (CCM). In the CLs, the catalyst nanoparticles (usually Platinum) supported on carbon particles (~20 – 50 nm), provide the electrochemically active sites for the reactions. The carbon supported catalysts are dispersed in an ionomer matrix, which provides the pathways for the protonic conduction to these sites. The pores in the CL enable the diffusion of reactants and products to and from reaction sites, while the carbon backbone conducts electrons. In contact to the CL is the MPL (50 – 100 µm)\(^3\), which is typically attached to the GDL (100 – 300 µm)\(^4\). The MPL is usually added as it has shown to enhance the PEMFC performance by reducing the electric and thermal contact resistances and improving the water management in the electrode\(^5\)\(^\text{-7}\). The MPL commonly consists of carbon particles impregnated with PTFE as a hydrophobic agent and binder, whereas the GDL is made from carbon fibres. These fibres are also often coated with PTFE to improve the water management in the cell. Both, MPL and GDL, act as conduits for electric and thermal energy, while their pores enable the diffusion of reactants and products to and from the CLs. The bipolar-plates on either side of the PEMFC distribute gases roughly, provide mechanical stability and serve as electric current collectors.

---

**Figure 1-1 Illustration of the PEMFC components and function**
1.2 PEMFC assembly

Several ways to fabricate and assemble the components and the PEMFC are reported in the research literature\textsuperscript{3}. However, the following section describes the most commonly used method, which is increasingly applied for large-scale manufacture. The components, CCM and GDL including the MPL, are fabricated individually and then assembled from sheet or roll-good materials to form the so called 5-layer membrane electrode assembly (MEA)\textsuperscript{3}. The general procedure is shown in Figure 1-2:

![Figure 1-2: Fabrication and assembly of the components (CCM and GDLs with MPLs) to the 5-layer membrane electrode assembly (MEA)](image)

The GDL basically consists of graphitized polymeric fibres (where volatile components were evaporated and predominantly carbon remains), which are woven or spun to form a thin paper-like sheet, and is commonly treated with PTFE as hydrophobic agent. Subsequently, the MPL is deposited onto the GDL in form of a highly viscous ink containing carbon and PTFE particles mixed in solvents. During the drying process, the solvents evaporate, the MPL adheres to the GDL fibres and the GDL/MPL material remains\textsuperscript{3}. The PEM on the other hand is a thin polymeric sheet. Although various PEM materials exist, Nafion\textsuperscript{®} remains the most commonly used material, which generally consists of a thin sheet of sulfonated PTFE\textsuperscript{8}. The PEM is conventionally coated with the CLs on either side resulting in the catalyst coated membrane (CCM). These sheets, the GDL/MPL materials and the CCM, are cut into the required size, positioned accordingly and finally (hot-)pressed to improve the adhesion between the CL and the MPL\textsuperscript{9}. The result is the 5-layer MEA as shown in Figure 1-3.
During this process, the CL-MPL interface develops, which has been found to affect the PEMFC performance by inducing sources of resistances\(^1\). On industrial scale, this assembly is done increasingly in ‘roll-to-roll’ processes, where the components are merged from roll-good materials. Roll-to-roll processes enable a reduction in manufacturing costs per unit and enhancements in quality control by shifting from batch- to roll processes\(^2,10,11\). The faster 5-layer MEA assembly inherently comes therein with less time to adhere the CL to the MPL, which amplifies the need for enhancements in the mating characteristics between the CL and MPL.

### 1.3 Effect of the CL-MPL interface on the PEMFC performance

The interface between the CL and MPL affects the performance of PEMFCs\(^1\), as it has been simulated in numerous modelling studies\(^12–16\). Ohmic, thermal and diffusional resistances arising at the interface affect the energy and mass transport during the PEMFC operation. These resistances arise due to material properties of the components and the morphology\(^17,18\), and due to liquid water formation in voids between the CL and MPL\(^19,20\) as illustrated in Figure 1-4.

Gaps between the CL and MPL along with cracks in the MPL were identified as water pooling regions, which can affect the reactant and product mass transport\(^14,21\). This accumulated water can reduce the limiting current density up to 20%\(^16\). Moreover, the liquid water can also amplify delamination effects of
the CL from the MPL during freeze-thaw cycles\textsuperscript{12,20}, which further disrupt the PEMFC performance. Ideally, the MPL surface adjusts to the CL surface excluding such gaps, however, these layers are rough and inherently enclose voids even after compression\textsuperscript{15}. When superimposing the surface profiles from the CL and MPL in modelling studies, the separation between the surface planes was found to account for up to 5 – 10 μm. The resulting void volume can accumulate 6 – 18% of the total liquid water in a PEMFC\textsuperscript{19}. A reduction of the surface roughness of the CL and MPL is expected to reduce this separation and, hence, the amount of accumulating liquid water\textsuperscript{19}. These interfacial gaps decrease the number of conductive pathways available for the electron transport through the carbon particles across the interface and thereby enhance the electric contact resistance (CR). Electrically non-conductive ionomer in the CL, and PTFE in the MPL obstruct the transport of electric energy and further amplify the resistances between these layers\textsuperscript{15,16,22}. In addition, the seminal hydration of the ionomer enabling the protonic conduction leads to a volumetric expansion of the ionomer\textsuperscript{23}, which affects the connectivity between the carbon particles in the CL\textsuperscript{24}. These properties usually measured in in-plane direction are expected to affect the CR in the through-plane direction. An increase in the compression pressure can reduce the electric and thermal CRs as well as the volume of the gaps at the CL-MPL interface\textsuperscript{15}, but it opposes the reduction in the porosity and thereby increases the mass transport resistances through the porous CL, MPL and GDL\textsuperscript{3}. Hence, an optimum compression is required to minimize electric and thermal resistances across the interface, while preserving a sufficiently open pore structure of the porous components. This complex interplay of material properties and operational parameters can result in significant resistances arising at the CL-MPL interface. Therefore, the investigation of the interfacial properties and mating characteristics can help to discover ways to reduce the impact of the interface and improve the PEMFC performance.

The research of this thesis aims on two sources for performance losses of the PEMFC correlated to the CL-MPL interface. Firstly, the interfacial morphology between the CL and MPL is investigated with a focus on the formation of interfacial gaps under compression pressure and with varying surface structures of the CL prior to the compression. Information about the morphology and gaps at the interface can be useful for improvements in the mating characteristics between the GDL/MPL and the CCM. A decrease of the amount of interfacial gaps without extensive compression during the assembly of the 5-layer MEA can enhance the performance of the PEMFC. Secondly, the electric CR as a function of compression pressure, relative humidity and the ionomer content and therefore varying surface structures of the CLs. Information about the CR and its dependencies on the PEMFC operating
conditions can be used to refine the accuracy of simulation studies on PEMFC electrodes, which usually neglect or underestimate the CL-MPL CR.

1.4 Literature review

1.4.1 Interface morphology between the CL and MPL of a compressed GDL-CCM assembly

Imperfections at the CL-MPL interface such as interfacial gaps or delamination deteriorate the PEMFC performance, as shown in the aforementioned modelling studies. All of these studies modelled the interfacial morphology from surface profile data, which was obtained by optical profilometry from fresh and uncompressed CL and MPL surfaces. From these models, the effect of the interface on the PEMFC performance was simulated. However, when the components (GDL/MPL and CCM) are stacked and compressed, the surfaces of the CL and MPL deform as carbon, PTFE and ionomer particles and agglomerates penetrate into voids and interfacial gaps. Few models included elastic deformation of the CL and MPL surfaces, however, a direct and non-destructive experimental evaluation of the interfacial morphology and the deformation of gaps can give a more accurate picture of the interface under compression. Scanning electron microscopy (SEM) imaging technology has been used to visualize existence of interfacial delamination from cross-sectional images of the PEMFC electrodes. To investigate the morphology between the CL and MPL and quantify the formation of gaps, the internal structure of the interface has to be evaluated. X-ray micro computed tomography (X-µCT) is a non-destructive technique that enables the characterization of the internal 3D microstructure of materials. In PEMFC technology, this technique has been widely used to assess the porosity distributions across different axes in GDLs, the effect of MPL cracks on the porosity and bulk porosity measurement of the GDLs and CLs. In terms of a GDL-CCM assembly including the CL-MPL interface, X-µCT has been used to compare the morphology of spray-coated and doctor-bladed CLs and to assess the relationship between compression and electrochemical activity within a fuel cell. Although X-µCT enables the direct visualization of the interfacial morphology, the technique has not yet been employed to investigate specifically interfacial gaps between the CL and MPL. Therefore, this research is the first to report the application of X-µCT technique on compressed GDL-CCM assemblies to investigate the formation of interfacial gaps.

