

Development of methods to improve automotive PEMFC degradation analysis

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vorgelegt von

Michael Obermaier M.Sc.

aus Ergolding

Berichter: Frau Univ.-Prof. Dr. Christina Scheu
Frau Univ.-Prof. Dr.-Ing.habil Brita Daniela Zander

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"The Earth is a fine place and worth fighting for."
Ernest Hemingway, Author

*"You never change things by fighting the existing reality.
To change something, build a new model that makes the existing model obsolete."*
Buckminster Fuller, Architect & Inventor

Abstract

Global warming and its harsh impact on the climate require a drastic reduction of greenhouse gas emissions. A significant contribution can be made in the traffic sector, where electromobility plays a key role. Electrified vehicles can be divided in hybrid electric vehicles, battery electric vehicles and fuel cell electric vehicles. Herein, fuel cell electric vehicles, being powered by polymer electrolyte membrane fuel cell (PEMFC) stacks, possess large driving ranges and short refueling times and are therefore especially interesting for long range transport and the logistic sector. PEMFCs consist of several components including gas diffusion layers, serving for adequate gas supply and water removal, a gas impermeable and proton conductive membrane as well as catalyst layers, where the electrochemical reactions take place. All of these components are prone to degradation. For the commercialization of fuel cell electric vehicles both a cost reduction and the achievement of durability targets is crucial. For the latter, knowledge about degradation mechanisms occurring during automotive PEMFC operation and the ability to detect those is of great importance.

This work contributes to the field by developing methods for an improved automotive failure analysis process as well as by clarifying life-time limiting degradation phenomena. In particular, three main degradation phenomena occurring in polymer electrolyte membrane fuel cells, namely fuel starvation degradation, membrane failure and changes of gas diffusion layer wettability properties are addressed.

In the first part of this thesis, different methods for the detection of membrane failure are evaluated for their application in an automotive fuel cell analysis process. Both model and real fuel cell systems are investigated. Detection via infrared thermography and helium-gas detection enable the spatial localization of membrane defects. Helium-gas detection is found to be more sensitive and less dependent on the material system. Detection via pressure drop and hydrogen crossover measurements are directly implementable at the fuel cell test station but are found to also depend on properties of the material system. The latter two methods do not allow a localization of the membrane defect and are less sensitive. As a result of a comprehensive comparison including detection limits, influence of the material

system and method handling, recommendations for the application of the different methods are given.

Secondly, a method based on cyclic voltammetry to determine wettability properties of gas diffusion layers is tested and adopted for an automotive failure analysis process. This method is important since gas diffusion layers are the key component for the water management within a PEMFC. The specific capacitance of the gas diffusion layer in an electrolyte is used as a measure for the wetted surface area and thus for the wettability properties of the gas diffusion layer. Systematic measurements show a correlation between operational parameters like electrolyte type or penetration time, as well as material parameters like gas diffusion layer morphology and the measured specific capacitance. The validity of the method to detect differences in wettability properties of the gas diffusion layer is demonstrated on several artificially and real automotive operation degraded samples. For a comprehensive understanding, detected changes in measured specific capacitance are correlated to ex situ degradation analysis results. The benefit of the method is shown by a comparison to static contact angle measurements, which reveals a higher sensitivity of the introduced method.

Finally, in the last part of this work, a comprehensive analysis of automotive PEMFC full size stacks is performed. Herein, degradation phenomena being correlated with local fuel starvation are investigated in depth. A degradation mechanism for the formation of geometric displacements of the membrane and for the formation of platinum deposition on top of the catalyst layer is postulated and supported by model experiments. Different degradation phenomena caused by fuel starvation, e.g. carbon corrosion induced cathode catalyst layer thinning, crack formation and catalyst degradation, are correlated. This enables the introduction of a fast indicator method for fuel starvation degradation. This method is applied to two automotive full size stacks being aged in a prototype vehicle and under fuel starvation conditions on a commercial fuel cell test station, respectively. The analysis reveals the heterogeneous distribution of fuel starvation degradation on single membrane electrode assemblies and at different cell positions within the full size stacks. In addition, the developed method for gas diffusion layer wettability detection is used to determine degradation distribution on both automotive full size stacks and is compared to the distribution of local fuel starvation degradation.

In summary, this work shows that method development and the application of the most suitable method can highly enhance a fuel cell analysis process. In addition, the importance of failure analysis and mechanism clarification for fuel cell development and the corresponding contribution to the reduction of greenhouse gas emission, is demonstrated.

Kurzzusammenfassung

Um die globale Erwärmung und die daraus resultierenden Folgen auf ein Minimum zu reduzieren, sind drastische Schritte zur Eindämmung von Treibhausgasemissionen notwendig. Elektromobilität kann und muss hier einen entscheidenden Beitrag leisten. Unter den elektrifizierten Fahrzeugen zeichnen sich Brennstoffzellen-elektrische Fahrzeuge durch eine hohe Reichweite und eine kurze Betankungszeit aus. Die darin eingesetzten Polymerelektrolytmembran-Brennstoffzellen bestehen aus mehreren Komponenten. Die elektrochemische Umsetzung von Wasserstoff und Sauerstoff findet in zwei Katalysatorschichten statt, welche durch eine gasundurchlässige, elektrisch isolierende, aber protonenleitende Polymermembran getrennt sind. Die Gasversorgung der Katalysatorschichten sowie der Abtransport von Produktwasser wird durch Gasdiffusionsschichten sichergestellt. Das Erreichen von Lebensdauerzielen stellt neben der Reduzierung der Gesamtkosten die größte Hürde für die kommerzielle Markteinführung von Brennstoffzellen-elektrische Fahrzeuge dar. Deshalb sind ein tiefgehendes Wissen über Degradationsmechanismen und die Fähigkeit, Degradationen effizient und detailliert zu analysieren, von immenser Bedeutung.

Diese Arbeit zielt darauf ab, einen Beitrag zur Verbesserung von Schadensanalysen im automotiven Bereich zu leisten. Ein besonderer Fokus liegt dabei auf Schäden durch Anodenunterversorgung, Membranschäden und einer Veränderung der Hydrophobizität von Gasdiffusionsschichten.

Im ersten Teil der Arbeit werden verschiedene Methoden zur Detektion von Membranschäden evaluiert und unter besonderer Berücksichtigung der Anforderungen im automotiven Umfeld verglichen. Für die Untersuchung werden sowohl Modellsysteme mit künstlich hergestellten Defekten, als auch Proben mit Membrandefekten aus realistischer automotiver Alterung herangezogen. Die Detektion mittels Infrarotthermographie und mittels Helium-Gas ermöglichen eine Lokalisierung des Defekts in der automotiven Zelle. Dabei ist die Helium-Gas-Methode sensitiver und weniger abhängig von Materialeigenschaften des verwendeten Systems. Die Detektion mittels Druckreduzierung und Wasserstoff-Crossover-Messungen lassen sich direkt am Prüfstand implementieren. Die Messergebnisse sind ebenfalls abhängig von Materialeigenschaften des verwendeten Systems. Sie ermöglichen

keine direkte Lokalisation des Defekts in der Zelle und sind weniger sensitiv. In einer Bewertungsmatrix, die unter anderem die Detektionsgrenzen, den Einfluss des untersuchten Materialsystems sowie die Handhabung berücksichtigt, werden Empfehlungen für den Einsatz der verschiedenen Methoden gegeben.

Im zweiten Teil der Arbeit wird eine Methode zur Bestimmung der Benetzbarkeitseigenschaften von Gasdiffusionsschichten, basierend auf spezifischen Kapazitätsmessungen mittels Zyklovoltammetrie, für den automotiven Schadensanalyseprozess modifiziert und getestet. Die gemessene Kapazität ist abhängig von der mit Elektrolyt benetzten Gasdiffusionsschichtoberfläche und kann daher als ein Messwert für die Benetzbarkeitseigenschaften herangezogen werden. Durch systematische Untersuchungen werden Korrelationen zwischen Versuchsparametern wie Elektrolytzusammensetzung und Benetzungszeit, Materialeigenschaften wie der Morphologie der Gasdiffusionsschicht und der gemessenen spezifischen Kapazität hergeleitet. Durch das Vermessen von verschiedenen, künstlich und real gealterten Proben wird die Fähigkeit, verschiedenste Degradationen zu detektieren, nachgewiesen. Um ein besseres Verständnis der detektierten Schadensarten zu bekommen, werden die Messergebnisse der unterschiedlich gealterten Proben mit verschiedenen ex situ Analyseergebnissen korreliert. Ein Vergleich zu statischen Kontaktwinkelmessungen, einer weit verbreiteten Methode zur Bestimmung der Gasdiffusionsschicht-Benetzbarkeit, zeigt eine erhöhte Detektionssensitivität der eingeführten Methode, was den Mehrwert der Methode nochmals verdeutlicht.

Im dritten Teil der Arbeit werden umfassende Schadensanalysen von automotiven Brennstoffzellenstacks mit anodenunterversorgungsbedingten Schadensmustern vorgenommen. Basierend auf den Ergebnissen von instrumenteller Analyse und Nachstellversuchen wird ein Degradationsmechanismus für die Bildung von Membranverformungen sowie für die Entstehung von Platin-Ablagerungen auf der Oberseite der Kathoden Katalysatorschicht postuliert. Verschiedene Schadensbilder, welche durch Anodenunterversorgung hervorgerufen werden, werden korreliert. Auf der Basis dieser Ergebnisse wird eine Methode zur schnellen Indikation von Anodenunterversorgungsdegradation eingeführt und auf zwei automotiven Brennstoffzellenstacks angewandt, welche unter realitätsnahen Bedingungen, wie beispielsweise im Betrieb in einem Prototypenfahrzeug, gealtert wurden. Die Ergebnisse zeigen den Verlauf der Anodenunterversorgungsdegradation auf Membran-Elektroden-Einheit und Stack-Ebene. Zusätzlich wird die im zweiten Teil der Arbeit entwickelte Methode zur Bestimmung von Gasdiffusionsschicht Benetzbarkeitseigenschaften eingesetzt, um die Degradation der Kathodenkatalysatorschicht und der Gasdiffusionsschicht zu korrelieren.

Die Ergebnisse dieser Arbeit zeigen, dass Methodenentwicklung und die richtige Methodenwahl den automotiven Schadensanalyseprozess entscheidend verbessern kann. Darüber hinaus wird die Bedeutung von Schadensanalyse und Schadensmechanismusaufklärung für die Entwicklung von Brennstoffzellen aufgezeigt.

Preface

The following publications contributed to this thesis:

Paper I

Comparative study of pinhole detection methods for PEMFC degradation analysis

M. Obermaier, K. Jozwiak, M. Rauber, A. Bauer, C. Scheu
Journal of Power Sources, 488, 229405 **2021**

Paper II

Gas diffusion layer wettability determination by cyclic voltammetry for automotive fuel cells

M. Obermaier, A. Bauer, M. Dalkilic, M. Rauber, C. Scheu
Fuel Cells, 21, 221-233 **2021**
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Paper III

Local Fuel Starvation Degradation of an Automotive PEMFC Full Size Stack

M. Obermaier, M. Rauber, A. Bauer, T. Lochner, F. Du, C. Scheu
Fuel Cells, 20, 394-402 **2020**

Paper contributions

Paper I: All co-authors supported M. Obermaier in the conceptualization of the work. M. Obermaier fabricated the test material, constructed the required cell hardware and performed the experimental work. K. Jozwiak supported the measurements on the fuel cell test station. The interpretation and discussion of the data was done by all authors. M. Obermaier wrote the manuscript. All co-authors edited and approved the paper.

Paper II: The concept of the work was done by M. Obermaier with support of all co-authors. Fabrication of the test material was done by M. Obermaier and supported by M. Dalkilic. M. Obermaier and M. Dalkilic performed the CV-measurements. M. Obermaier carried out the ex situ degradation analysis. All authors interpreted and discussed the data. M. Obermaier wrote the paper, which was edited and approved by all authors.

Paper III: M. Obermaier developed the concept of the work which was edited by the co-authors. The ex-situ degradation analysis was done by M. Obermaier. In situ data were acquired by the BMW fuel cell development department. All authors were involved in the interpretation and discussion of the data leading to the postulated degradation mechanism. The manuscript was written by M. Obermaier and edited and approved by all authors.