1.4.2 Electric contact resistance at the CL-MPL interface

The electric contact resistance (CR) arising at the interface between the CL and the diffusion media (GDL with or without MPL) directly affects the PEMFC performance. However, only few experimental
attempts to evaluate the CR have been reported, which can be explained by the complexity involved in separating the contact from the bulk resistance of these not free-standing layers. An overview of the relevant studies in comparison to the research in the present thesis is given in Table 1-1.

Nitta et al.37 studied the electric CR between the CL and GDL without the MPL, and their research pointed out the significance of the electric resistance arising at the interface. The authors evaluated the CR along with other resistance contributions as a function of compression pressure in-situ in a symmetrical H₂/N₂ cell. They concluded the dominance of the CL-GDL CR among all ohmic resistance contributions in a PEMFC (50 – 60% at 1 – 1.7 N·mm⁻²) and moreover reported the non-linear decrease of the CR from 44 to 7.8 mΩ·cm² with increasing compression from 0.66 – 4.71 N·mm². They suggested the evaluation of the CR arising between the MPL in contact to the CL in a further study. The addition of the MPL to the GDL is expected to decrease the CR, as it has been shown by Ye et al.38. In this study, the in-plane bulk and contact resistances of different GDL materials (both with and without MPL) were studied in a linear resistivity setup, where the GDL/MPL is in contact to copper bars representing the electrodes. The authors reported on the effects of the addition of a MPL to GDL, but the electric resistance contributions (bulk and contact) were measured towards copper surfaces, not the CL surfaces. In contrast, the CR between the CL and the MPL was investigated by Kleemann et al.11 who employed a mixed in-plane/through-plane four-point-probe (4PP) resistivity setup to examine the relation between the mechanical properties of GDL materials (both with and without MPL) and the electric bulk and contact resistance contributions. The authors also reported the inverse relationship between compression pressure and the CL-MPL CR, ranging from 90 to 0 mΩ·cm² at compression pressures between ~0.05 and 2 N·mm⁻². However, the experimental setup required the choice of an offset to evaluate the CR, i.e. the authors assumed the CR to be 0 mΩ·cm² at highest compression pressure of 2 N·mm⁻². Therefore, the values underestimate the magnitude of the CR arising at the CL-MPL interface, which is demonstrated in the present research. Makharia et al.36 presented an estimate for the ohmic CL-MPL CR of 3.4 mΩ·cm² obtained in a non-disclosed experimental setup, which was used to validate results obtained by electrochemical impedance spectroscopy (EIS). The main emphasis of their study was placed on the evaluation of polarization losses using EIS, where the measured ohmic resistance included all ohmic contributions of the PEMFC components and their interfaces. An extended evaluation and discussion of the CR was out of scope of their research and therefore not presented.

Aside from these experimental studies, Swamy et al.18 developed an analytical model for the CL-MPL CR as a function of compression pressure. The authors used material properties and the surface
roughness profiles (obtained by optical profilometry) of the mating surfaces as input data. Their results show the non-linear decrease of the CR from 2.5 to ~1 mΩ-cm$^2$ with the increase in compression pressure from 1 to 3 N-mm$^{-2}$. Moreover, the roughness of the surfaces and the elastic modulus of the GDL were found to have a significant impact on the CR. Their study suggests that a drop of 50% in the roughness of both surfaces or the Young’s modulus of the GDL leads to a drop in the CR of 40% and 45%, respectively.

From this discussion, it is clear that the experimental evaluation and discussion of the ohmic resistance arising at the CL-MPL interface is still necessary.
<table>
<thead>
<tr>
<th>Purpose of the study</th>
<th>Makharia et al.</th>
<th>Nitta et al.</th>
<th>Kleemann et al.</th>
<th>Ye et al.</th>
<th>Swamy et al.</th>
<th>Present study</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Breakup of polarization losses in PEMFC</td>
<td>Evaluation of the CR between the CL and GDL</td>
<td>Correlation of mechanical properties with resistances of GDL materials</td>
<td>Determination of bulk and contact resistances of GDL and CL</td>
<td>Simulation of the effects of surface roughness and Young’s modulus on the CR</td>
<td>Evaluation of the CR between the CL and MPL</td>
</tr>
<tr>
<td>Approach</td>
<td>In-situ beginning of life (BOL) and non-disclosed measurements for validation</td>
<td>In-situ BOL measurements</td>
<td>Ex-situ measurements</td>
<td>Ex-situ measurements</td>
<td>Analytical model</td>
<td>Ex-situ measurements</td>
</tr>
<tr>
<td>CL/MPL</td>
<td>Y/Y</td>
<td>Y/N</td>
<td>Y/Y</td>
<td>N/Y</td>
<td>Y/Y</td>
<td>Y/Y</td>
</tr>
<tr>
<td>Electrical resistance measurements</td>
<td>EIS and non-disclosed setup</td>
<td>EIS</td>
<td>Mixed in-plane/trough plane 4PP</td>
<td>In-plane 4PP</td>
<td>Through-plane 4PP</td>
<td></td>
</tr>
<tr>
<td>GDL/MPL material</td>
<td>PTFE treated Toray paper (proprietary treatment)</td>
<td>SGL Sigracet® 10BA</td>
<td>Toray TGP-H-060, non-specified roll goods</td>
<td>Toray TGP-H-120, wet-proofed carbon cloth, MPL with 20% PTFE</td>
<td>SGL Sigracet® 25BC</td>
<td></td>
</tr>
<tr>
<td>CL/MEA</td>
<td>Custom CLs (ionomer/carbon I/C = 0.4 and 0.8)</td>
<td>Gore Primea® Series 5510</td>
<td>Non-specified MEA</td>
<td>Pure carbon particle pseudo-CL</td>
<td>Custom CLs (I/C = 0.3, 0.6 and 0.9)</td>
<td></td>
</tr>
<tr>
<td>Compression pressure</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
<td>N</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>Y</td>
</tr>
<tr>
<td>CR (mΩ·cm²)</td>
<td>3.4</td>
<td>8 - 44</td>
<td>0 - &gt;100</td>
<td>-</td>
<td>0.5 – 3.5</td>
<td>2.5 – 62</td>
</tr>
</tbody>
</table>
1.5 Contribution of this work on the CL-MPL interface advancement

This research investigates two of the sources for performance losses correlated to the CL-MPL interface – the interfacial morphology and the electric CR between the CL and the MPL.

1. X-μCT is employed to obtain 3D datasets of compressed CCMs and GDLs to study the interfacial morphology between the CL and MPL. Specifically, the formation of interfacial gaps between the layers as a function of compression and surface roughness of the CL were studied. The origin and dimension of gaps and the interfacial gap area (fraction of the interface separated by gaps) were studied and quantified. Scanning electron microscopy (SEM), energy dispersive X-ray technique (EDX) and optical profilometry were also used to characterize these materials and to link the compressed structure to the underlying material characteristics. The results provide additional insights into the interfacial morphology between the CL and MPL and point towards pathways to improve the mating characteristics between these two components in the 5-layer MEA assembly.

2. In a separate experiment, the CR is investigated at different operational conditions (relative humidity and compression pressure) for CLs with different ionomer contents in contact to the MPL of a commercial GDL. The CR is evaluated in a custom 4PP ex-situ experimental setup, which allows the deconvolution of the resistance contributions by applying a measurement protocol formulated in this study. In contrast to previous studies on the CL-MPL CR, this study reports as a novelty the fully separated CR values of CLs with different compositions as a function of compression pressure and relative humidity (RH).

Figure 1-2 presents an overview of the content in this thesis. The two experimental modules are part of publications submitted to journals.
Figure 1-5: Thesis structure overview
2. **Experimental methods**

This section details the sample preparation, the choice of carrier substrates for the CLs and the used physical characterization tools. The image processing and analysis steps of the cross-sectional images obtained by X-\(\mu\)CT technique are presented and the experimental setup used for the electric resistance measurements is described.

2.1 **Materials and sample preparation**

A CCM is commonly fabricated by depositing layers of colloidal CL ink onto a PEM using techniques such as (electro-) spray-coating\(^{39,40}\), decal transfer method\(^{41,42}\) or screen printing\(^3,43\). The coating process is followed by heat treatment and eventually hot-pressing, during which the solvent is evaporated and the adhesion of the CL to the membrane is improved\(^{42}\).

For this research, three different CLs with increasing ionomer/carbon (I/C) ratios of 0.3, 0.6 and 0.9 were prepared, as these ratios are in the commonly used ranges of ionomer content in the CLs. As both studies (interfacial morphology and electric CR evaluations) were done in different experimental setups, different base substrates for the CL deposition were required. Figure 2-1 shows the substrates, the spray-coating process and the finished CL samples on the different substrates.

![Figure 2-1: CL fabrication onto a) different substrates via b) spray coating of the CL inks on the substrates, c) finished CLs on Nafion PEM and GCC disk](image)

For the CR measurements, the CLs were deposited on conductive gold-coated copper (GCC) disks. Ideally, the CR should be measured with the current lines being perpendicular to the interface in the through-plane direction, which is difficult to achieve for a CL supported on a membrane. The solid GCC disks as substrates for the CLs prevented any structural damages due to handling of the layers, while simultaneously providing the necessary through-plane conductivity for the measurements. For the
interfacial morphology evaluations, the CLs were deposited on a Nafion® 117 PEM (purchased from Fuel Cell Store). The lower density of the membrane as compared to metallic substrates allowed a better differentiation of the materials on the cross-sectional images generated by the X-ray μCT technique. Both experiments, the CR and the interfacial morphology evaluations, were done in contact to the MPL of a Sigracet® 25BC GDL (purchased from Ion Power).

Two of the deposition methods were tested in the course of this thesis: the thin-film application via a doctor-blade and the spray-coating of the CLs directly on the carrier substrates. One of the major differences between the application methods was the control over the thickness of the deposited CL. The doctor-blade enabled a precise adjustment of the CL thickness, whereas it only could be measured indirectly during or subsequent to the spray-coating process via techniques such as SEM or optical profilometry. However, the trials to apply thin CLs using a doctor-blade on the carrier substrates or on a PTFE sheet for a subsequent decal transfer did not result in CLs with satisfactory consistency and quality. The applied CL inks formed large droplets and an irregular dispersion of the CL ingredients depending on the ink viscosity. Furthermore, large cracks and flakes developed in the CLs during the solvent evaporation, which can be explained by the poor adhesion of the ink to the gold coating on the carrier substrates used for the CR measurements. In contrast, the relatively slow and gradual application via spray-coating resulted in CLs with relatively homogeneous consistency without flake or crack formation, but with differences in the CL thickness. Variations in the CL thickness are commonly used to control the amount of catalyst in the CL and hence the electrochemical active surface area. However, the interface between the CL and MPL is predominantly affected by the surface structures as compared to the layer thickness. Therefore, the application via spray-coating was chosen to fabricate the CL samples for this thesis. The three CLs with different ionomer/carbon (I/C) ratios and surface structures were fabricated by spray-coating the CL inks simultaneously onto two different substrates without a subsequent hot-pressing step. During the hot-pressing procedure, the adhesion of the CL to the PEM is improved by applying compression pressure at elevated temperatures onto the CCM using PTFE blanks. Again, since the surface structures of the CLs are predominantly affecting the interfacial morphology, the hot-pressing was not required. For the CL inks, commercially available Cabot Vulcan® XC72R carbon powder (purchased from Fuel Cell Store), LIQUion® solution LQ-1105 containing 5% NAFION® (1100 EW) by weight (from Ion Power) were mixed with isopropanol (from Fisher Scientific) and de-ionized water as solvents. The amounts of the ingredients were determined by weight, mixed and subsequently ultrasonicated for 3 hours to assure proper dispersion of the particles in the ink. During the spray-
coating process, the base substrates were fixed on a heating plate at a temperature of 80°C, while the ink was deposited in multiple layers to facilitate the solvent evaporation.

2.2 Surface profilometry, SEM imaging and EDX analysis

2.2.1 Scanning electron microscopy – energy dispersive X-ray analysis
The macroscopic structure and chemical composition of the MPL of the GDL and the CLs were studied using scanning electron microscopy (SEM, Hitachi SU 3500) and energy dispersive X-ray analysis (EDX, Helios NanoLab 650 Focussed Ion Beam SEM). EDX analysis enables elemental mapping of a sample surface by stimulating the emission of characteristic X-rays of a specimen. Therefore, the sample surface is targeted with a high energy beam of charged particles (electrons or protons). These particles excite electrons in the shells of an atom. When an electron of an inner shell is excited, the resulting hole is occupied from an electron of the higher energy outer shell, and the difference in energy is emitted in form of characteristic X-rays. EDX allows elemental mapping of distinct locations on the sample surface, and in the present study it was used to compare the distribution of ionomer on the CL surfaces. Since Fluorine is a characteristic component of the ionomer, its content is used as a representative for the ionomer content in the surface asperities of the CLs.

2.2.2 Optical profilometry
Moreover, the surface roughness of the MPL and the three fabricated CLs were evaluated by optical profilometry (WYKO NT1100 optical profilometer). Interferometry optical profilers measure height variations of surfaces using the wavelength of light as a ruler. Generally, these height variations are measured as optical path differences between the sample surface and a reference surface. Inside a profilometer, light is split by a beam splitter. Half of the light is passing through the focal plane of a microscope, while the other half is reflected by a reference mirror. Interference of the beams occurs at distinct wavelengths, which can be detected by a digital camera as light or dark fringes. From this data, surface profiles can be reconstructed, which are used to evaluate amplitude and statistical surface parameters. In the present study, the arithmetic roughness $R_a$ was evaluated as a means to compare the surface roughness between the CLs and the MPL. From a surface profile such as illustrated in Figure 2-2, $R_a$ is calculated as the average deviation of the profile height $y$ from the mean line.
2.2.3 X-ray micro-computed tomography

The internal microstructure of the compressed GDL-CCM assembly was studied using X-ray microcomputed tomography (X-µCT, Zeiss MicroXCT-400 system). In X-µCT technology, cross-sectional images of the sample are generated by measuring the attenuation of X-rays penetrating through the sample. Different material densities attenuate X-rays to a different degree, i.e. denser material attenuates to a higher degree and appears in brighter grey-tones on the image as shown in Figure 2-3.

During the scanning process, the sample is rotated and moved in axial direction, such that a stack of cross-sectional images is generated. From these image stacks, a 3D dataset can be reconstructed using various types of image processing software (such as ImageJ).

2.3 X-µCT investigation of interfacial morphology

2.3.1 GDL-CCM assembly preparation

The study focusing on the formation of interfacial gaps was conducted by analyzing six compressed GDL-CCM assemblies, which enclosed the CL-MPL interface. Each assembly consisted of an in-house
fabricated pseudo-CL (without catalyst particles) on the membrane, compressed against the MPL of a GDL in a custom clamping setup made from Ultem PEI (Polyetherimide, purchased from McMasterCarr). The GDL-CCM assemblies used for the X-µCT scans consisted of small sections, 2 x 4 mm, of the GDL and the CCM, which were compressed in a clamping setup shown in Figure 2-4.

![Illustration of the clamping setup compressing the GDL-CCM assembly](image)

**Figure 2-4: Illustration of the clamping setup compressing the GDL-CCM assembly**

Each GDL-CCM assembly was enclosed in a pair of clamping pieces and compressed by tightening two Nylon screws to achieve compressions of 30 or 50% by volume with the calculated thickness of the uncompressed GDL-CCM assembly as reference. Either 4 or 5 layers of 76.2 µm (3 mil) thick Kapton® were used as spacers to achieve separation widths of 305 or 381 µm, representing approximately 50% and 30% volumetric compression of the GDL-CCM assemblies. These compressions were chosen as they correlate to a compressive strain of approximately 1.7 MPa and > 2.5 MPa, respectively. The former value is commonly applied as compression pressure in PEMFC systems, while the latter is used during the assembly of the GDLs and the CCM to compress and adhere the layers during the 5-layer MEA preparation.

### 2.3.2 X-µCT scanning procedure

X-µCT imaging was employed to acquire a 3D image of the internal microstructure of the compressed GDL-CCM assemblies within the clamping setup shown in Figure 2-2. These clamping setups were glued to an aluminium stud, which was then clamped in the X-µCT vice to ensure the stability during the scans. For each scan, 2500 radiographs, scanning 360 degree, were acquired each with an exposure time of 8 s and a voxel size of 2 µm. The radiographs were used to reconstruct a 3D volume of the GDL-CCM assembly. The final 3D datasets were 1050 x 1050 x 950 voxels. This procedure provided a stack of 950 cross-sectional images of a GDL-CCM assembly showing the CL-MPL interface.
For a voxel size of 2 µm, the spatial resolution is 3.7 µm, meaning that features of at least 3.7 µm in equivalent spherical radius can be identified assuming that 27 (3³) voxels are required to resolve a feature within a 3D dataset. As illustrated in Figure 2-5, the spatial resolution is larger than the average pore size within the CL and MPL bulk. Thus, the solid material and the void space within these layers appeared as single phase within the 3D dataset.