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List of abbreviations

ACL	Anode catalyst layer
BEV	Battery electric vehicle
BET	Brunauer–Emmett–Teller
BSE	Back-scattered electron
CCL	Cathode catalyst layer
CCM	Catalyst coated membrane
CE	Counter electrode
CL	Catalyst layer
CV	Cyclic voltammetry
Cu	Copper
E	Electrode
EDS	Energy dispersive X-ray spectroscopy
FCEV	Fuel cell electric vehicle
GDL	Gas diffusion layer
GDE	Gas diffusion electrode
HEV	Hybrid electric vehicles
IR	Infrared
MEA	Membrane electrode assembly
MPL	Microporous layer
Nf	Nafion
PEMFC	Polymer electrolyte membrane fuel cell
PI	Polyimide
Pt	Platinum

PTFE	Polytetrafluorethylen
RE	Reference electrode
RHE	Reversible hydrogen electrode
r.h.	Relative humidity
Ru	Ruthenium
SE	Secondary electrons
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
WE	Working electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRM	X-ray microscopy

List of symbols

α	Temperature coefficient of a resistor
ΔH	Reaction enthalpy
ΔT	Temperatur rise above a pinhole
ϵ	Dielectric constant
λ	Wavelength
σ	Stefan-Boltzmann-constant
Φ	Electrical potential
A	Area measured by BET, normalized to the circular measurement area of the CV setup
A_{BET}	BET area
c	Speed of light
C_{DL}	Double layer capacitance
c_E	Electrolyte concentration
C_H	Helmholtz double layer capacitance
C_{GC}	Gouy and Chapman double layer capacitance
C_S	Stern double layer capacitance
C_{spec}	Specific capacitance
d	Pinhole diameter
f_i	Focal distance of optical lens
F	Faraday constant
G	Geometry factor
h	Planck constant
I	Current

I_C	Capacitive current
j	Current density
J	Joule's constant
k_B	Boltzmann constant
l	Distance between condensator plates
L	Electromagnetic spectral radiance
M	Magnification
$Q_{Cond.}$	Outgoing heat flow according to thermal conduction
Q_{Joule}	Heat flow according to Joule heating
R	Universal gas constant
R_f	Filament resistance
R_f^0	Reference resistance at zero degree Celsius
S_i	Distance of object/image from focal plane
T	Absolute temperature
T_1	Temperature of the filament
T_2	Temperature of the cylindrical cell
T_{av}	Average temperature of MEA without pinhole
T_{max}	Maximum temperature on MEA e.g. at pinhole position
z	Charge number of the ions

Chapter 1

Introduction

“We are killing our planet. Let us face it, there is no planet B.” (Emmanuel Macron, 2018)[1]. With this statement the French president pointed out the severe challenge the society has to solve - the threatening climate catastrophe resulting from global warming. Indeed, global warming is “killing” the planet’s biodiversity, as for instance a study investigating 976 species reported that about 47 % of the world’s local extinctions during the 20th century can be ascribed to global warming [2]. In addition, our “planet A” is going to undergo severe changes, as for example the temperature rise of today can lead to the disappearance of about 28 % – 44 % of the present-day glacier volume over the next centuries [3]. In addition to losing the planets diversity, global warming will also have severe effects on global life, ranging from impact on human health and security, supply insecurity, and an impact to the economy [4, 5]. Increasing natural catastrophes like storms, floods or droughts will lead to food and water insecurity as well as to heat-related illnesses, vector-borne and water-borne diseases. In addition, natural catastrophes will lead to population displacement, which could not only result in stress and mental trauma for the climate refugees but also to conflicts and violence [4][5].

Therefore, 197 countries agreed 2016 in the Paris agreement on “holding the increase in global average temperature well below 2 °C above pre-industrial levels” [6]. Despite the agreement, global carbon dioxide (CO₂) emissions further increased until 2019 [7]. The decrease in CO₂ emissions in 2020 is most likely an exception caused by the Covid-19 pandemic [8, 9]. The urgency to act now is additionally shown by the fact, that the last five years have been the hottest years on record [10].

In order to still meet the goal of the Paris agreement, the emission of greenhouse gases like CO₂ has to be drastically reduced. According to the international energy agency, about 25 % of global CO₂ emissions, about 29 % of CO₂ emissions in the European Union and about 23 % of CO₂ emissions in Germany are caused by

transportation (status 2017) [11]. Therefore, many countries are aiming to strongly reduce the CO₂ emissions of the transport sector. For instance, the goal of the German government is to have an almost carbon free transport system by the year 2050 [12]. By the year 2030, the CO₂ emission of the transportation sector should be decreased by around 40 % compared to the emissions of the year 1990 [13]. The fact that traffic numbers will still increase in the future makes this goal even more challenging [14, 15].

Within the transport sector most CO₂ emissions are caused by road transportation. For instance, in the European Union this share is 72 % [16]. In order to reduce the CO₂ emissions of the traffic sector, transportation has to be shifted to rail and ship. In addition, public transportation has to be enforced and low and zero emission road transport has to be increased. The European Union aims to reduce the car-fleet emission targets by 15 % and 37.5 % for the years 2025 and 2030, respectively, compared to the 2021 target. Similarly, the van-fleet emission targets should be reduced by 15 % and 31 % for the years 2025 and 2030, respectively, compared to the 2021 target [17].

In this context, electromobility is considered as a key development to enable a reduced carbon footprint in the transportation sector [18]. In general there are three types of electrified vehicles, namely hybrid electric vehicles (HEVs), battery electric vehicles (BEVs), and fuel cell electric vehicles (FCEVs) [19–21]. Hybrid electric vehicles use both a conventional and an electric powertrain. Depending on the vehicle type, an electric engine is used to support the combustion engine or to drive the vehicle fully electric for a limited distance. Among HEVs, plug-in hybrid electric vehicles are able to recharge the battery by an external current source and are thus able to drive fully electric with energy from the electric grid without using gasoline. Battery electric vehicles use electric energy stored in batteries to power an electric engine without possessing a combustion powertrain. The capacity of the battery, which defines the driving range, allows longer full electric driving than plug-in hybrid electric vehicles. Additional range extenders, which exemplarily generate electricity from gasoline, can be used to extend the driving range. Finally, FCEVs complement the electrified vehicles. They use a polymer electrolyte membrane fuel cell (PEMFC) to convert chemical energy stored in hydrogen to electric energy to power an electric engine. To increase the power output, several hundreds of PEMFCs, form a fuel cell stack. FCEVs possess large driving ranges (> 500 km) and short refueling times (< 8 min) [22]. In particular for heavy vehicles, fuel cells offer a weight advantage compared to energy storage in batteries. This makes fuel cells especially interesting for an emission free powertrain for trucks, buses and heavy passenger cars like sport utility vehicles [23]. The overall efficiency of FCEVs is however lower than for BEVs. As for BEVs, a green mobility with FCEVs is only possible when electricity from renewable energy sources is used for hydrogen production via water electrolysis. The most probable scenario of a future low-emission mobility is a combination of all mentioned electrified vehicles, wherein BEVs are more appropriate for short range drives and low weight vehicles while FCEVs are

more suitable for long range drives and heavy weight vehicles [22, 23].

While BEVs are already mostly commercialized, FCEVs are not yet launched as series vehicles. Only a few car manufacturer have small-series vehicles (Toyota Motor Corporation, Hyundai Group, Honda Motor Company Ltd, Daimler AG) [24], or are planning to launch them in the near future like the BMW Group [24, 25]. Most important milestones for the commercialization of FCEVs are both a cost reduction and the fulfillment of durability targets [22]. Regarding costs, membrane electrode assembly (MEA) costs of a PEMFC are projected to decrease with increasing quantity. Therefore, especially the costs of the fuel cell system have to be lowered in addition to a reduction of the catalyst costs [22]. Besides costs also the durability of the fuel cell system has to be increased to meet the requirements of a typical vehicle lifetime of about 6000 h to 7000 h. [26]. Durability targets of the European Fuel Cells and Hydrogen Joint Undertaking for the fuel cell system of light duty vehicles are given by 5000 h, 6000 h and 7000 h for the years 2020, 2024 and 2030, respectively. Durability is hereby defined as the time passed until 10 % of power degradation is reached [26]. The fuel cell system of buses are targeted to outlast 20000 h, 24000 h and 28000 h by the years 2020, 2024 and 2030, respectively. Similar targets are also established by the United States Department of Energy [27] and the Chinese society of automotive engineers [28].

In order to improve the fuel cell durability, failure analysis is of great importance and is therefore widely addressed in literature [29–41]. Degradation phenomena range from the stack-level down to the micro- and nanometer scale. Accordingly, for an optimized failure analysis, different methods have to be developed and adopted to automotive applications.

1.1 State-of-the-art fuel cell analysis

State-of-the-art fuel cell analysis typically combines several methods ranging from in situ methods like electrochemical techniques to ex situ characterizations like microscopic and spectroscopic techniques. Depending on the degradation phenomena under investigation, different characterization techniques are suitable. A detailed description about different analysis methods is given in literature [29–31], wherefore only the most important methods are introduced in this section. Microscopic techniques like optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to investigate morphology changes from the micro- to the nanometer scale. Cryo cross section polisher enables herein the preparation of suitable cross-sections [42, 43]. Insights to catalyst characteristics can be accessed via X-ray diffraction (XRD), enabling an estimation of the catalyst crystallite size and crystal structure [29, 30]. Different spectroscopic techniques like energy dispersive X-ray spectroscopy (EDS) or X-ray photoelectron spectroscopy (XPS) are used for the determination of the elemental composition [29, 30]. The composition can also be evaluated by thermogravimetric analysis and

inductively coupled plasma mass spectroscopy. Information about surface area and porosity can be obtained by gas-adsorption and mercury porosimetry measurements [44–49]. In addition, several electrochemical characterization techniques exist [29–31]. For instance, the electrochemical active surface area of the catalyst in the cell can be estimated by cyclic voltammetry or CO-stripping. The hydrogen crossover within a cell can be accessed by linear sweep voltammetry.

For automotive fuel cell development, a continuous development of characterization techniques to improve the detectability of degradation phenomena as well as to increase the analysis efficiency is crucial. In addition, methods are adopted and optimized for automotive applications. For example, segmented current density measurements [30, 31, 50], which enable the spatially resolved determination of e.g. current density and temperature, are adopted to automotive applications of large-scale PEMFCs by several authors [51–55]). Another example of the adoption of a state-of-the-art measurement technique to automotive fuel cells and fuel cell stacks is given by electrochemical impedance spectroscopy [56–58]. This method allows the calculation of different MEA properties like membrane resistance, charge transfer resistance, double layer capacitance or diffusion resistance by applying appropriate impedance models.

Besides the adaption of methods to automotive application the development of new methods is also crucial in fuel cell degradation analysis [59]. In the field of electrochemical characterization, several techniques based on electrochemical impedance spectroscopy were developed, including total harmonic distortion analysis [60–62], distribution of relaxation time [63], techniques analyzing at single frequencies [56, 57] and differential impedance analysis [64]. The analysis of single frequencies instead of a whole frequency band enables herein a fast in situ diagnostic of single cells and stacks, which is in particular important for application in FCEVs.

A first example in the field of ex situ techniques is given by the development of a non-destructive optical microscopy test method for a quick and reliable quantitative characterization of catalyst layer defects is highly promoting MEA manufacturing [59]. Another method development that led to a better understanding of degradation phenomena is given by three-dimensional electron tomography. It was introduced in the field of fuel cell characterization to improve the understanding of how the morphology of catalyst nanoparticles is changing during accelerated stress tests [65–68]. Herein, three-dimensional transmission electron microscope tomography was applied exemplarily to reveal the morphology of platinum/ ruthenium (Pt/ Ru) catalyst nanoparticles before and after potential cycling [68]. In combination with results of cyclic voltammetry it was concluded that dissolution/ dealloying of the catalyst particle was the main catalyst related degradation mechanism during start/stop operation.

The benefit of method development is additionally shown by the technique of X-ray computer tomography enabling MEA imaging while being non-destructive. An improvement of the method was for instance performed by acquiring tomograms

without sample cutting [69]. Further development allowed to separate the different material phases [70, 71]. Applied in failure analysis, X-ray computer tomography allowed, among others, the analysis of membrane failures such as layer thinning or crack formation [72–74].

Method development was also applied to improve the determination of wetting behavior of the gas diffusion layer (GDL) surface. Hydrophobic properties of GDLs can be accessed by several methods [75–81], where static contact angle measurements are widely applied [80, 81]. They possess however only low sensitivity [81]. A sensitivity improvement was for instance made by the introduction of sliding angle characterization [81–83]. A further technique with improved sensitivity compared to static contact angle measurements is the determination of wetted surface area by cyclic voltammetry as demonstrated for carbon cloth material under acidic conditions [84–86]. Due to the importance of GDL wettability determination this technique is characterized and adopted to an automotive fuel cell analysis process in this study.

Due to this wide range of method development, often a variety of different analysis methods exist for the characterization of specific degradation phenomena, each possessing different advantages and drawbacks. For instance, membrane defects can, among others, be detected by pressure drop tests [87–89], hydrogen crossover measurements [89–96], relaxometry [88], infrared-thermography (IR-thermography) [34, 87, 90, 92–94, 97–99], detection of a test gas [100] or impedance spectroscopy [92, 96]. For an efficient and detailed analysis, the selection of the most appropriate method according to the requirements is crucial. Therefore, comparative studies of different methods are very beneficial. A comparison of different techniques for the detection of membrane defects used in automotive applications is performed in this work.

Method development and a proper selection of the analysis techniques both aim to enhance the fuel cell analysis process targeting to correlate observed degradation phenomena to underlying reasons and thus to reveal the degradation mechanism. Several studies performed degradation analysis on differently sized single PEMFC and PEMFC stacks [101–113]. However, only few studies exist on the degradation analysis of automotive size stacks [111–115]. An analysis of the whole stack is however important since altered degradation patterns can occur throughout the automotive stack due to different operation conditions and stack dimensions. Therefore, failure analysis of an automotive full size stack including the revealing of specific degradation mechanisms is also in the focus of the present work.