Figure 2-5: Pore size distributions of the CL, MPL, GDL and the interfacial gaps²⁶,³²,⁴⁶

Moreover, a portion of the GDL pores and the interfacial gaps between the CL and MPL are smaller than the spatial resolution and cannot be viewed in the 3D dataset. However, as the highest potential of water accumulation is accompanied with relatively large continuous voids¹⁶,¹⁹, the resolution achieved with the X-µCT is sufficient to capture such gaps.
2.3.3 Image processing and analysis

Post processing of the cross-sectional images and the 3D dataset was performed with the open source software ImageJ\textsuperscript{47}. In these images, each grey tone is allocated to a material density, i.e. a lighter grey tone refers to a higher material density. The relatively dense Nafion® membrane, the CLs, as well as the carbon fibres and PTFE phases are shown in light grey tones. The highly porous but packed MPL is shown in intermediate grey tones and void space in dark grey to black tones. To extract the information about CL-MPL interfacial gaps, the cross-sectional image stacks were processed following the sequence of steps shown in Figure 2-4 and described in the subsequent section.

![Processing steps of the cross-sectional images](image)

Figure 2-6: Processing steps of the cross-sectional images showing the GDL-CCM assembly in the clamping setup with a) the original image, b) cropped to the CL-MPL-interfacial region showing the CL, a part of the MPL and membrane after enhancing the contrast, c) after application of the 3D-median filter and the threshold function, d) reconstructed 3D dataset

First, all the acquired cross-sectional images (e.g. Figure 2-6a)) in the stack were aligned along the x-y-z axes of the global coordinate system and cropped to an area of 0.08 mm x 2 mm. Each cropped image showed the CL enclosed by a section of the membrane and the MPL (Figure 2-6b)). Second, noise was removed using a 3D-median filter, which averages the grey tone spherically around a particular voxel. The median filter has been successfully applied in prior studies\textsuperscript{4,26,27,31} of GDL and CCM materials, although it slightly reduces the edge sharpness. Third, the image was binarized (Figure 2-6c)) using the MaxEntropy threshold function to segment the solid material from the voids. This function uses as a threshold value the greyscale tone with the maximum inter-class entropy (uncertainty of a greyscale tone) of the image stack histogram. In general, the choice of the threshold value significantly affects the
segmentation of solid material and void space \(^{48}\) and commonly has been solved by either applying Otsu’s method \(^{26,30}\) or a manually chosen global threshold value \(^{4,27,48}\). Otsu’s method statistically correlates the threshold grayscale tone to the minimum weighted variance in the image histogram. In comparison, the manually set threshold values are fitted, such that investigated material parameters (the porosity or GDL fibre diameter) obtained via X-\(\mu\)CT match to values obtained by standardized analytical methods \(^{49}\) (mercury intrusion porosimetry or SEM imaging). In this work, a statistical threshold function was found to provide better segmentation as compared to the manual method, and further the MaxEntropy function was found to be superior compared to Otsu’s method. A 3D view of the segmented voids and cracks in the interfacial region is shown in Figure 2-6d). The black edges on the side of the figure represent the edges of the clamping setup, which were cropped prior to the subsequent image analysis.

The segmented 3D datasets were then analysed to determine the interfacial gap area \(A_{\text{gap}}\) (fraction of CL-MPL interface area separated by gaps) and the areal crack density \(A_{\text{crack}}\) (MPL crack area per interfacial area). The procedure is shown in Figure 2-7 for a section of the segmented 3D dataset.

![Image analysis starting from a) section of a segmented 3D dataset, b) its projection in through-plane direction, c) binarized projection (for \(A_{\text{void}}\) and d) cross-section of the MPL showing only cracks (for \(A_{\text{crack}}\)](image)

To determine the interfacial void area, all of the gaps between MPL and CL and cracks in the MPL visible in the 3D dataset were projected onto a plane. First, the gaps/voids segmented in the 3D datasets (Figure 2-7a)) were projected onto a plane from a distance of approximately 20 \(\mu\)m from the mean CL-MPL interface plane (Figure 2-7b)). This projection was then binarized (Figure 2-7c)) and used to evaluate the interfacial void area \(A_{\text{void}}\) by dividing the number of black pixels by the total number of pixels (equation 1):

\[
A_{\text{void}} = \frac{\text{Black pixels}}{\text{Total pixels}} \quad (1)
\]
In this equation, the void area $A_{\text{void}}$ equals to the sum of the interfacial gap area $A_{\text{gap}}$ as well as the areal crack density $A_{\text{crack}}$ of the MPL, as both depict regions of missing contact between the CL and MPL. The difference between interfacial gaps and cracks can be found in their behaviour under compressive strain. With increasing compression, the volume of interfacial gaps becomes smaller, whereas the volume of cracks in the MPL remains relatively constant and decreases only slightly due to limited lateral migration of particles in the MPL. To separate the interfacial gap area $A_{\text{gap}}$ from the cracks in the MPL, the areal crack density $A_{\text{crack}}$ was subtracted from $A_{\text{void}}$. The areal crack density $A_{\text{crack}}$ was evaluated by applying equation 1 on the in-plane cross-section of the MPL at a distance of 5 μm from the mean CL-MPL interface (Figure 2-7d)). At this distance, only cracks corresponding to the MPL were visible. This image processing and analysis procedure was carried out for all six compressed GDL-CCM assemblies.

2.4 Electric contact resistance at the CL-MPL interface

The electric through-plane resistance contributions of the components and their interface were evaluated ex-situ in a custom made four-point-probe (4PP) setup shown in Figure 2-6. In conventional through-plane two-point-probe (2PP) setups, the bulk and contact resistances are separated by stacking multiple samples and measuring the resistance. The bulk resistance of the samples are calculated from a resistivity given by the manufacturer, and thereby one or more resistance contributions or dependencies are frequently neglected. Mixed in-plane/through-plane 4PP setups also require simplifications as e.g. including an offset in the resistance measurements (0 mΩ·cm$^2$ at given compression pressure) or simply do not allow the separation of the bulk and contact resistances. To separate the through-plane CR contribution, the voltage drop corresponding to the sample should ideally be measured where the current forcing electrode contacts the sample surfaces. This can be achieved with micro-probes placed directly on the sample surface, as in a setup shown in Figure 2-8.

![Figure 2-8](image)

**Figure 2-8:** a) the 4PP setup in a climate chamber, b) an illustration of the main components, the four sensing probes are placed at each of the planes (A, B, C, D), c) the current forcing electrode with the circular micro sensing probe in the center.
The 4PP setup used in the present study enables the deconvolution of the through-plane bulk and CR of anisotropic samples to the current forcing electrode and thereby overcomes the limitations of commonly employed resistivity setups\textsuperscript{54}. The setup employs four voltage sensing probes at different interface planes (A, B, C and D in Figure 2-8b)). By changing the combination of the voltage sensing probes during the resistance measurements (combinations A-D, A-C, B-D or B-C), the bulk and CR contributions of the sample and the electrodes can be separated. In order to account for the in-plane anisotropy of the GDL materials, a circular arrangement of the voltage sensing probes was used to average out inhomogeneous in-plane resistances\textsuperscript{54}. The two circular micro-sensing probes (shown in Figure 2-6c)) placed on the sample surfaces (planes B and C) directly measure the voltage drop from the pure sample bulk resistance. This was achieved by placing the thin-walled (∼10 µm) circular voltage sensing probe as close as possible to the current forcing electrode (with average distance of 15 – 20 µm) while still being insulated from the electrode.

However, as the total resistance of an assembly consisting of a GDL/MPL on the CL/GCC disk (referred to as ‘Sample’ in Figure 2-6b)) arises from the contributions of the resistances of the individual components (GDL/MPL and CL/GCC) and their interface (CL-MPL), a measurement protocol was developed to separate this CL-MPL CR. This protocol involved as follows:

1. Conditioning of the GDL/MPL and the CL/GCC disk at a pre-set relative humidity (RH) and temperature for 3 hours. In this time, the RH in the climate chamber is adjusted and the water content in the ionomer in the CL equilibrated.
2. Evaluation of the individual bulk resistances at increasing compression pressure of
   a. the GDL/MPL sample
   b. CL/GCC disk sample
3. Evaluation of the bulk resistance at increasing compression pressure of the assembly consisting of the CL/GCC disk pressed against the MPL of the GDL and thereby forming the CL-MPL interface.