1.2 Objective of the thesis

The aim of this thesis is to reveal life-time limiting degradation mechanisms for automotive scale PEMFCs and PEMFC stacks as well as to develop and adapt methods for an improved automotive failure analysis.

One major cause of fuel cell failure is membrane degradation [32, 33, 35, 37, 38, 116]. Several different methods exist to determine membrane defects like pinholes or membrane thinning but a systematic comparison of various techniques for automotive size cells is mostly missing. As a central part of this thesis, different methods for the detection of membrane defects are adopted to automotive applications and compared to each other. Since the determination of membrane defects in the beginning state and the detection of defects on different degraded and non-degraded material systems is crucial, a special focus is put on the influence of the material system. In addition, the minimal detectable pinhole sizes and the applicability for automotive fuel cells is addressed.

Another degradation phenomena leading to severe performance loss is the increase of the gas diffusion layer wettability [36, 39, 83, 117], which is addressed in the second part of this thesis. A sensitive measure for changes in GDL wettability is the capacitance between the GDL and an electrolyte, which is determined by cyclic voltammetry. In this thesis the method is modified and adapted to be used in an automotive fuel cell analysis process. For a comprehensive understanding of the method, the correlation between operational or material parameters (e.g. electrolyte type, penetration time, GDL morphology and surface structure) and measured specific capacitance is investigated. The detection of different kinds of GDL degradation is crucial for the applicability of the method in an automotive fuel cell analysis process. Therefore, different artificially and real-operation aged GDLs are analyzed with both the introduced method and different ex situ analysis techniques. Finally, the benefit of the method with regard to sensitivity is examined by a comparison to static contact angle measurements.

In the last part of the thesis, fuel starvation degradation, as a third severe degradation phenomena [32, 36, 39] is investigated. For this purpose, two automotive full size stacks, being operated in a prototype vehicle and under automotive driving conditions at a test station, respectively, are analyzed. Fuel cell development requires a deep understanding of the degradation phenomena and its underlying degradation mechanism. Therefore the different degradation phenomena on the catalyst coated membrane are characterized and explained in detail. In particular, the aim is to postulate a degradation mechanism of a type of catalyst degradation, which has not been reported in literature up to date. As conditions on cell and stack level can highly influence degradation, knowledge about the distribution of degradation on single cells and within the stack is important. This leads to a better understanding of the degradation development and of the influence of stack and cell parameters. Full size stacks consist of several hundreds of cells, wherefore an analysis of the distribution of fuel starvation degradation within the stack is very time-consuming. Therefore, a fast indication method for fuel starvation degradation on the stack level is developed and applied to two automotive full size stacks being aged under realistic automotive conditions.

Chapter 2

Fundamentals of automotive PEMFCs and their degradation phenomena

In the following chapter the fundamental basics of fuel cells and their degradation are presented. Specifically, the components of FCEVS with special regard to automotive PEMFCs are described. The function of different PEMFC stack components is explained and an overview of their degradation is given. Herein, conditions leading to the observed degradation phenomena are discussed. More information about fuel cells can be found in [29, 118–120] and a more detailed description of fuel cell degradation is given in [29, 32–41, 116, 118, 121–124].

2.1 Structure of Fuel cell electric vehicles and PEMFCs

Fuel cell electric vehicles consist of several components [18, 20, 21, 125–127]. Its structure is illustrated in figure 2.1. FCEVs are driven by an electric engine, being supplied with electricity from the fuel cell system. Herein, chemical energy stored in hydrogen is electrochemically converted to electrical energy. Excess heat is dissipated by a cooling system. The hydrogen is usually stored in a gas tank with an absolute pressure of up to 70 MPa [18, 21, 126]. Hydrogen tanks typically consist of a metallic or polymer inlet, which is supported by carbon fibers [20, 126, 127]. The fuel cell system is composed of a fuel cell stack and additional periphery like compressors, humidifiers, electrical units and controllers, which are necessary to run the stack at high performance. A high-voltage battery is used to store electrical energy or to provide additional electric energy [18, 20, 21, 125, 127]. An automo-

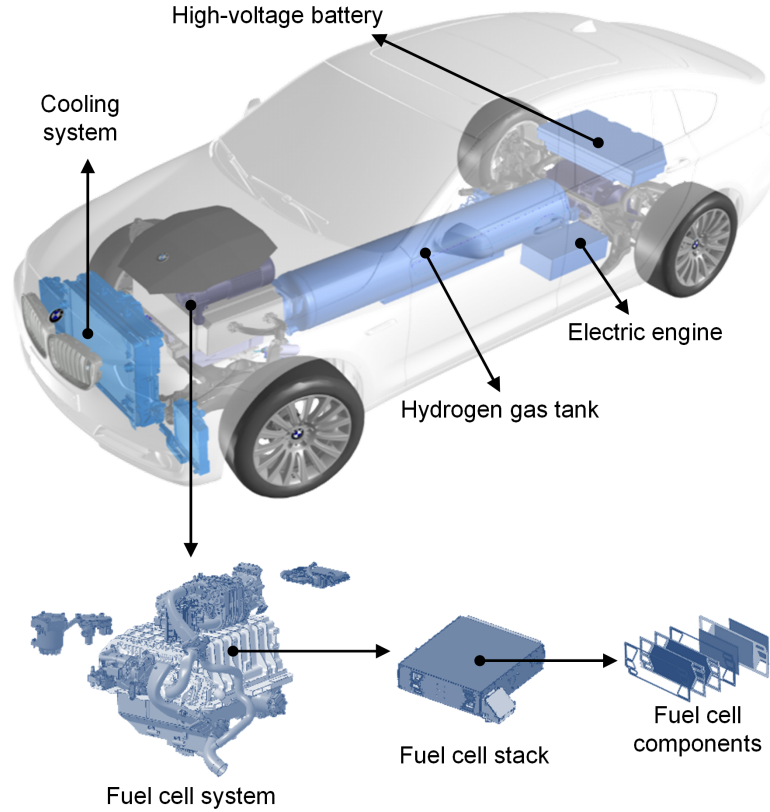


Figure 2.1: Schematic of a fuel cell electric vehicle. The fuel cell system is powering an electric engine and can be supported by a high-voltage battery. Within the fuel cell system, several PEMFCs forming a fuel cell stack convert ambient air and hydrogen from a gas tank to water and electric energy. Excess reaction heat is radiated to the ambient by a cooling system. Image modified after [128].

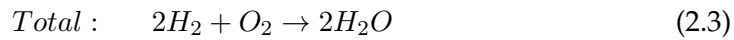
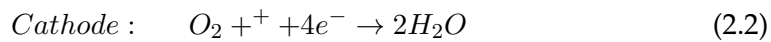
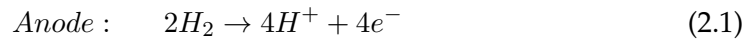
tive fuel cell stack, being the central part of the fuel cell system, consists of several hundreds (> 350) of single low-temperature PEMFCs possessing an active area of approximately 300 cm^2 [18, 21, 54, 126]. As illustrated in figure 2.2, PEMFCs are made up of several components [31, 120].

Metallic bipolar plates are used as flow fields to distribute the reaction gases and the coolant over the cell. Within a stack, the bipolar plates distribute fuel (anode) and air (cathode) at the opposing sides of the bipolar plate [127]. In the middle of the bipolar plate, a coolant, usually a water-glycol mixture, is supplied to control the temperature of the cell. In addition, bipolar plates serve as current collectors. Membrane electrode assemblies (MEAs), as shown in figure 2.2 are placed in be-

tween two bipolar plates. They enable the conversion of hydrogen and oxygen to water and electricity. MEAs consist of gas diffusion layers, electrodes and a polymer membrane [31, 120] and are usually laminated into a subgasket, which serves as sealing point and electrical insulator between two bipolar plates.

Gas diffusion layers serve for a homogeneous gas supply and a good water management at the active area. In addition, they need to have good thermal and electrical conductivity to ensure low ohmic losses and a homogeneous temperature distribution [31, 120]. As shown in figure 2.2, they usually consists of a substrate like carbon paper or carbon cloth and a microporous layer (MPL) applied onto it. For good water removal properties, GDLs are usually treated by an hydrophobic agent like polytetrafluorethylen (PTFE) and are morphologically optimized for appropriate water management [129].

Electrochemical reactions take place at the anode and cathode electrodes, which are separated by a proton conducting, but gas impermeable and electrical insulating polymer membrane, like Nafion [31, 120]. As illustrated in figure 2.2, each electrode, consists of a porous structure of ionomer and catalyst particles, which are distributed on a carbon support. Therefore, electrodes are also referred to as catalyst layers (CLs). Anode and cathode electrodes are also named anode catalyst layer (ACL) and cathode catalyst layer (CCL), respectively. For electrochemical reactions a three-phase boundary has to be present at the catalyst particle. This three-phase boundary, determining the electroactive area, is formed by electron conducting porous carbon support, proton conducting ionomer and reaction gas within the pores. To increase the electrochemical active surface area, nanostructured catalyst particles are often used. As shown in equation 2.1, hydrogen is oxidized at the anode. Protons are then migrating through the membrane to the cathode where oxygen from the air is reduced and water is formed (see equation 2.2). The total reaction is shown in equation 2.3. Under standard conditions (1.0 atm, 25 °C) the electrode potential of the O_2/H_2O redox couple is 1.23 V versus standard hydrogen electrode [31].



If the two CLs are applied to the membrane, they form the so-called catalyst coated membrane (CCM) [31, 120]. Another approach is to apply the CLs to the GDL to form gas diffusion electrodes (GDEs).

Fuel cell performance, which is often correlated to the obtained power density output, can be increased by several factors including cell geometry, humidity, temperature and pressure of the reactant gases [37, 130–138]. For instance high humidification leads to enhanced proton conduction of the ionomer and can also lead to an increase in electrochemically active surface area of the CL. However, accumulation of water and the corresponding blockage of active sites has to be avoided. Therefore, the operating conditions have to be chosen carefully.

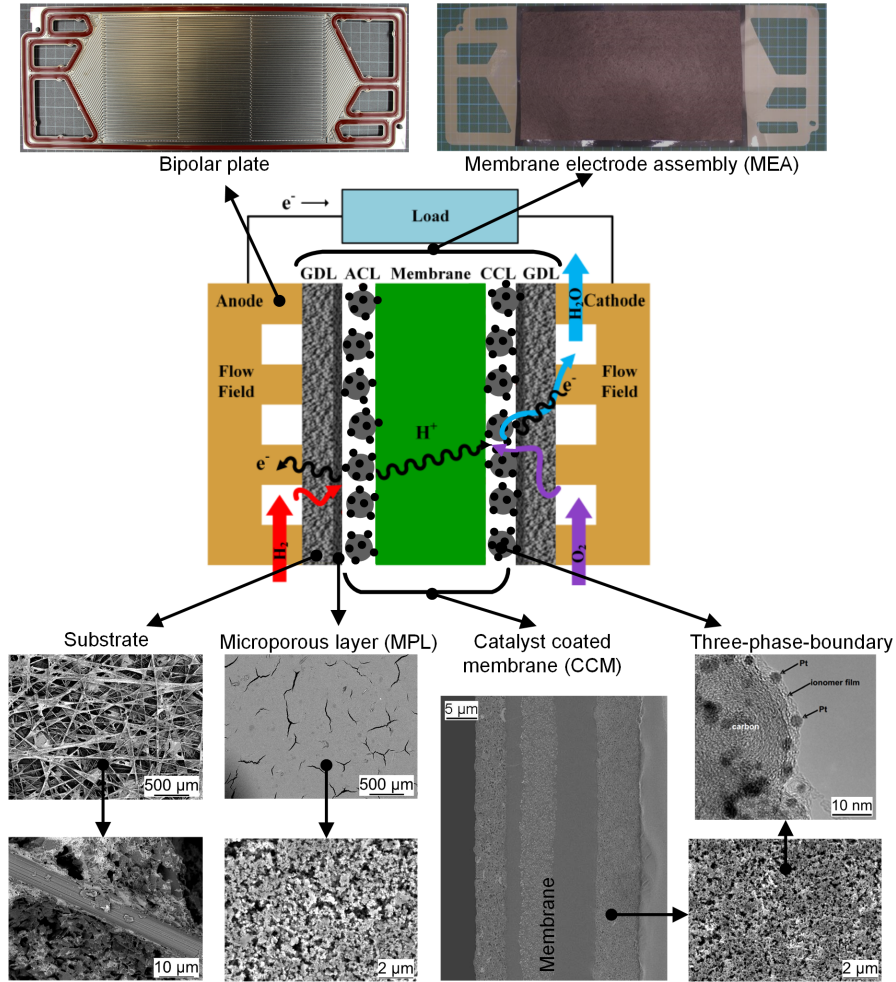


Figure 2.2: Schematic of different components of a PEMFC. Photographs of a bipolar plate and a MEA [51, 52] are shown as well as SEM micrographs of a GDL substrate, of a MPL and of a CCM. In addition, higher magnifications of a GDL fiber and the porous structure of a MPL and of a CCL are shown. A TEM micrograph, modified after [139], shows a three-phase boundary at the Pt-catalyst particles consisting of electron conductive carbon, proton conductive ionomer and gas permeable pores.

2.2 Overview of fuel cell degradation phenomena

Automotive PEMFC stacks are complex systems, which are prone to several kinds of failures. The different failure modes range from the stack level down to the microscopic level. Depending on the applied operation conditions, different degradation mechanisms occur for individual components. Figure 2.3 gives examples for different degradation phenomena on the stack, MEA and material level. The stack

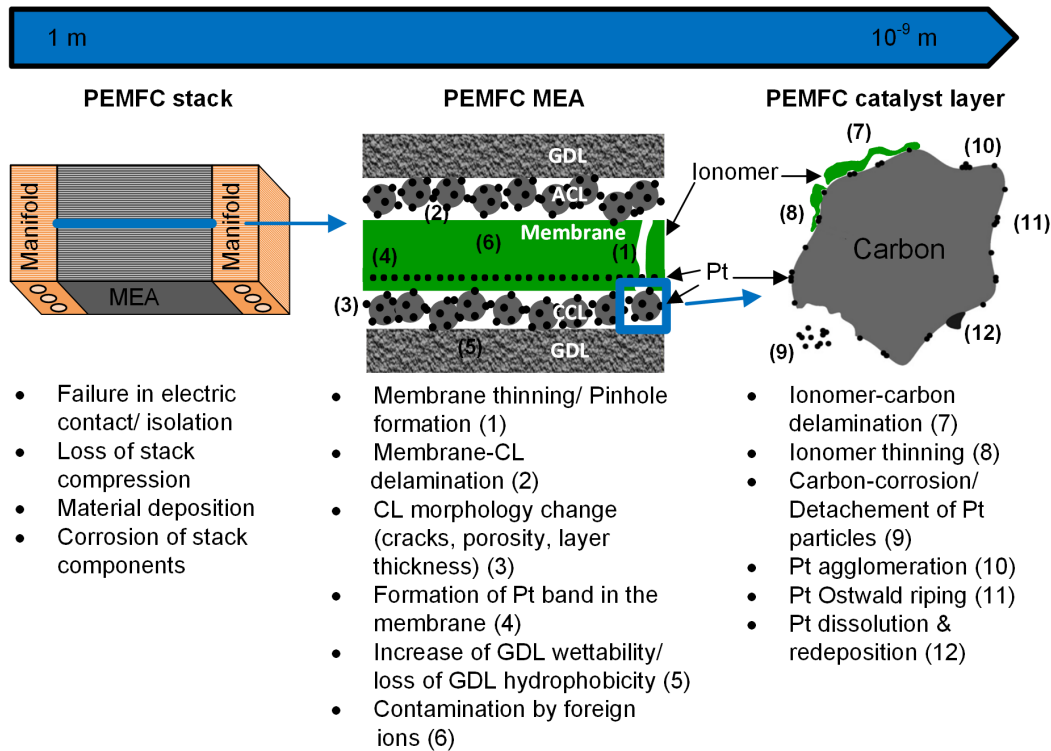


Figure 2.3: Overview of some important degradation mechanisms in PEMFCs on stack level (left), MEA level (center) and material level (right). Image on the right is modified after [122]. The blue line on the left side indicates the position of a single MEA in the stack. A cross-section of the MEA is given in the center and an individual carbon support particle with Pt catalyst is shown on the right.

is prone to electrical failures such as short-cuts or electrical insulation defects. In addition, corrosion or redeposition of material stemming from other components can be observed on e.g. casing, bipolar plates, current collectors or media ports. The components of the MEA suffer e.g. from morphology changes like crack and hole formation, material loss or thinning, delamination between different components or change of material properties. In particular for high performance automotive applications, cells are liable to fuel starvation degradation [32, 36, 39] resulting in severe carbon corrosion and degradation of the catalyst. Fuel starvation degradation occurs, when the active sites of the anode CL are undersupplied by hydrogen. It is therefore highly correlated to water removal properties of the GDL [36, 140–145]. In addition, membrane degradation, including thinning and pinhole formation, is also considered as a major failure mode limiting fuel cell durability [32–34, 38, 116, 146]. In the following GDL, membrane and CL degradation will be described in more detail.

2.2.1 Degradation of the membrane and the ionomer

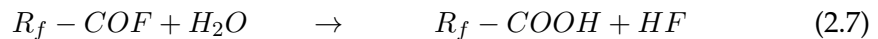
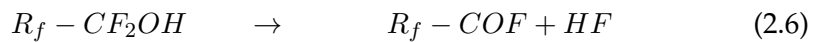
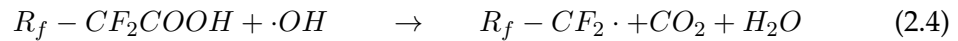
Within the MEA, the ionomer in the membrane serves for electrical insulation and gas separation between the two electrodes, while providing protonic conductivity. In the CL the ionomer provides protonic conduction, which is relevant for the formation of an electroactive three-phase boundary. According to its different requirements, ionomer degradation ranges from loss of electrical insulation and proton conductivity to mechanical failures resulting e.g. in the loss of gas separation properties of the membrane. All of these degradation phenomena are highly performance relevant [32, 33, 35, 37, 38, 116]. Decreased protonic conductivity of the ionomer leads to a performance reduction due to ohmic losses. Reaction gases being directly combusted due to gas separation failure of the membrane lead to efficiency losses. Membrane degradation can be classified in chemical, mechanical and thermal degradation [38, 120]. In addition, degradation due to contamination can occur. These different types of degradation are briefly discussed in the following.

2.2.1.1 Contamination with foreign ions

The presence of foreign ions like metal cations, that originate from degradation of metal components of the fuel cell system like bipolar plates, tubes, humidifiers or catalyst particles, lowers the proton conductivity of the ionomer [147]. Furthermore, the hydration state of the membrane is lowered due to the presence of metal ions [148–150], which additionally reduces the proton conductivity. Finally, metal ions can accelerate the chemical decomposition of the ionomer [147].

2.2.1.2 Chemical decomposition

Chemical decomposition of the polymer occurs due to attack of hydroxyl- or hydroperoxyl-radicals at the polymer endgroups with residual hydrogen-containing terminal bonds [151]. Hydroxyl and hydroperoxyl-radicals are formed by decomposition of hydrogen peroxide. The latter originates from the direct reaction of hydrogen and oxygen at catalytic sites of the electrode or at a catalyst band in the membrane. Another formation path of hydrogen peroxide is given by oxygen oxidation at potentials < 0.695 V [152]. According to equation 2.4 to 2.7 one decomposition cycle leads to the formation of a new -COOH group, which is again prone for another radical attack. Thus, decomposition leads to a complete “unzipping” of the polymer chain [32].



Chemical decomposition is increased by increasing hydrogen peroxide formation, which is directly correlated to the gas crossover through the membrane. Several

conditions lead to an increased gas crossover including membrane thinning, membrane pinhole and crack formation, increased gas partial pressures at the catalytic sites [153, 154], high voltages close to open circuit voltage [155–157], high temperature [155] and low relative humidities [155, 156, 158, 159]. In addition, the contamination with foreign metal ions is supposed to increase the hydrogen peroxide formation resulting in increased chemical degradation [120]. Therefore, also high relative humidities can accelerate the chemical decomposition of the ionomer by promoting the formation of metal ions, which originate from metallic fuel cell components [151].

For a more detailed description of the chemical decomposition the interested reader is referred to [147].

2.2.1.3 Mechanical degradation

Mechanical membrane degradation is a stress-induced process. When the applied stress exceeds the yield strength of the membrane, membrane deformation occurs [32], which can lead to local membrane thinning or pinhole and microcrack formation [147, 160]. The mechanical properties of the membrane can be altered by chemical and thermal degradation processes [147]. Low relative humidities make the membrane additionally brittle and fragile [38, 161–165].

Stress can be induced by several factors. Changing relative humidity leads to swelling and shrinkage of the membrane, thus introducing a mechanical stress in the membrane [99, 166, 167]. A similar but less pronounced effect is given for temperature changes. Mechanical clamping induces additional mechanical stress. Furthermore, differential pressure between anode and cathode leads to mechanical stress at the membrane [147]. Local peaks of the membrane stress can occur e.g. due to nonuniform current distribution [168, 169], non-uniform membrane hydration [170, 171] and non-uniform contact areas due to bipolar plate channels and ribs [120, 163, 172, 173]. Thus, the degradation state of the membrane often varies at different positions within a single CCM.

Besides membrane deformation, mechanical membrane degradation can also occur due to membrane puncturing [32] e.g. by fibers of the GDL substrate.

An improvement of mechanical stability of the membrane can for instance be achieved by the introduction of a PTFE reinforcement [166, 167].

2.2.1.4 Thermal degradation

Low temperature polymer membranes are designed to be stable in an operation range below 100 °C. Therefore, local temperature rises during operation can lead to severe membrane damage. Increased temperature (> 100 °C) can result from poor stack and cell cooling, increased current densities or small membrane defects allowing a direct combustion of hydrogen and oxygen at the catalyst sites. Pinholes in the membrane can result in a self-worsening effect. The defect size can be increased by the thermal input, leading to an increased gas crossover, which will

again lead to a further temperature rise, resulting in additional membrane degradation. This can finally lead to fatal membrane failure.

The membrane is prone to different thermal degradation mechanisms. Temperature induced dehydration of the membrane could lead to condensation of two sulfonic acid groups, lowering the proton conduction [147]. In addition the condensation of two sulfonic acid groups is a possible source of radicals leading to chemical membrane degradation [174]. Secondly, temperatures above the glass transition temperature of the polymer (110 °C) lead to a rearrangement of the polymer, resulting in a morphology change of the membrane [175, 176]. Finally, thermal decomposition of the polymer is reached at temperatures around 250 °C [38, 177, 178].

2.2.2 Degradation of the gas diffusion layer

Within a MEA, GDLs serve for electrical conduction between CL and bipolar plate, distribution of reactant gases and water management. Thus, they are a highly performance relevant component [179, 180]. Good water management means both water removal to prevent CL flooding and the prevention of dehydration of the membrane [181]. Reduced mass transport properties and corresponding fuel cell flooding due to GDL hydrophobicity loss, e.g. caused by a decreased PTFE content, lead to a performance loss of the cell as found by several groups [38, 103, 120, 182, 183]. In addition, degradation induced morphology changes at the GDL can also lead to a cell performance loss by altering electric conduction, water removal and permeability properties of the GDL [182, 184–186].

GDL degradation can be separated in mechanical and physicochemical degradation [129]. Mechanical degradation like fiber breakage, crack and void formation, altered porosity and PTFE detachment are usually caused by GDL compression, freeze/thaw cycles and gas-flow erosion. This can lead to changes in electrical conductivity, mechanical strength and water management properties [181]. Likewise physicochemical degradation due to carbon corrosion and dissolution can also alter the electrical, mechanical and water management properties by surface oxidation, detachment of PTFE and morphology changes [129, 181]. In the following the most common failure modes are discussed.

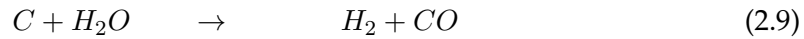
2.2.2.1 Compression of the gas diffusion layer

On the one hand, GDL compression is improving the contact between single fibers and the contact to the CL and bipolar plate. Thus, the MEA performance is increased by reducing the electrical through-plane resistance [187, 188]. In addition, the contact resistance between bipolar plate and GDL is reduced [188]. However, on the other hand, GDL compression is found to decrease the permeability [187–189], and hydrophobicity [190–192] of the GDL. Underlying degradation patterns are fiber breakage [190, 193], a decrease in surface roughness and crack formation

[190], as well as fracture and detachment of PTFE coating [193, 194]. In particular, cyclic compression leads to severe degradation of the GDL [129, 190].

2.2.2.2 Carbon corrosion

In general, carbon corrosion describes the oxidation of carbon to carbon dioxide or carbon monoxide as described in equations 2.8 and 2.9 [122]:



The reaction is thermodynamically possible at a potential of 0.2 V vs. reversible hydrogen electrode (RHE), but a considerable oxidation does not occur below a potential of 0.6 V vs. RHE [195]. High electrode potentials can in particular be reached during start/stop operation or during reactant starvation [34, 124, 196]. Besides an increasing potential, the reaction rate increases with increasing temperature [197, 198] and increasing relative humidity [33, 199, 200]. In addition, oxidizing agents like hydrogen peroxide can also lead to severe carbon corrosion [201]. Carbon corrosion is accelerated by the presence of catalyst particles or metal ions like Pt^{2+} [202], which is one reason why the MPL is more prone to carbon corrosion degradation than the GDL substrate as it can be in direct contact to Pt particles of the CL and can be reached more easily by diffusing Pt-ions from the CL [85, 203]. Decreased hydrophobicity properties of the GDL [204] can e.g. be correlated to carbon corrosion induced PTFE detachment [85, 202]. Water removal properties can be additionally altered due to morphology changes [205] like a porosity increase of the GDL, resulting in an enhanced space for water accumulation [85]. Deteriorated mechanical and electrical properties after carbon corrosion induced mass loss are found due to macropore formation, a loss of bonding strength between carbon fibers of the substrate and the MPL, and a decreased fiber thickness [204, 206]. Finally, also a decrease of gas permeability properties of the GDL is found due to carbon corrosion degradation [204].

2.2.2.3 Other kinds of gas diffusion layer degradation

Additional GDL degradation can be caused by freeze/thaw cycles, gas erosion or dissolution.