The CL-MPL CR was then calculated by subtracting the resistance contributions of the GDL/MPL and the CL/GCC from the assembly resistance following equation 2:

\[ R_{\text{CL-MPL}} = R_{\text{GDL/MPL-CL/GCC}} - R_{\text{GDL/MPL}} - R_{\text{CL/GCC}} \]  

(2)

In Eq. 2, \( R_{\text{CL-MPL}} \) represents the CL-MPL CR and \( R_{\text{GDL/MPL-CL/GCC}} \) the total resistance of assembly. \( R_{\text{GDL/MPL}} \) and \( R_{\text{CL/GCC}} \) are the bulk resistances of the GDL/MPL and the CL on the GCC disk, respectively. To
calculate the area specific resistance, which is commonly used to present sheet resistances of PEMFC materials, \( R_{C(CL-MPL)} \) was multiplied with the nominal area of the CL sample of 2.37 cm\(^2\). The compression pressure applied to the sample was varied pneumatically, while the climate chamber (Tenney Engineering Inc.) in which the setup was placed, enabled the control of the temperature and RH. The resistance measurements were done with a micro-ohmmeter (Agilent 34420A) at increasing compression from 0.34 to 4.06 N-mm\(^2\) at a RH of 20, 50 and 80% for all CL compositions. As the bulk resistance for the GDL and CL depends on the compression pressure\(^{11,53}\), the measurement of the bulk resistance was done at each compression pressure and the average values were used to evaluate the CL-MPL CR.
3. Results and discussion

The following sections detail the results of both experiments, the CR measurements and the interfacial morphology studies, and the findings are discussed.

3.1 Surface roughness and structure of the MPL and CL samples

The surface structures of the CL and MPL define the interfacial morphology and the development of interfacial gaps under compression. Furthermore, the electric CR is determined by the conductive pathways available for the electron transport, which are affected by the morphology and composition at the interface. Therefore, physical characterization of the CL and MPL surfaces was done prior to the assembly and the compression to correlate physical surface properties with the results of the X-μCT and the CR resistance measurements. Generally, the three CLs (CL 1, CL 2 and CL 3) with different ionomer contents (I/C ratios of 0.3, 0.6 and 0.9, respectively) and the MPL exhibited different macroscopic surface structures, as shown on the SEM images in Figure 3-1.

![SEM images of the CL surfaces at magnifications of 200x and 2000x and the MPL surface at 100x and 1000x](image)

Figure 3-1: SEM images of the CL surfaces at magnifications of 200x and 2000x and the MPL surface at 100x and 1000x

It can be seen from Figure 3-1 that CL 1 showed a relatively smooth surface with irregular peaks and valleys, whereas CL 2 and CL 3 featured fractal structures. EDX analysis revealed that the bright web-like structures of CL 2 and the darker areas in CL 3 contained a higher ionomer content as compared to their surrounding features. These different surface structures were a result of a combination between the deposition method and the base CL compositions. The ionomer and solvents (alcohols) in the CL ink act as surfactants due to their amphiphilic nature, which tend to accumulate along liquid/solid and liquid/air interfaces and thereby reduce the surface tension. With different ionomer contents in the CL inks, the interfacial interactions change and the macroscopic surface structures are affected. These different macroscopic surface structures are known to influence the surface roughness when the CLs are spray-coated directly on the substrate without a subsequent hot-pressing step. The surface roughness of the
CLs and the MPL were evaluated by optical profilometry, which measured the surface roughness parameters from images as shown in Figure 3-2.

![Profiler images of CLs and MPL surfaces](image)

**Figure 3-2**: Images and statistical data of the CL and MPL surfaces obtained by optical profilometry

To increase the reflectivity of the samples and therefore the quality of the image obtained by optical profilometry, the surfaces can be coated with a metallic coating by physical vapor deposition (e.g. sputter deposition\(^{17}\) or electron beam evaporation\(^{56}\)). However, the deposition of an additional layer in nanometer thickness slightly distorts the sample surface, and makes the sample useless for the following CR measurements. The CL and MPL samples prepared in the present study did not require an additional metallic coating to enhance the reflectivity in contrast to the study reported by Hizir et al.\(^{17}\). Visual comparison of the profilometry images of the uncoated samples obtained in the present study and the gold-coated samples presented by Hizir et al. revealed similar reflectivity. This can be explained by the difference in the used profilometer models and possibly a difference in the reflectivity of samples. The roughness measurements delivered the arithmetic roughness \(R_a\) along with the root mean squared roughness \(R_q\) as well as the maximum profile height \(R_t\) and the average distance \(R_z\) between highest peak and lowest valley in a sample. \(R_z\) and \(R_t\) were found to depend strongly on the profilometry measurement depth (the distance in z-direction in which the profilometer scans the surface), if the sample is not perfectly reflective and exhibits only few spots of missing surface data (black spots on images in Figure 3-2). Both, \(R_a\) and \(R_q\), provided an indication of the order of roughness of the CLs with a similar trend (roughness of CL 1 < CL 2 < CL 3). \(R_q\) was generally slightly increased as compared to \(R_a\), as a surface peak or flaw affects the root mean squared parameter due to its underlying equation more. In the subsequent sections, \(R_a\) is used to correlate the surface morphology to the results obtained by the \(X-\mu\)CT and electric CR measurements.
The average roughness parameters $R_a$ for each of the three CLs and the MPL are listed in Table 3-1, where each value is based on 5 measurements covering an area of 231 μm x 308 μm per sample.

Table 3-1: Average surface roughness $R_a$ of the CLs and the MPL of the GDL

<table>
<thead>
<tr>
<th>Sample</th>
<th>Roughness $R_a$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL 1 (I/C 0.3)</td>
<td>1.00 ± 0.01</td>
</tr>
<tr>
<td>CL 2 (0.6)</td>
<td>1.37 ± 0.09</td>
</tr>
<tr>
<td>CL 3 (0.9)</td>
<td>2.77 ± 0.12</td>
</tr>
<tr>
<td>25BC MPL</td>
<td>5.26 ± 1.09</td>
</tr>
</tbody>
</table>

From Table 3-1, the average roughness parameters $R_a$ increased from 1.00 ± 0.01 μm to 1.37 ± 0.09 μm and 2.77 ± 0.12 μm with increasing ionomer content of CL 1, CL 2 and CL 3, respectively. In comparison to the CLs, the roughness parameter of the MPL ($R_a$ of 5.26 ± 1.09 μm) was considerably larger, and about twice the value of CL 3. These values are in order with surface roughness parameters for a commercial CL of a CCM and MPL reported by Hizir et al.\textsuperscript{17}. In addition, the MPL exhibited irregularities such as cracks and holes that interrupted the continuity of the MPL surface. Examples of these defects are shown in Figure 3-3.

![SEM images of the surface irregularities as a) fine cracks and b) dents and holes in the MPL](image)

Figure 3-3: SEM images of the surface irregularities as a) fine cracks and b) dents and holes in the MPL

Irregularities in the MPL surface arise from GDL fibres translating through the MPL and emerging at the surface, and from large pores in the GDL serving as a substrate for the MPL, into which the MPL sags\textsuperscript{21,25}. Cracks as shown in Figure 3-3a) can arise along protruding GDL fibres and are amplified due to bending-induced stress of the GDL\textsuperscript{22,57,58}. Dents and holes as shown in Figure 3-3b) presumably occur when the viscous MPL ink is deposited onto the GDL surface and the ink intrudes into relatively large surface pores between the carbon fibres. Such irregularities in the MPL surface can result in interfacial gaps when in contact with the CL surface, which is presented in the following chapters.
3.2 X-µCT investigation of interfacial morphology

3.2.1 Origin and area of interfacial gaps

Using the 3D X-µCT datasets, the origin of the interfacial gaps within all six GDL-CCM assemblies, along with the interfacial gap areas $A_{\text{gap}}$ and areal crack densities $A_{\text{crack}}$ were investigated. The Figures 3-4 to 3-6 present different features of interfacial gaps and cracks within the GDL-CCM assembly. Figure 3-4 provides an overview of crack occurrence in the 3D-dataset of CL 2 compressed 30% by volume.