Mechanical stress during freeze/thaw cycles due to volume expansion of freezing water is found to damage PTFE coating and binder, leading to increased electronic conductivity, but decreased gas permeability [207].

In addition, the narrow channels of the bipolar plate lead to high gas velocities causing erosion of the GDL material in particular in the presence of liquid water [129]. As described by several authors, gas erosion can lead to material and hydrophobicity loss [208, 209] by damaging the MPL [210] e.g. due to crack formation.

Finally, prolonged water exposure of the GDL can lead to dissolution of the carbon material [205, 209, 211], and the formation of hydroxides and oxides on top of carbon fibers and on top of the microporous carbon network of the MPL [211–213]. This results in both morphology changes and a decreased hydrophobicity [205, 209, 211, 214]. Material loss as observed by several authors [205, 209, 211] can not only lead to altered mechanical and electrical properties but also to an altered water management of the GDL [186, 205, 209, 211, 214]. Typical degradation phenomena are increased porosity [186, 205], crack formation [129], and a damaging and a loss of PTFE [215–217], wherein the latter is still under debate [205].

2.2.3 Degradation of the catalyst layers

Electrochemical reactions during fuel cell operation take place at the CL. Therefore, CL degradation is very critical for PEMFC performance and durability [32–34, 36, 39, 122–124]. A reduction of the electrochemical active area can occur due to several reasons, as depicted in figure 2.4.

Firstly, the electrochemical active area can be reduced by a decrease of the geometric surface area of the catalyst particle by dissolution, Ostwald ripening, particle agglomeration and particle coalescence [29, 32, 65, 123, 218, 219]. Secondly, a detachment of catalyst particles from the electric conductive carbon support or from the proton conductive ionomer can cause a decrease of the electrochemical active surface area. Finally, a reduced electrochemical active surface area can be established by catalyst poisoning, which can occur due to surface adsorption of impurities like CO, S, NO_x or Cl [220, 221].

In the following, the most dominant CL degradation phenomena are explained in more detail. An in-depth investigation of CL degradation of two automotive full size stacks is described in chapter 6.

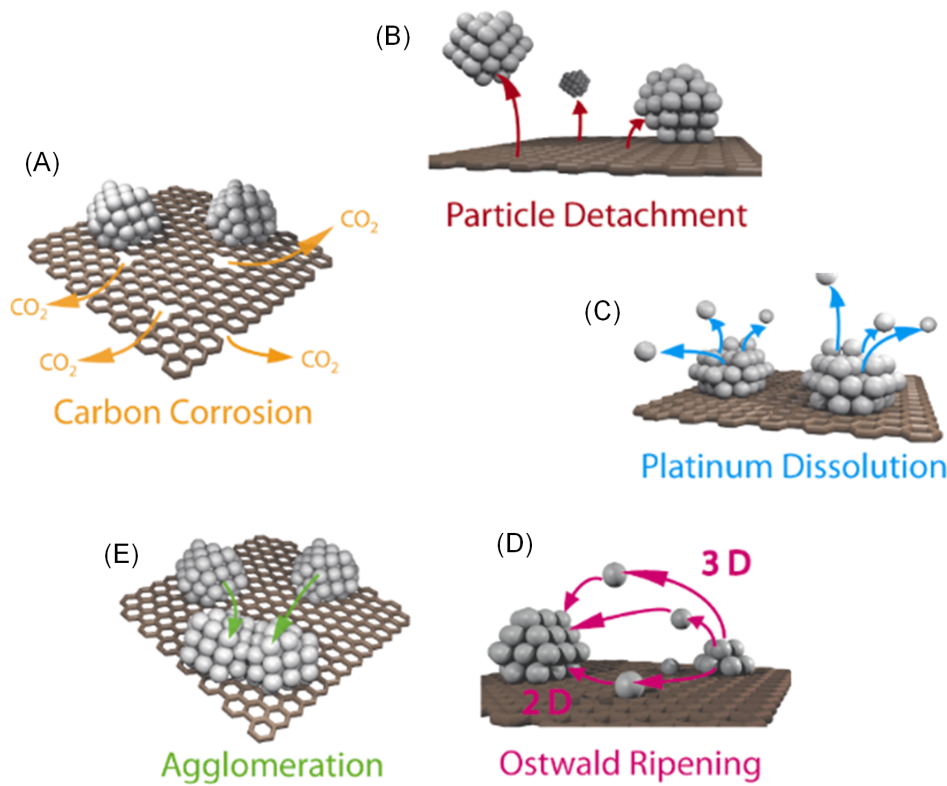


Figure 2.4: Illustration of different CL degradation mechanisms. (A) Carbon corrosion, (B) particle detachment, (C) platinum dissolution, (D) Ostwald ripening, (E) particle agglomeration. The image is modified after [218].

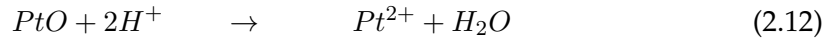
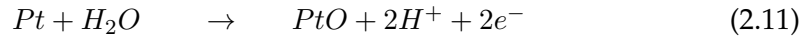
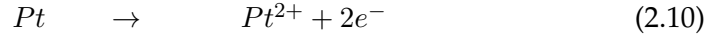
2.2.3.1 Carbon corrosion

Carbon corrosion of the CL, as illustrated in figure 2.4 (A), follows the same reaction as explained in section 2.2.2.2. This leads to different degradation phenomena. Catalyst layer thinning and crack formation decrease the electrical conductivity of the CL [222]. In addition, a collapse of the CL resulting in a loss of porosity leads to a severe decrease in gas permeation [34].

Besides morphological changes, carbon corrosion can also induce the detachment of catalyst particles from the carbon support (see figure 2.4 (B)), which leads to a loss of active sites [223]. In addition, the formation of surface oxides results in an increased hydrophilicity of the CL, which can lead to CL flooding and decreased gas permeability of the CL [34, 224, 225]. It has to be mentioned here that the extend of the degradation is dependent on the carbon support used, wherein graphitized carbons are less prone to oxidation degradation as compared to amorphous carbons [199].

2.2.3.2 Catalyst dissolution and Ostwald ripening

Catalyst dissolution (see figure 2.4 (C)) occurs at elevated potentials (> 1.0 V vs. RHE [32]) due to both a direct oxidation (see equation 2.10) and an oxidation with an intermediate surface oxide (see equation 2.11 and 2.12) [226–228]:



The dissolution rate depends on the pH value, the temperature, the humidity as well as on the amplitude and dynamics of the applied potential [29, 226, 229–234]. After dissolution Pt-ions are free to migrate. Platinum-ions being dissolved in water can be washed out and can then be found in the fuel cell excess water [235]. In addition, Pt-ions are able to migrate within the ionomer and are deposited when being reduced by hydrogen [123, 232, 236–242], which can diffuse from anode to cathode. Thus, a Pt band within the membrane can be formed [123, 236, 238–241]. The driving force for Pt-ion migration is given by the potential gradient between anode and cathode. Finally, dissolved Pt-ions can also redeposit on other catalyst particles (see figure 2.4 (D)) leading to catalyst particle growth and thus a reduction of electrochemical active surface area [243–245]. This process is also known as Ostwald ripening.

2.2.3.3 Particle agglomeration and coalescence

Another mechanism leading to a decreased surface/volume ratio and thus to a decreased electrochemical active surface area is particle agglomeration and coalescence (see figure 2.4 (E)). During the process, two catalyst particles grow together via surface diffusion [65, 219, 246–248]. Herein, the driving force is to lower the total surface energies of catalyst nanoparticles [122]. A contact between different catalyst particles can be established by migration of whole Pt particles or by carbon corrosion induced catalyst particle detachment.

Chapter 3

Characterization techniques for PEMFC failure analysis

In the following chapter a short introduction to PEMFC failure analysis is given. Firstly, the general process for performing PEMFC failure analysis is described. In the second part, different characterization techniques and methods are introduced, which are used for fuel cell failure analysis. A focus is put on microscopic techniques, which can be applied to reveal fuel starvation degradation and its underlying mechanism. In addition, the working principles of IR-thermography, gas detection, pressure drop and hydrogen crossover measurements being used for pinhole detection are explained. Finally, cyclic voltammetry is described as a technique to determine GDL wettability. For a more detailed description of PEMFC characterization techniques the reader is referred to [30, 31, 121, 249, 250].

3.1 Stack and single cell analysis processes

Failure analyses are important for PEMFC development. Based on the results, strategies for system improvements like material selection, component design and operation conditions are suggested. Herein, a standardization of the failure analysis process including nomenclature, preparation, analysis and documentation simplifies problem solving approaches. Figure 3.1 illustrates the typical steps of a failure analysis according to [251]. In terms of a fuel cell stack the process starts by describing and documenting the condition of the fuel cell stack including imaging of optical abnormalities as well as the collection of electrochemical in situ data measured during stack operation. Information about the stack itself and its history is gathered, which could be relevant for the interpretation of the analysis results. Failures on stack components like bipolar plate and MEA, observed during the

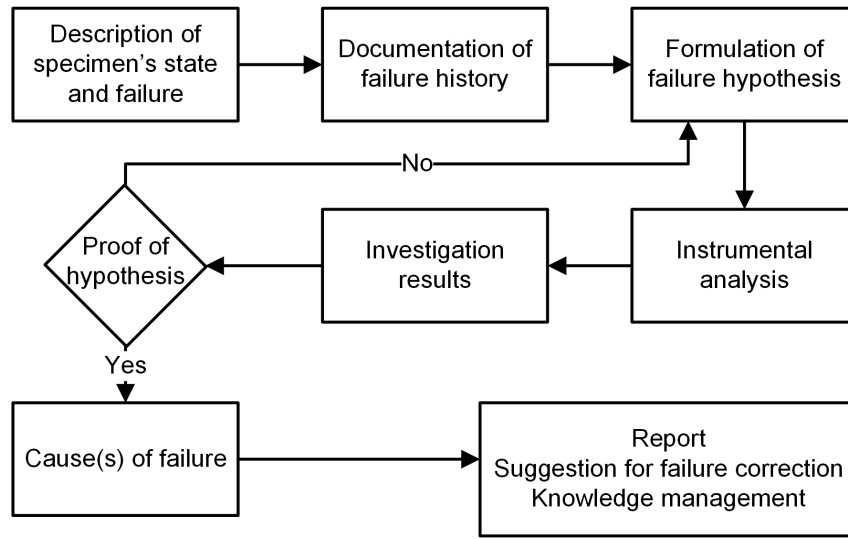


Figure 3.1: Flowchart illustrating the process of failure analysis according to [251].

stack disassembly are also described and documented. Based on both the failure description and background information, failure hypotheses are formulated and prioritized. In the next step, hypotheses are checked with instrumental techniques. Herein, the selection and application order of appropriate methods for the material system under investigation is highly relevant for a detailed and systematic analysis. Therefore, the creation of an investigation plan considering sample collection and preparation, application order of methods and possible model experiments is crucial. For instance, non-destructive methods like electrochemical operando methods or optical microscopy should be performed prior to MEA disassembly, cutting of specific samples or the application of other destructive methods. Spatial distributions of degradation phenomena are monitored with the help of the cell number within a stack and by using a localization matrix of a single MEA. Evaluation of instrumental analysis results and their comparison to reference values enables the confirmation or disproof of the failure hypothesis. In the latter case new hypotheses have to be formulated and verified. In the former case, as far as it is possible, the reason for the failure should be determined. Herein, the primary reason for the failure and its interaction with different influencing factors like operating conditions should be formulated. Consequently, suggestions for preventing the failure should be given. Finally, reporting the results of the failure analysis is important for both the distribution of the obtained information and the knowledge management. As described above a good instrumental analysis is crucial for PEMFC failure analysis. The most important methods used in this work are introduced in the following.

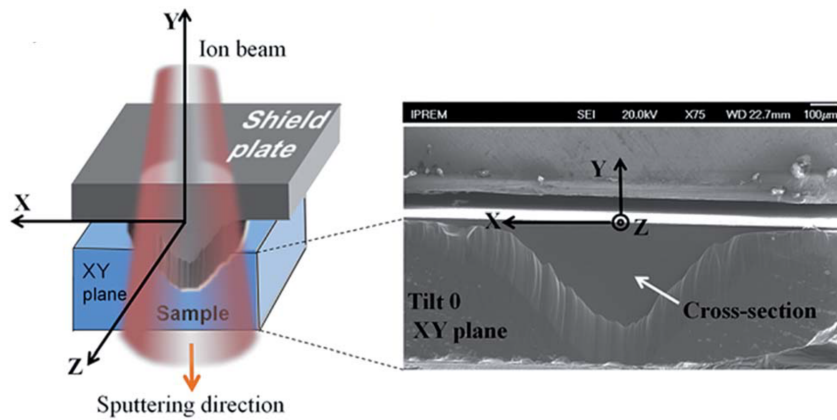


Figure 3.2: Schematic of a cross section polisher using an ion beam and a shield plate. A secondary electron image of a cross section obtained in a scanning electron microscope is shown on the right. Image adapted from [42] with permission from The Royal Society of Chemistry.

3.2 Cross section preparation

Preparation of sample cross sections is an important tool in fuel cell analysis, which gives insights to different layers and their interfaces. Different methods for cross section preparation exist including mechanical polishing, laser polishing or polishing with a focused ion beam. Although cross sections being made with an ion beam are strongly limited in size, they show a smoother surface with less damage of the cross section surface compared to mechanical cutting or laser polishing [252] [253]. By applying a circular ion beam, cross sections with a size of up to 1000 μm can be produced. As shown in figure 3.2, samples are positioned below a shielding plate in order to get a planar cross section [254]. In the polishing process, gas ions e.g. Argon ions are accelerated by an applied voltage. Due to their specific kinetic energy, they remove specimen atoms during the collision process. The acceleration voltage is used to set the Argon ion energy, which should be low enough to avoid artifacts but high enough to enable acceptable milling times. In order to increase the polished cross section area, the sample is shifted relative to the ion beam. During the milling, samples suffer from thermal impact and electrical charging. To overcome this problem the sample is placed between two supporting layers enabling discharging of the sample, giving mechanical strength and enabling thermal conduction. The thermal impact on the sample can be additionally reduced by liquid nitrogen cooling, which is especially important for thermally sensitive samples like the polymer membranes used in fuel cells.

3.3 Microscopy

As already described in section 2.2, many degradation phenomena of fuel cells occur on the micro- and nanoscale level. Therefore, magnified imaging is crucial for fuel cell degradation analysis. The working principle of optical and scanning electron microscopy, which are mainly applied in this work is described in the following.

3.3.1 Optical microscopy

The basic principle of optical microscopy is the use of two lenses to obtain a magnified image of the object. A more detailed description is given in [255, 256]. The light path of a typical microscope, creating a real final image, is illustrated in figure 3.3 (A). Light rays are coming from an object being placed in a distance S_1 relative to the first lens, which is larger than the focal length f_1 of the first lens. They form an intermediate magnified and inverted image at a distance S_2 behind the first lens. The magnification of the first lens is given by $M = -\frac{S_2}{S_1}$. A negative magnification value indicates an inversion of the image. The position of the intermediate image S_2 is given by the lens equation $\frac{1}{f_1} = \frac{1}{S_1} + \frac{1}{S_2}$. The second lens with focal length f_2 , positioned at a distance $S_3 > f_2$ from the first image, creates the further magnified final image at a distance S_4 behind the second lens. For digital optical microscopy a camera is used to capture and digitize the image.

When the first image is placed in a distance $S_3 < f_2$ of the second lens, a virtual image is created, which can be focused to a real, further magnified image on the eyes retina by the human eye lens (see figure 3.3 (B)).

The image quality of optical micrographs can be optimized by several factors, wherein illumination is a key parameter. In addition, back light illumination can be used for imaging transparent samples or to detect and localize holes in the sample. A useful advancement in optical microscopy are three-dimensional optical microscopes, which enable three-dimensional image reconstruction by capturing a series of images in different focal planes. Herein, the stacking or reconstruction software analyses the images in order to extract sharpest pixel points. In this work, a three-dimensional optical microscope is used to obtain information of PEMFC components like bipolar plates, CLs, CCMs or GDLs as well as to detect pinholes within CCMs.

3.3.2 Scanning electron microscopy

The working principle of scanning electron microscopy is based on the interaction of electrons with the matter of the investigated sample. The following explanation is based on [258–260], where a detailed description of scanning electron microscopy is given. For image acquisition, an electron beam is scanned over the sample and scattered electrons or other signals such as X-rays are detected at each

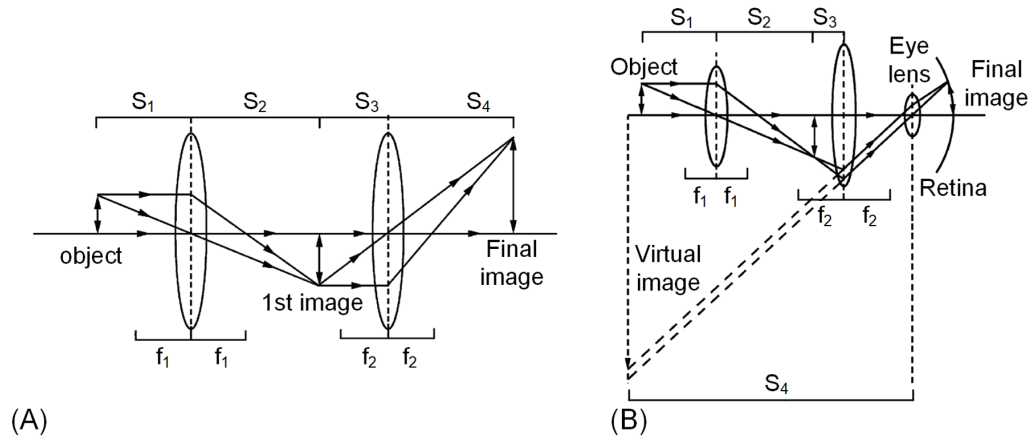


Figure 3.3: Optical path showing the magnification principle of an optical microscope for a real image being captured e.g. by a camera (A) and for a virtual image being viewed by a human eye (B). Figure modified after [256].

position. Electrons can be scattered elastically or inelastically when interacting with the specimen. The penetration depth of the electrons is defined as the depth where the energy of the electron is decreased to the thermal energy [257]. It depends on the electron energy and the interaction with the specimen and is therefore strongly dependent on the specimen composition. Large atomic numbers of the specimen lead to stronger electron scattering and therefore to a decreased penetration depth [258, 259]. The various signals are all generated up to this depth, but the escape depth is different. As illustrated in figure 3.4, differently scattered electrons give different depth information of the sample. Electrons being removed from the specimen atoms and leave the surface are called secondary electrons (SE). Secondary electrons possess only a small energy of a few electronvolt and are thus only able to escape the material in the very proximity of the surface area. Therefore, they give detailed topographical information of the sample surface [258–260].

By quasi-elastic scattering, primary electrons are deflected in a large angle. Electrons being scattered by an angle larger than 90° are called back-scattered electrons (BSE). Due to the quasi-elastic scattering they suffer only a negligible energy loss and escape from a deeper region of the sample. The scattering angle is highly dependent on the nucleus charge, which is directly correlated to the atomic number of the specimen. Thus, the intensity of back-scattered electrons is increasing with increasing atomic number, wherefore back-scattered electrons can be used for material contrast imaging in addition to topographical imaging. The topographical information of back-scattered electrons is however reduced compared to secondary electrons [258–260].

Inelastic scattering of the primary electron cannot only remove electrons from the outermost shell but can also cause the excitation of electrons from inner shells.

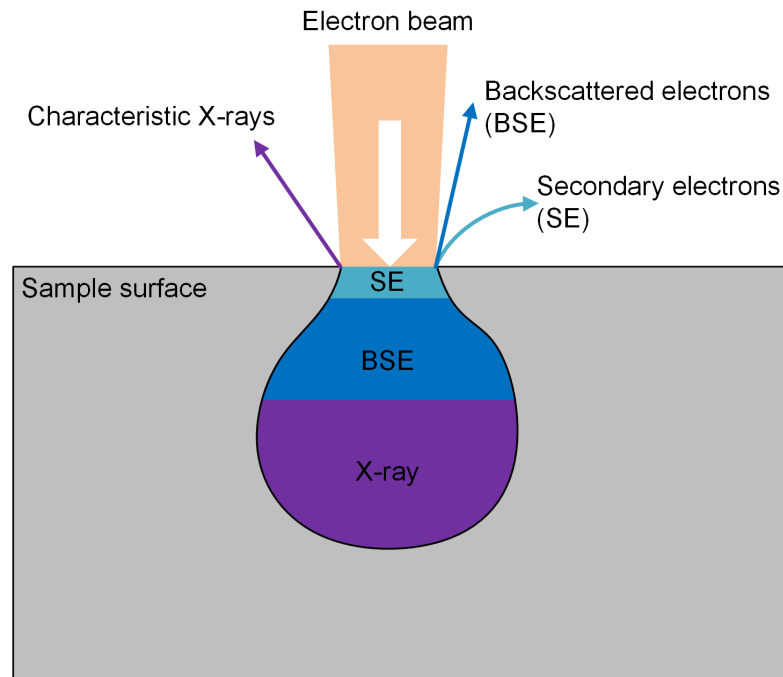


Figure 3.4: Overview of the electron beam penetration depth and the depths where different signals (SE, BSE, X-rays) can escape and leave the sample. Image modified after [261].

Outer shell electrons filling the empty site of an inner shell lead to the emission of X-rays that are characteristic for the energy levels of the specific atom. Detection of these characteristic X-rays can be used to investigate the element composition of the specimen. This method is called energy dispersive X-ray spectroscopy. [258, 259].

The image acquisition of scanning electron microscopy can be improved by various settings. For example the the acceleration voltage, the aperture size and the spot size can be varied. In addition, or the an extraction voltage can be applied.

In this work, scanning electron microscopy is used for high-resolution imaging and the determination of elemental composition of different fuel cell components like GDLs and CLs.

3.4 Pinhole detection methods

Within the MEA, the membrane serves for protonic conduction, electronically insulates both electrodes and separates the gases supplied to both electrodes. As already described in section 2.2.1, a decrease of protonic conduction, electronic insulation and gas separation properties can lead to severe performance losses. Especially direct combustion of hydrogen and oxygen due to membrane failure is a

critical safety issue of the fuel cell. Thus, the detection of membrane defects like small pinholes is important in fuel cell degradation analysis. Pinholes can serve as an indicator for the state of the membrane or can be the starting point for fatal membrane failure. Several pinhole detection approaches exist, whereof four promising and widely used methods IR-thermography, helium-gas (He-gas) detector, pressure drop technique and hydrogen crossover measurements) are studied in this work. Their basic working principle are described in the following.

3.4.1 Detection with infrared-thermography

The principle of pinhole detection with IR-thermography is based on the exothermic reaction of oxygen of ambient air with hydrogen permeating through the membrane and membrane defects. This reaction takes place at the catalytic sites of the electrode, where both hydrogen and oxygen are present.

Permeation through a non-defective membrane is approximately constant throughout the membrane. According to the corresponding exothermic reaction, this leads to a homogeneous increase of the electrode temperature. Increased hydrogen combustion above a pinhole leads to a stronger local temperature rise at the electrode. Due to thermal conduction, also the temperature of the MEA's GDL is increased, which can be captured by the IR-camera. Figure 3.5 (A) shows an example measurement setup. The IR-camera is placed above a MEA clamping device with a perforated top plate. The holes in the top plate enable an access of ambient air to the MEA and an imaging of the MEA surface. The top plate shown in the figure only possesses holes in the center of the plate. For imaging of the whole MEA surface, a plate with a complete perforation of the MEA area has to be used. At the lower side of the clamping device the MEA is supplied with hydrogen gas. As depicted in figure 3.5 (B), a quantification of the temperature rise can be made by subtracting the average GDL temperature of a non-defect region from the maximum GDL temperature measured above the pinhole. The exact position of the pinhole on the MEA can be documented by using a localization matrix, as exemplarily shown in figure 3.5 (C). For temperature measurements, IR-cameras use the principle that every body above zero temperature emits electromagnetic radiation. The detection of the radiation intensity enables the calculation of the sample's surface temperature. The electromagnetic spectral radiance L of a black body is given by Planck's law [262]:

$$L = \frac{2\pi hc^2}{\lambda^5} \cdot \frac{1}{\exp\left(\frac{hc}{\lambda k_B T}\right) - 1}, \quad (3.1)$$

where c is the speed of light, k_B the Boltzmann constant, h the Planck constant, λ the wavelength of the radiation and T the absolute temperature. A black body is herein an idealized physical body adsorbing all incoming electromagnetic radiation. The emission spectrum of a black body is only determined by its temperature and is independent on its shape and composition. According to Planck's

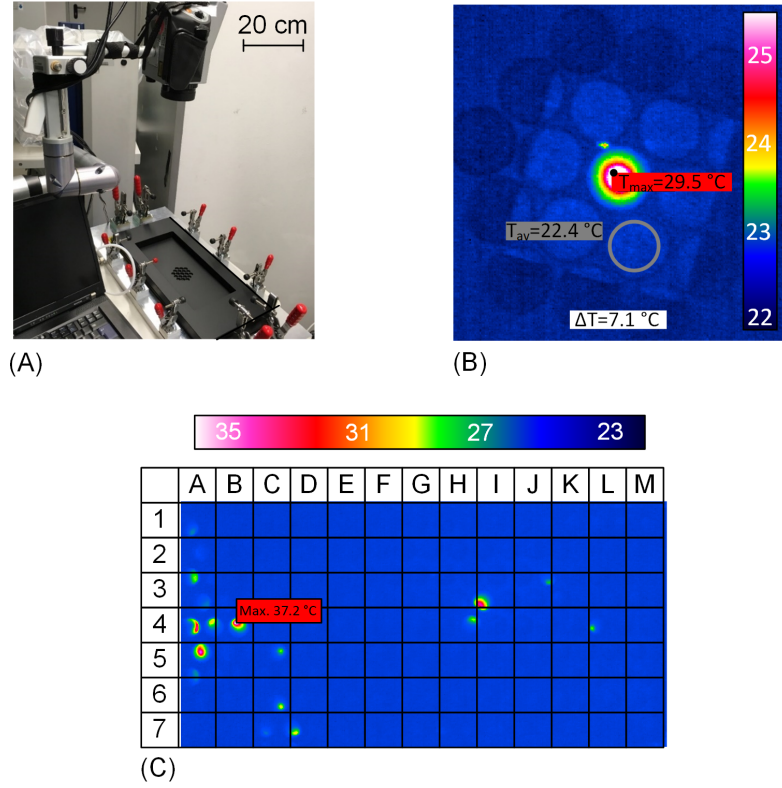


Figure 3.5: (A) Example setup of an IR-camera above a MEA clamping setup enabling oxygen and hydrogen gas supply to both sides of the MEA. Holes in the top plate of the clamping device allow an imaging of the MEA surface. (B) IR-thermography image showing the measured GDL temperature rise of $\Delta T = 7.1^\circ\text{C}$ above an artificial pinhole in the CCM. The temperature rise ΔT is calculated as the difference between the GDL temperature above the pinhole and the average GDL temperature of a non-defect region. (C) Localization of pinholes on a IR-thermography image of an MEA with the help of a localization matrix.

law the emitted intensity is increasing with increasing temperature while the peak wavelength is decreasing. A simplified correlation of temperature and emitted intensity is obtained by integrating the intensity over all wavelength, leading to the Stefan-Boltzmann-law [262]:

$$L = \sigma T^4, \quad (3.2)$$

where σ is the Stefan-Boltzmann-constant.