![Figure 3-4: In-plane cross-sections of the reconstructed 3D dataset through a) the transition region from fibrous GDL to the MPL and b) the MPL with cracks and gaps at the CL-MPL interface in dark grey tones. Part c) shows the interfacial gaps induced by cracks in the MPL (1), cracks in the MPL without surrounding gaps (2) and gaps induced by the surface roughness of the layers (3)](image)

In-plane cross-sectional views at the GDL-MPL and CL-MPL interfaces of the unsegmented dataset are shown in Figure 3-4a) and b), while c) presents a projection of the segmented cracks and interfacial gaps at the CL-MPL interface. The circles between all three images indicate cracks that translate the entire MPL, and thus join the GDL to the CL. Some of the cracks in the MPL, identified as 1a and 1b, are surrounded by dark grey tones indicating the presence of interfacial gaps. Other cracks, e.g. 2, are not surrounded by interfacial gaps. Several additional light grey spots, e.g. 3, are also present. Examination of these 3D datasets has shown that that MPL cracks 1a and 1b and surrounded by CL-MPL interfacial gaps are located in the centre of a large pore on the surface of the GDL. It is hypothesized that these cracks formed because the MPL sagged into the large GDL pore and then fractured because of the missing mechanical support of carbon fibres. This relationship between large gaps and cracks in the MPL, and interfacial gaps in the CL, is further visualized in the video in Appendix A (Video: Interfacial_gap_formation). The use of a thicker MPL could compensate for the missing support of GDL
fibres and the sagging of the MPL, however, as the MPL thickness increases, the diffusional resistances of reactants and products as well as the electric and thermal resistances increase\(^\text{59}\). A reduction of the sagging and perforation of the MPL and the coherent formation of interfacial gaps could be achieved by reducing the size of the pores on the GDL surface serving as substrate for the MPL deposition. A close-up view of an MPL crack induced gap (such as 1a and 1b in Figure 3-3) is shown in Figure 3-5, providing the full geometry of the crack and the large gap at the CL-MPL interface in different views.

![Figure 3-5: Interfacial gap (1) induced by a crack in the MPL (2) with the underlying CL (3) shown in light grey tones, a) top- and b) side-view, c) the 3D volume](image)

As can be seen in Figure 3-5, the interfacial gap spans over a considerably larger area of the underlying CL than the crack. In the literature, cracks within the MPL were identified as efficient initiation points for the liquid water transfer through the GDL during the operation of a PEMFC\(^\text{60,61}\). Such large gaps around cracks potentially bundle the product water of the reactions in the CL, remove it through the MPL crack and thereby amplify the observed concentration of liquid water at the crack outlet into the GDL\(^\text{62}\). However, its beneficial effect on the water management opposes a deteriorating effect on the conduction of electricity, heat and reactants across the interface\(^\text{15}\). In addition to large MPL cracks and large MPL-crack induced gaps, relatively small interfacial gaps (grey spots identified as 2 in Figure 3-4 and magnified in Figure 3-6 were found.
These gaps are thought to form due to the surface roughness features of the CL and the MPL\textsuperscript{17,18,25} and were found throughout the CL-MPL interface irrespective of large irregularities in the MPL or the CL surfaces. During PEMFC operation, product water can accumulate in voids like the one shown in Figure 3-6 without the possibility for the water to evacuate through MPL cracks\textsuperscript{60,61}. The resulting water filled voids block reactants from diffusing across the CL-MPL interface towards the catalytic sites in the CL\textsuperscript{13,15}.

Interfacial gaps induced both by MPL cracks and by surface asperities of the CL and MPL were found within all six GDL-CCM assemblies. The interfacial gap area $A_{\text{gap}}$ and areal crack density $A_{\text{crack}}$ was quantified for all GDL-CCM assemblies and the results are presented in Figure 3-7.
The values for $A_{gap}$ and $A_{crack}$ represent averages of 9 measurements, where either the threshold value or the projection distance (see Figure 2-5 and description for information) of the gap/crack was varied. Varying the threshold value by 1 grey tone resulted in an average difference in $A_{gap}$ of 0.4%, while varying the projection distance by 1 μm resulted in an average difference of 0.31% as compared to the values shown in Figure 3-7. As can be seen in the figure, the largest $A_{gap}$ of 15.89% was found at 30% compression between the MPL in contact to CL 1, which had the smoothest surface ($R_a$ of 1.00 ± 0.01 μm) among all investigated CL samples. Smaller $A_{gap}$ values with 6.00% and 5.89% were observed under similar compression for CL 2 and CL 3, respectively, where both exhibited rougher surfaces ($R_a$ of 1.37 ± 0.09 μm for CL 2 and 2.77 ± 0.12 μm for CL 3). Since $A_{crack}$ of all GDL-CCM assemblies was similar (1.53 to 2.44%), the large difference between $A_{gap}$ of the CL 1 samples and the CL 2 and CL 3 samples must predominantly arise from surface roughness induced gaps (such as shown in Figure 3-6). A possible explanation is the larger difference in surface roughness for the CL and the MPL ($\Delta R_a = R_{a,MPL} - R_{a,CL}$). $\Delta R_a$ of the GDL-CCM assemblies containing CL 1 ($\Delta R_a$ of 4.26 μm) was larger as compared to the values found for CL 2 ($\Delta R_a$ of 3.95 μm) and CL 3 ($\Delta R_a$ of 2.49 μm). A higher $\Delta R_a$ between the two layers can result in a higher fraction of interfacial gaps, whereas a lower $\Delta R_a$, i.e. large surface features of a rough and soft surface opposing an also rough surface, adjust and enclose fewer gaps, as illustrated in the insets of Figure 3-7. Hence, a reduction in $\Delta R_a$ can result in a decrease in the interfacial gap area, which was also proposed to some degree by Swamy et al.\textsuperscript{18}. The authors suggested that the reduction of the surface roughness of CL and MPL decreases the separation width between the layers. As shown by the results of the present study, this finding can be refined to the reduction of the relative difference between the surface roughness $\Delta R_a$, i.e. approximating the roughness of both surfaces. Additionally, the increase in compression from 30% to 50% generally leads to a reduction of the interfacial gap area of all GDL-CCM assemblies (by 59%, 11.6% and 39.6% for CL 1, CL 2 and CL 3, respectively) irrespective of the apparent difference in roughness $\Delta R_a$. Under compressive strain, the carbon, PTFE and ionomer undergo a plastic deformation and are forced to migrate into pores and interfacial gaps\textsuperscript{11,18}. Therefore, a reduction in the interfacial gap area can be achieved by adjusting the roughness to reduce $\Delta R_a$ along with the increase in the compression pressures.

### 3.2.2 Roundup

The results show that interfacial gaps are forming throughout the CL-MPL interface depending on the surface roughness and morphological irregularities of the CL and MPL, and decrease with increasing compression. From the X-µCT 3D datasets, it was found that the largest continuous interfacial gaps were
occurring in proximity of cracks in the MPL. These are hypothesized to form due to the presence of large pores on the surface of the GDL, where the MPL sagged into the pore and cracked as a result of missing mechanical support of carbon fibres. Relatively small gaps were induced throughout the CL-MPL interface by the surface roughness features of the layers. The highest interfacial gap area (fraction of interfacial area separated by gaps) was found for the GDL-CCM assembly with the largest difference between the surface roughness parameters of CL and MPL. Lower interfacial gap areas were found for GDL-CCM samples with rather similar roughness parameters of CL and MPL. A higher compression resulted in a lower fraction of interfacial gaps, as carbon, PTFE and ionomer undergo a plastic deformation under compressive strain and are forced to migrate into pores and gaps.
3.3 Electric contact resistance

3.3.1 Effect of compression pressure and CL composition

The contact resistance (CR) between two components depends on the intrinsic properties of the materials, of the composition (fraction of electrically conductive vs. non-conductive material), and the interfacial morphology. The morphology is furthermore affected by the operational conditions in the PEMFC as compression pressure and relative humidity (RH). To elucidate the effect of different compositions of the CL on the CR, measurements were done at increasing compression pressure and at varying RH. For all measurements, the GDL/MPL material remained the same, hence, the results present the effect of the CL composition and surface structure on the CR.

The ionomer contents of CLs usually lies in the range of 20 and 50 wt.%\textsuperscript{39,8,63,64}. Variations in the ionomer content have shown to affect the CL structure and, hence, the PEMFC performance\textsuperscript{8}. An increase in the ionomer content enhances the protonic conductivity of the ionomer matrix in the CL\textsuperscript{23} along with a decrease in the bulk porosity of the layer\textsuperscript{64}. Moreover, the increase in the ionomer content also increases the electric in-plane resistance\textsuperscript{8} and is expected to affect the CR towards the MPL, which is studied in this thesis. Figure 3-8 presents the CL-MPL CR ($R_{CL\text{-}MPL}$) of the three CLs with different I/C ratios, evaluated at compression pressures between 0.34 and 4.06 N·mm\textsuperscript{-2} and at 20% RH towards the MPL. The evolution of the interfacial resistance captures the effect of ionomer content on the interfacial properties, specifically, the effect on the electronic pathways formed at the carbon-carbon contact points between the two layers. As can be observed from Figure 3-8, the evolution of $R_{CL\text{-}MPL}$ for all three CLs showed the non-linear decrease with the increase in the compression pressure. Although the magnitudes of $R_{CL\text{-}MPL}$ were different for the three CLs, the general trend remains the same, which is in agreement with the reported literature\textsuperscript{11,37}. 
The CRs measured for CL 1 and CL 2 were found to be of similar order for compression pressures higher than 1 N mm\(^{-2}\). In contrast, the CR for CL 3 was found to be 42 – 79% higher than the values for CL 1 and CL 2. The magnitude of the CR values obtained for CL 1 and CL 2 are comparable to the bulk resistances of wet-proofed GDL materials\(^{53}\), while the CR for CL 3 is comparable to the GDL/bipolar plate interface\(^{54}\).

The observed variation in the \(R_{C(CL-MPL)}\) for the CLs arises from a combined effect of the micro structures on the surfaces and the CL composition. To correlate the electrical measurements with these effects, physical characterization of the CL surface was performed using SEM, EDX and surface profilometry. As can be observed in the SEM images (Figure 3-1 and 3-9), the surface morphology depends on the composition of the CL. However, these roughness features shared some common structural similarities, the surface asperities with peaks and valleys (named spot A and B in Figure 3-9), which were distinguished from images obtained by optical profilometry (Figure 3-2).
Figure 3-9: SEM images showing the CL surface morphologies with varying ionomer content. Spot A and Spot B in the images correspond to the peaks and valleys on the CL surfaces used for EDX mapping.

As discussed in chapter 3.1, the physical interactions between the CL ink components (carbon particles and ionomer) in combination with the deposition method determine the macro structures formed on the CLs surface\textsuperscript{22,39,63}. The interfacial interactions between the solid and liquid components result in a localized difference in the ionomer content within the sprayed ink, which in turn affects the macroscopic structures of the CLs during the deposition and drying processes\textsuperscript{60}. In order to obtain quantifiable values for these surface structures, surface profilometry was done and the average roughness $R_a$ was evaluated for each of the CL samples and the MPL (Table 3-1). The roughness ($R_a$) for the MPL was found to be higher than the CL surface roughness. The general trend for the roughness $R_a$ showed that with increasing ionomer content the roughness increases. The highest roughness was observed for CL 3 among the three CLs used in this study. The structural features on the CL surface arose from the migration of components (ionomer and carbon particles) during the drying process, which resulted in a non-uniform ionomer composition on the CL surface. The variation in the composition of the ionomer was determined by EDX measurements at different locations. The EDX measurements were done to evaluate the fluorine content in the CL, which is an elemental component in the Nafion polymer\textsuperscript{3}, therefore its content can be used as an indicator for the ionomer content at the different surface asperities. The measurements were done at the peaks and valleys, shown as spot A and B, respectively, in Figure 3-9. The measured fluorine content averaged for 5 measurements at these asperities is listed in Table 3-2 along with the mean values for the CL surfaces.

Table 3-2: Fluorine content of the CL surface asperities obtained by SEM-EDX

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fluorine content (wt.%</th>
<th>Spot A (Peak)</th>
<th>3.3 ± 0.1</th>
<th>3.3 ± 0.1</th>
<th>3.3 ± 0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL 1</td>
<td>9.8 ± 1.6</td>
<td>5.2 ± 1.6</td>
<td>8.7 ± 1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CL 2</td>
<td>27.1 ± 6.2</td>
<td>8.7 ± 1.8</td>
<td>17.9 ± 10.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CL 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As expected, the mean fluorine content increased from CL 1 to CL 3. However, the fluorine content at the peaks (Spot A) was found to be higher than at the valleys (Spot B) for CL 2 and CL 3, and similar for CL 1. The increase in the ionomer at the peaks corresponding to the surface structure arose from the agglomeration due to interfacial interactions between the CL ink components during drying of the spray-coated layer\textsuperscript{39,40}. Since the ionomer is electronically insulating, these variations affected the local current distribution at the interface, and thereby the measured CR.

The measured resistance values were correlated with the structural and compositional aspects of the CL surfaces. Since the similar GDL material (Sigracet\textsuperscript{®} 25BC) was used for all CR measurements, the MPL surface structure and coverage of the PTFE was expected to remain constant for all the samples. The relative comparison of $R_{C(CL-MPL)}$ at 0.34 N-mm$^{-2}$ revealed that the values found for CL 3 were 79\% higher as compared to CL 1. In the present study, CL 1 and CL 2 exhibited relatively lower roughness ($R_a = 1.00 \pm 0.01$ μm and $1.37 \pm 0.09$ μm, respectively) as compared to CL 3 ($R_a = 2.77 \pm 0.12$ μm). At low compression pressures, the peaks of the CL and MPL surfaces are primarily in contact\textsuperscript{19}, and a relatively large interfacial gap area reduces the number of pathways for electrons as shown in Figure 3-10 for the case of CL 1 in contact to the MPL at 50\% RH.

![Figure 3-10: CR between CL 1 and the MPL (RH = 50\%) at increasing compression, and the interfacial gap area at 1.7 and 4.1 N-mm$^{-2}$. The insets show the projections of the 3D datasets at the particular pressure, from which the gap area was calculated.](image)

As can be seen in the insets of Figure 3-10 and the calculated interfacial gap areas, at lower compression (1.7 N∙mm\(^{-2}\)) a larger fraction of the CL-MPL interface is separated by gaps as compared to the case of high compression pressure (4.06 N∙mm\(^{-2}\)). Moreover, the peaks of the rougher CL 3 (spot A in Figure 3-9) revealed 3 and 9 times the concentration of fluorine and hence the ionomer content, as compared to CL 2 and CL 1 respectively. The higher roughness additionally reduces the number of carbon-carbon contact points, responsible for the electron transport. The high fluorine concentration at the top surface of these peaks suggests that a higher number of carbon particles on the surface are masked with the electrically insulating ionomer. Therefore, the high \(R_{C(CL-MPL)}\) of CL 3 was an effect of the relatively rough surface in combination with the significantly higher ionomer content in the peaks of the CL. The difference between \(R_{C(CL-MPL)}\) of the CL compositions was found to decrease at higher compression pressures. With increasing compression, the voids between the CL and MPL diminish, the peaks and valleys flatten out and the interfacial gap area decreases. As a consequence, the area available for the electron transport increases (increase in the carbon-carbon contact points), which results in a lower CR. As the roughness features flatten out, the number of carbon-carbon contact points depends on the fraction of the surface covered by the ionomer. The \(R_{C(CL-MPL)}\) values at high compression pressure highlights the effects of PTFE and ionomer towards the CR, where the masking effects of these electronically insulating components dominate. A comparison at the maximum compression pressure of 4.06 N∙mm\(^{-2}\) shows that \(R_{C(CL-MPL)}\) of CL 3 is 42% higher than the value found for CL 1. At this compression, \(R_{C(CL-MPL)}\) is controlled by the ionomer content (measured as fluorine wt.%), which was found approximately 2.5 and 6 times higher for CL 3 as compared to CL 2 and CL 1, respectively. Therefore, the CR at low compression pressure highlights the effect of the surface roughness, whereas at high compression pressure it predominantly depends on the surface coverage by the ionomer.

### 3.3.2 Effect of relative humidity and CL composition

The protonic conductivity of the Nafion ionomer depends strongly on the degree of humidification\(^{65}\), which is an integral part of the PEMFC functionality. The hydrated sulfonic acid groups of the Nafion electrolyte enable the selective transport of protons through the ionomer matrix\(^3\). However, hydration of the ionomer matrix also causes swelling of the ionomer\(^{24}\). In the CL, the carbon particles are embedded in the ionomer matrix and any deformation of this matrix will invariably affect the contact characteristics between carbon particles. As it has been shown in earlier works, the swelling of the ionomer in the CL leads to a decrease in the electronic conductivity through the CL bulk due to reduction in the carbon-carbon contact points\(^{23,66}\). In addition to the bulk resistance, the ionomer swelling is
expected to affect the CR at the CL-MPL interface by inducing deformations in the surface asperities, which has been studied here. Studies were conducted to substantiate the effect of humidification (RH of 20 – 80%) on $R_{C(CL-MPL)}$ for the CLs and the results are shown in Figure 3-11.