For measurements of real bodies, the emissivity of the sample has to be taken into account, which is a measure for an actual emitted intensity of a real body compared to an ideal black body. It is dependent on wavelength, temperature as well as on material and surface properties like roughness. Media between the measured surface and the detector can additionally alter the measured intensity. In case of air as

medium, humidity and carbon dioxide are well known adsorbents of IR-radiation. Finally, it has to be considered that the measurement device might be restricted to a specific wavelength range, which can have an additional influence on the measured temperature. For a more detailed description of IR-imaging the interested reader is referred to [262].

In this work, IR-thermography is used to detect membrane defects, which are documented in a MEA localization matrix. In the example shown in figure 3.5 (B), several defects are found at positions A1, A2, A4, A5, B4, C5, C6, D7, I3, H4, J3 and L4.

3.4.2 Detection with gas detector

For gas detection a thermal conductivity sensor, that identifies gases according to their specific thermal conductivity is used. It detects changes of the thermal conductivity of a test gas compared to a reference gas, which is usually ambient air.

Thermal conductivity detectors consist of a filament being surrounded by a cylindrical cell. The test gas flows through the cylindrical cell with a specific flow rate, thus creating a thermal contact between the filament and the cylindrical cell. By applying a current I through the filament, its temperature increases. The temperature of the filament is hereby determined by the incoming heat flow Q_{Joule} according to Joule heating at the filament resistance R_f and the outgoing heat flow according to thermal conduction towards the cylindrical cell via the test gas $Q_{Cond.}$ [263]. These are given by

$$Q_{Joule} = \frac{I^2 R_f}{J} \quad (3.3)$$

$$Q_{Cond.} = G(T_1 - T_2)\kappa, \quad (3.4)$$

where J describes Joule's constant, T_1 and T_2 the temperature of the filament and the cylindrical cell, respectively, and G a geometry factor. R_f can be calculated by measuring the voltage at the filament for the applied current.

By using a filament with a temperature dependent resistance, the filament temperature can be calculated from the following equation [263]:

$$R_f = R_f^0(1 + \alpha T_1), \quad (3.5)$$

where the resistance R_f^0 describes the reference resistance at 0 °C and α describes the temperature coefficient.

If the gas composition changes, the deviated thermal conductivity between the filament and the cylinder leads to an altered heat flow and thus to an changed filament temperature. This results in an altered filament resistance. Changes in the filament resistance are thus a measure for the test gas composition and can be used for the detection of different test gases.

Since the thermal conductivity measurement is strongly dependent on ambient conditions a reference cell, working with a reference gas (usually ambient air) is

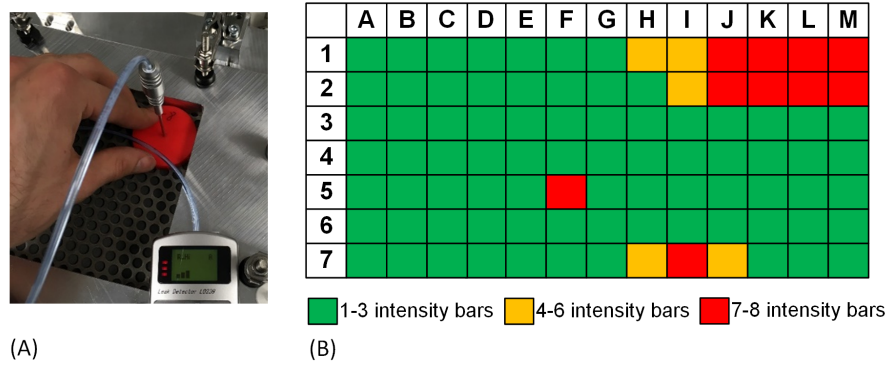


Figure 3.6: (A) Photograph showing the experimental setup of a He-Gas detector with a funnel at the detector's tip. The investigated MEA is placed below a perforated clamping plate. (B) Localization of pinholes on the MEA with the help of a localization matrix.

often used. The resistance difference is measured with a Wheatstone bridge. Thus, differences in thermal conductivity of the gases within both cells are determined. For a more detailed description of the working principle the interested reader is referred to reference [263].

In this work a thermal conductivity detector possessing a qualitative helium gas detection with an intensity bar graph ranging from a value of one to eight was used to detect membrane defects. The setup described in section 3.4.1 is used and helium gas is supplied to the lower side of the MEA. The helium gas, which is permeating through the membrane and membrane defects is detected by the thermal conductivity sensor. Since the tip of the detector is very small, funnels with different sizes are used to scan the MEA surface, as illustrated in figure 3.6 (A). Different funnel sizes lead to different measurement accuracies, with smaller funnels showing a higher accuracy and thus a higher sensitivity. The decrease in pinhole detection sensitivity with increasing funnel size is explained by the decreasing ratio of gas crossover through the pinhole to diffusive background gas crossover through the membrane. At this point a compromise between time effort and sensitivity has to be made with smaller funnels being more sensitive but more time consuming during the scanning process. For localization of pinholes the qualitative measured He-flow through the membrane defect is compared to background helium flow by diffusion through the membrane. The result is documented in a MEA localization matrix (see figure 3.6 (B)).

3.4.3 Pressure drop technique

Measurement setup and principle of the pressure drop technique are shown in figure 3.7. MEAs are placed in a common fuel cell test hardware, mechanically com-

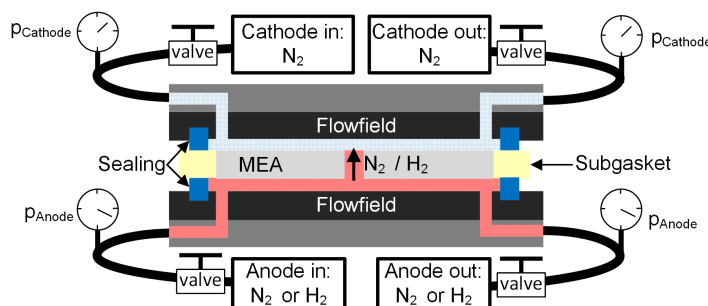


Figure 3.7: Schematic of the experimental setup for pressure drop and hydrogen crossover measurements. Anode gas (N_2 for pressure drop and H_2 for hydrogen crossover measurements) crosses the membrane towards the cathode via diffusive flow through the bulk membrane and convective flow through the pinhole. Convective flow is enhanced by a differential pressure between anode and cathode. Gas crossover induced pressure changes and hydrogen oxidation currents are monitored.

pressed with a specific clamping pressure and supplied by nitrogen gas at both anode and cathode. Before starting the measurement a sufficient long waiting time is recommended in order to assure proper conditioning (diminishing of temperature and pressure oscillations) of the cell. The waiting step depends on the cell setup and test station used and has typically a duration of a few minutes. Usually, the external leakage is determined by pressurizing both electrodes to a specific pressure and monitoring the pressure loss at both electrodes in a first step. In a second step, a differential pressure between anode and cathode as illustrated in figure 3.8 (A) is established and the pressure change of both electrodes is monitored. The leak rate being calculated from the relative pressure change between the two electrodes is corrected by the external leakage and normalized to a specific measuring time. The method is dependent on several factors including gas temperature and humidity as well as gas composition and volume. According to the ideal gas law the pressure drop through a membrane defect is increasing with decreasing volume. Low temperatures and low relative gas humidities increase the convective gas crossover e.g. through pinholes, while the diffusive gas crossover e.g. through the membrane is decreased [147]. Convective and diffusive gas crossover is additionally dependent on the type of gas used. Finally, it has to be mentioned, that increased internal leakages can be caused by a large single membrane defect, several small membrane defects or membrane thinning. In this work, these could not be distinguished by this method. In this work, the pressure drop method is used to detect pinholes in artificial and real degraded MEAs.

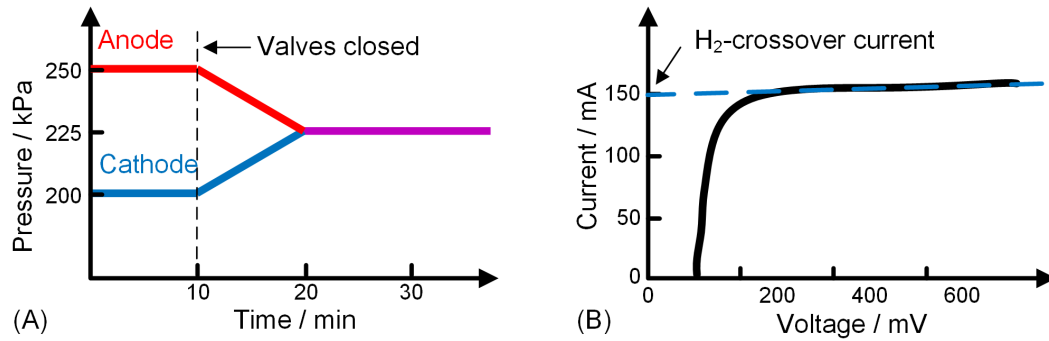
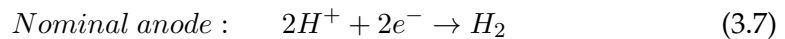
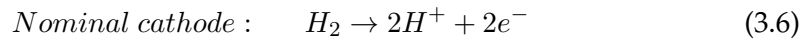


Figure 3.8: (A) Pressure versus time plot used in the pressure drop technique, showing equalizing of different pressures at anode and cathode due to gas crossover through a pin-hole. (B) Current-voltage curve (linear sweep voltammogram) used in hydrogen crossover measurement showing the oxidation current of crossover hydrogen as a function of the applied potential. The intercept of the linear approximation (dashed line) at high potentials corresponds to the hydrogen crossover current.

3.4.4 Hydrogen crossover measurements

For hydrogen crossover measurements a fuel cell test hardware as illustrated in figure 3.7 is used and hydrogen and nitrogen are supplied to anode and cathode, respectively. In the following the basic working principle is explained. Herein, the nomenclature of the electrodes according to standard fuel cell operation are used, neglecting the exact definition of anode and cathode. By applying a positive potential at the cathode with respect to the anode, crossover hydrogen is oxidized at the cathode (see equation 3.6). Due to the potential and concentration gradient, protons formed at the cathode migrate back to the anode, where they are reduced to hydrogen again (see equation 3.7).



When connecting anode and cathode a current flows due to the oxidation and reduction of hydrogen. This current is mainly dependent on the electric and proton conductivity of the MEA, the amount of crossover hydrogen at the cathode and the applied potential between anode and cathode. When linearly increasing the potential between anode and cathode, as performed in linear sweep voltammetry, a potential current correlation as shown in figure 3.8 (B) is obtained. During the linear sweep the potential is swept between the open circuit voltage of the hydrogen/nitrogen system and a potential at which all of the crossover hydrogen is instantaneously oxidized [264]. As indicated in figure 3.8 (B), the current-voltage curve can be approximated by a straight line at high potentials. The intercept of this approximated straight line is a measure for the hydrogen crossover in the cell,

while its slope at higher potentials is a measure for the electric cell resistance. Peaks at potentials around 0.2 V vs. reversible hydrogen electrode are given by the hydrogen desorption of the Pt catalyst and are reduced at lower scan rates.

The hydrogen crossover is influenced by several factors including gas temperature, relative humidity and gas pressure. By decreasing the gas temperature and the relative humidity, the convective gas crossover e.g. through pinholes is increased, while the diffusive gas crossover e.g. through the membrane is decreased [146]. Increasing partial and absolute differential pressure leads to an increase in diffusive and convective hydrogen crossover, respectively. In addition, a sufficient high humidity is required in order to ensure proton conductivity of the membrane.

In this work, measured hydrogen crossover values are compared to reference values of non-perforated begin-of-life MEAs, which enables the detection of membrane defects. As for the pressure drop method, it has to be mentioned that increased hydrogen crossover currents can be caused by a large single membrane defect, several small membrane defects or membrane thinning, which could not be distinguished in this work.