![Graph a) showing contact resistance vs. pressure for different RH levels.](image1)

![Graph b) showing contact resistance vs. relative humidity for different I/C ratios.](image2)

**Figure 3-11:** Experimental results for the effect of RH on $R_{C(CL-MPL)}$ for a) CL 1 and b) $R_{C(CL-MPL)}$ at a compression pressure of 1 N·mm$^{-2}$ for the three CL at varying RH from 20 to 80%

As can be seen in Figure 3-11a), the values for $R_{C(CL-MPL)}$ approximately doubled with the increase in RH from 20 to 80% throughout the range of compression pressure from 0.34 to 4.06 N·mm$^{-2}$. This increase in the $R_{C(CL-MPL)}$ with the increase in RH was observed for all three CL compositions (Figure 3-11b)). The volumetric swelling of the ionomer affects the carbon-carbon contact points at the interface, which results in the resistance increase with humidification of the assembly$^{23}$.

A comparison of the range for $R_{C(CL-MPL)}$ obtained in the present research to the CR values reported in literature is shown in Figure 3-11. The minimum $R_{C(CL-MPL)}$ was obtained for CL 1 (I/C ratio of 0.3) at a RH of 20%, while the highest $R_{C(CL-MPL)}$ was obtained for CL 3 (I/C ratio of 0.9) at a RH of 80%. All the measured values for $R_{C(CL-MPL)}$ of the different CL compositions at varying RH and compression pressure lie within these minimum and maximum values and are used to compare to the CRs reported in the literature.
As can be seen in Figure 3-12, the non-linear decrease with increasing compression pressure observed in the present research is in agreement with the earlier works. This decrease with increasing compression is an effect of the deformation of the surface asperities of the stacked CL and MPL\textsuperscript{15,18} and thereby increasing carbon contact points. However, the experimental values reported by Kleemann et al.\textsuperscript{11} underestimate the $R_{\text{CL-MPL}}$, which can be explained by the choice for the offset to enable the CR evaluation with their setup. The authors assumed the CR to be negligible at highest compression pressure (0 mΩ·cm$^2$ at 2 N·mm$^{-2}$) and correlated the gain in resistance with decreasing compression to the increasing CR. On the other hand, the experimental values reported by Nitta et al.\textsuperscript{37} were higher than the highest $R_{\text{CL-MPL}}$ obtained (CL 3 at 80% RH) in the present studies, as their results represent the CR between the CL and the GDL without a MPL, which was found to dominate the ohmic resistance contributions in their PEMFC setup. The results show that using an MPL enhances the contact properties to the CL and hence leads to a decrease in the CR. The ability of the MPL to enhance the mating characteristics with a rough surface has also been observed in earlier studies\textsuperscript{38,54}. In relation to the results presented by Nitta et al.\textsuperscript{37}, the contribution of the CL-MPL CR can account for up to 11 – 55% of the total ohmic resistance in a PEMFC. These results indicate that depending on the ionomer content and RH, the CR between the CL and the MPL can have a significant contribution towards the total ohmic resistance of a PEMFC.
3.3.3 Roundup
Generally, a non-linear decrease in the CR between the CL and MPL with increasing compression pressure was observed for all CL compositions. The deformation of the surface asperities with increasing compressive strain enhances the contact points between carbon particles and leads to a reduction in the CR measured between the CL and MPL. The electrically insulating ionomer in the CL masks the carbon particles available for the electronic conduction. This insulating effect increases with higher ionomer contents and thereby increasing CRs. The effect of RH and the water uptake of the ionomer on the CR was also studied. The increase in RH from 20 to 80% resulted in approximately the doubling of the CR for all CL compositions, which is attributed to ionomer swelling with the uptake of water. A correlation of the surface properties of the CL (characterized by SEM, EDX and optical profilometry) with the measured resistance showed a dependence of the CR on the surface roughness and the ionomer content on the surface asperities.
4. Conclusions

This work reported the results of ex-situ investigations of 1) the interfacial morphology, specifically the formation of interfacial gaps between the catalyst layer (CL) and micro porous layer (MPL) and 2) the electric contact resistance (CR) arising at the interface. The interfacial gaps were studied for assemblies consisting of compressed gas diffusion layers (GDLs) on catalyst coated membranes (CCMs), where either the compression or the CL surface structure (and roughness) was varied. In a separate experiment, the CR was studied as a function of compression pressure and relative humidity (RH) for CLs with different compositions (ionomer/carbon ratios of 0.3, 0.6 and 0.9) towards the MPL of a commercial GDL.

The key-findings from the investigation of the interfacial morphology are:

1a. The highest interfacial gap area of 15.9 % (fraction of interfacial area separated by gaps) was found for the GDL-CCM assembly with the largest difference between the surface roughness parameters of CL and MPL. Lower interfacial gap areas (6.00% and 5.89%) were found for GDL-CCM assemblies with relatively similar roughness parameters of CL and MPL. The gap area was found to decrease by 11.6 – 59% with an increase in compression from 30 to 50% by volume.

1b. The largest continuous interfacial gaps were occurring in proximity of cracks in the MPL, which are hypothesized to form due to the presence of large pores on the surface of the GDL. In such relatively large pores, the MPL sagged into and cracked as a result of missing mechanical support of the GDL carbon fibres.

1c. Relatively small gaps were induced throughout the CL-MPL interface by the surface roughness features of the CL and MPL.

The findings presented here have not been reported in the literature before, and can contribute to the CL-MPL interface advancement, while pointing towards further work in this area. From the X-µCT 3D datasets, a reduction of the interfacial gap area can be achieved by adjusting the roughness parameters of the CL and MPL to improve the mating characteristics along with the increase in compression. Moreover, the fraction of MPL crack induced interfacial gaps to the CL can be manipulated by modification of the GDL serving as a substrate for the MPL. Looking ahead, the GDL and MPL manufacturing process could be adjusted to manipulate the occurrence of holes and dents in the MPL.
and the formation of interfacial gaps. Smaller pores on the GDL surface serving as a substrate influence the development of holes and dents in the MPL. Also, by texturing the CL and MPL surfaces their mating characteristics and thereby the formation of interfacial gaps could be influenced. However, to validate these hypotheses, further testing is needed.

The key-findings from the electric contact resistance measurements are:

2a The increase in compression pressure resulted in the decrease of the CR for all CL compositions. The minimum CR found for the CL with lowest ionomer content at low RH was in order of bulk resistances of GDL materials\textsuperscript{57}. The maximum CR found for the CL with the highest ionomer content at high RH was in order of the contact resistance arising at the GDL/flow field plate interface\textsuperscript{54}.

2b The increase in the RH from 20 to 80\% resulted in approximately the doubling of the CR for all CL compositions, which is attributed to ionomer swelling with the uptake of water.

The methodology and the information on the electric CR can improve our understanding of transport phenomena of PEMFCs and assist in modelling the interfacial transport. The results presented here in comparison to the study reported by Kleemann et al.\textsuperscript{11} show, that the commonly used experimental data for validation of simulation studies underestimates the arising CR. Moreover, from the results of both ex-situ experiments presented in this thesis, the CR could be affected by the assimilation of the surface roughness features of the CL and MPL. A decrease in the interfacial gap area due a lower relative difference in the roughness parameters of CL and MPL increases the number of pathways available for the electron transport at similar compression pressure.

4.1 Future work

The findings presented in this study should be considered in future work aiming on the mating characteristics between the two layers, CL and MPL. In general, the GDL/MPL fabrication process could be adapted, such that fewer gaps will be enclosed between the surfaces, which affect the contact resistance, but more importantly, the water management in the PEMFC. Additionally, simulation studies focusing on the CL-MPL interface could include the information presented here.

Suggestions include:

- During the GDL fabrication, the GDL pore sizes could be varied, such that the number and density of cracks in the MPL changes and, hence, the occurrence of interfacial gaps towards the CL is affected.
• Moreover, the surface of the MPL could be engineered to assimilate the roughness parameters of CL and MPL. Experimental tests would involve the manufacture of GDL/MPL materials with varying crack densities, the measurement of the gap area using X-μCT, and electrochemical tests with the different GDL/MPL materials.

• In simulation studies, the effect of different dimension of interfacial gaps on the water management could be modelled with a focus on large funnel-shaped gaps around cracks in the MPL. Also, models including ohmic resistance contributions should us the data presented here for validation, as the CR usually has been underestimated in previous studies.
References


47. ImageJ - Image processing and analysis in Java. at <http://imagej.nih.gov/ij/>