3.5 Cyclic voltammetry for the determination of wetted surface area

The method to determine the wettability of GDL samples, which is applied in this work, is based on the principle of double layer formation between a liquid electrolyte and a solid conductor or electrode. A GDL and an aqueous electrolyte are used as electrode and liquid electrolyte, respectively. A double layer, as shown in figure 3.9, describes two layers of opposite polarity at the solid-liquid interface. One layer is formed at the solid surface and the second one is formed within the electrolyte. Thus, a capacitance at the solid-liquid interface is created. The double layer capacitance can be measured by cyclic voltammetry (CV) and can be used as a qualitative measure of GDL surface area being wetted by the electrolyte.

Different models exist to describe the capacitive behavior of the double layer. In a first approximation of Helmholtz et al. [265], a double layer can be described as a solid-state capacitor (see figure 3.9 (A,I)). This results in a linear decrease of the potential with increasing distance from the solid/electrolyte interface (see figure 3.9 (A,II)). The capacitance C_H of this so called Helmholtz double layer is given by [119]:

$$C_H = \frac{\epsilon}{4\pi l}, \quad (3.8)$$

where ϵ is the dielectric constant and l the distance between the plates of the capacitor.

Another approach introduced by Gouy and Chapman [266, 267] describes the double layer with a diffuse layer model. As illustrated in figure 3.9 (B,I), ions performing thermal motion in the electrolyte are supposed to form a diffuse rather

than a rigid layer. By assuming the ion distribution to be Maxwell-Boltzmann distributed, the potential decreases exponentially with increasing distance to the solid/electrolyte interface (see figure 3.9 (B,II)). The capacitance C_{GC} is given by [119]:

$$C_{GC} = zF \sqrt{\frac{2\epsilon c_E}{RT}} \cosh\left(\frac{zF\Phi}{2RT}\right), \quad (3.9)$$

where z describes the charge number of the ions, F the Faraday constant, c_E the electrolyte concentration, R the universal gas constant, T the absolute temperature and Φ the applied potential.

In addition, Stern et al. [268] introduced a model describing diffusely distributed ions, which are immobilized close to the solid/ liquid interface, thus combining the models of Helmholtz and Gouy-Chapman (see figure 3.9 (C)). The capacitance is then given by [119]:

$$\frac{1}{C_S} = \frac{1}{C_H} + \frac{1}{C_{GC}} \quad (3.10)$$

For further models describing the double layer capacitance like the triple layer model, the interested reader is referred to reference [119].

In addition to the double layer capacitance, also pseudocapacitance can contribute to the total measured capacitance. Pseudocapacitance is based on physisorption of an electrolyte ion on the surface of the solid material. Unlike double layer formation, pseudocapacitances are formed by an adsorption process including a reversible one-electron-reaction. The amount of the pseudocapacitance strongly depends on the surface material of the solid, wherein a high pseudocapacitance can be reached for transition metals like platinum [269].

Double layer capacitance and pseudocapacitance can be measured by potentiostatic cyclic voltammetry. During the cyclic voltammetry measurements, the potential of the working electrode is scanned with a specific rate in a triangular shape between two set-potentials and the corresponding current is measured. The potential scan is reversed when reaching the end potential, scanning back to reach the start potential and thus closing one cycle [271]. As illustrated in figure 3.10, electroactive species are reduced during the forward scan, while they are (re-)oxidized during the backward scan. Cyclic voltammetry is therefore often used to investigate reduction/oxidation processes as well as electron transfer-induced chemical reactions [272]. Herein, the peak potential and peak shape as well as the reversibility of the oxidation and reduction peaks give information about the oxidation and reduction processes. With regard to PEMFCs, adsorbed hydrogen and Pt are oxidized in the H-desorption region and OH-adsorption region during the forward scan, respectively (see figure 3.10). During the backward scan, Pt and protons are reduced in the OH-desorption and H-adsorption region, respectively. When no electroactive species are present, only a capacitive current due to charging of the double layer and pseudocapacitance between electrolyte and working electrode is measured. The measured capacitance is hereby a qualitative measure for the surface area of the electrode being in contact with the electrolyte. The capacitive

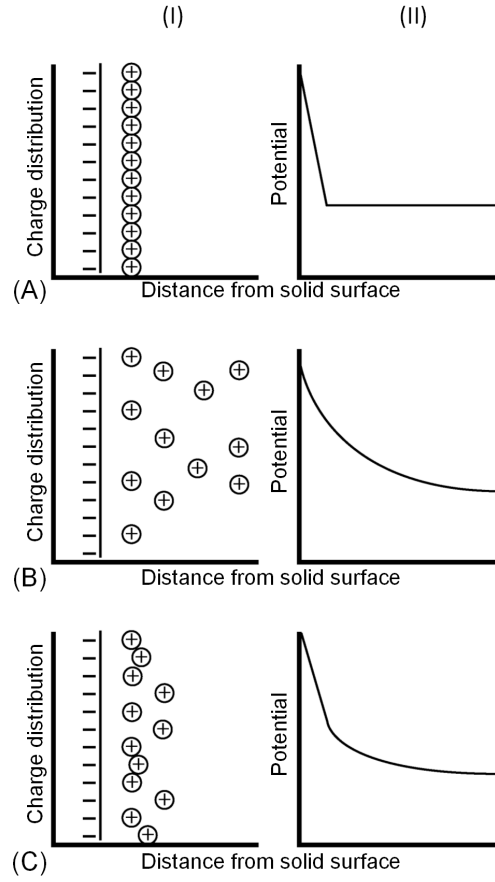


Figure 3.9: Schematic of different double layer models and the corresponding distance-dependent potential: (A) Helmholtz model, (B) Gouy-Chapman Model, (C) Stern Model. (I) shows the charge distribution and (II) shows the potential as a function of the distance from the solid surface. Figure modified after [270].

current I_C is given by the capacitance C and the potential change with time $\frac{d\Phi}{dt}$:

$$I_C = C \frac{d\Phi}{dt}. \quad (3.11)$$

Thus, an increase in the potential scan rate $\frac{d\Phi}{dt}$ also increases the capacitive current, wherefore the measured capacitive current is often normalized to the potential scan rate in order to extract the double layer capacitance C_{DL} .

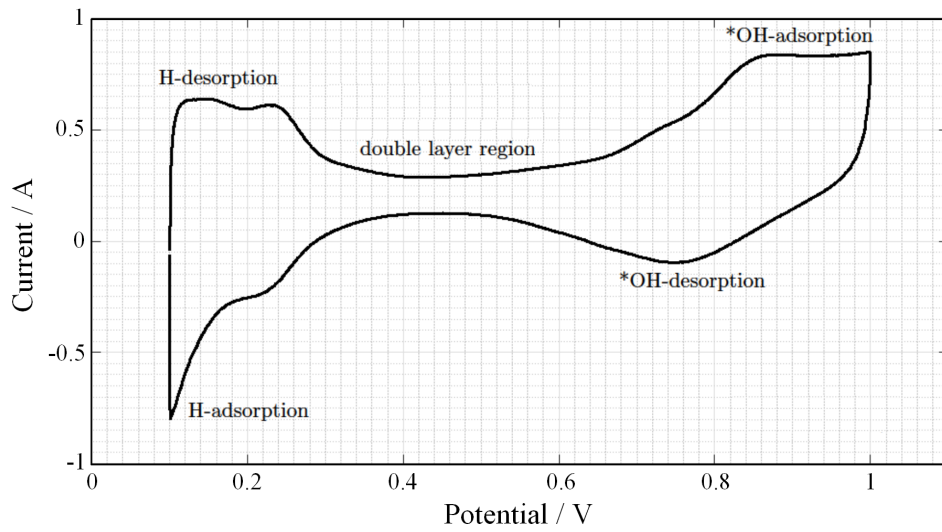


Figure 3.10: Schematic of cyclic voltammogram of a PEMFC MEA. Electroactive and double layer potential regions are indicated in the voltammogram. Figure taken from [273].

Chapter 4

Comparative study of pinhole detection methods for PEMFC degradation analysis

This chapter is a modified version of a research article that was submitted in the Journal of Power Sources [274]. In brief, the following topic is addressed. Knowledge gained by fuel cell degradation analysis is important for meeting durability targets and thus for the commercialization of polymer electrolyte membrane fuel cells. Herein, the application of the most appropriate characterization method is crucial depending on which degradation mode is dominating. One major failure mode in polymer electrolyte membrane fuel cells is the formation of pinholes in the polymer membrane. In this work, a systematic study of four promising methods for pinhole detection is performed, namely detection via IR-camera, via He-gas detection as well as via pressure drop and hydrogen crossover measurements between anode and cathode. In particular, detection limits as well as influences of the material system and other relevant factors are discussed. Finally, a comparison of the different methods and a recommendation for their practical application is given to optimize detection of membrane defects in the field of failure analysis. The most successful ones are then tested for the analysis of real automotive stacks before and after operation.

4.1 Literature review

It is well agreed in literature that pinhole formation in the polymer electrolyte membrane is a main degradation mode [32, 33, 35, 37, 38, 116] leading to cell performance decrease and fatal cell and stack failure [275]. Thus, even the detection of

small pinholes, which are usually not noticed during fuel cell operation [275], is important. Several pinhole detection methods are used in literature ranging from bubble test [87, 90], gas detection [100], pressure drop method [87–89], hydrogen crossover detection [89–96], segmented current measurement [91, 276], relaxometry [88], cell voltage decay [96, 277], impedance spectroscopy [92, 96], and detection via IR-thermography [34, 87, 90, 92–94, 97–99].

The application of the appropriate method for a certain analysis task is important. Thus, an overview and comparison of different analysis methods can be very helpful for the selection of a suitable method. For instance, Moor et al. [87] compared the methods of leak test and relaxometry at the fuel cell test station with IR-thermography for pinholes with a minimum diameter of 75 μm . They found leak test and relaxometry to be fast analysis tools, while IR-thermography was more sensitive and able to localize the pinhole position on the membrane-electrode assembly. Asghari et al. [89] compared and combined the methods of IR-thermography, open circuit voltage decay, and hydrogen crossover current measurements to detect and localize pinholes within fuel cell stacks, without stack disassembly. In accordance with Moor, they concluded that all techniques investigated are able to detect leakages but that a combination of several techniques is more accurate in leakage detection and localization. However, detection limits as well as the influence of the MEA type and hardware components are still mostly unclear. In this chapter, a systematic and detailed comparison of four pinhole detection methods (IR-thermography, gas detection, pressure drop, hydrogen crossover) is given. For the study different test systems are used, mimicking real MEAs, with well-defined pinhole diameters down to 5 μm to investigate the detection limits. Material systems with different Pt content and/ or different morphology of the gas diffusion layer are tested to determine their influence. Finally, two state-of-the-art MEAs taken from automotive midsize-stacks are analyzed with regard to pinhole detection via IR-thermography and helium-gas detection. One stack is analyzed before begin-of-life, the other one is investigated after 1300 h of driving.

4.2 Experimental details

4.2.1 Material characterization methods

Optical microscopy (Keyence VHX-6000) was used to determine size and shape of artificial pinholes as well as to check possible morphology changes of MEA components before and after applying the various pinhole detection methods. Cross sections of different gas diffusion electrodes/ gas diffusion layers were prepared with a cryo cross section polisher (JEOL IB-19520CCP) and studied by scanning electron microscopy (FEI Quanta FEG 650). A measure for the gas permeability of different GDEs/ GDLs was performed by a Gurley-Densometer (Model 4118). Samples are placed with the MPL side facing the upper clamping plate of the Gur-

ley measurement system, resulting in the gas first permeating the MPL before permeating the substrate. The measured Gurley number was inversely proportional to the gas permeability. It has to be mentioned here that measured gas permeability is mostly determined by the MPL and electrode structure of the investigated GDEs/GDLs. GDE/GDL thickness were measured with a universal micrometer (Frank PTI 16502, tip diameter 5 mm, applied pressure 125.2 kPa).

4.2.2 Investigated materials

A typical MEA is made of GDLs, electrodes, and a polymer membrane. GDLs typically consist of a substrate like carbon paper or carbon cloth (i.e. networks of carbon fibers) and a microporous carbon layer. The electrodes are in contact to this microporous carbon layer and are built of a porous carbon support on which the nanometer-sized Pt catalyst particles are located. The electrode together with the GDL form a GDE. The polymer membrane in the center of the two electrodes is a proton conductive ionomer [120]. In the present work, three different MEA test systems, differing in the type of membrane, the electrode and GDL properties as well as in the aging/degradation state of the membrane and electrodes were investigated.

The GDL type on the anode side was identical for all test systems (GDL 1) and had a Gurley number of $(219 \pm 30) 10^{-2} \text{ sec cm}^{-3}$, which was inversely proportional to the permeability.

At the anode of test system I, only GDL 1 without electrode was applied. A polyimide (PI) foil with a thickness of 15 μm was used to mimic the membrane. Within the polyimide foil artificial pinholes with different diameters (5 μm , 10 μm , 30 μm , 50 μm , 100 μm , 200 μm , 300 μm , 500 μm) were created by laser drilling, preventing lid formation, which can be observed when punching with micro-needles [146]. Polyimide was chosen due to its high temperature stability enabling the fabrication of circular shaped pinholes (see figure 4.1 (A)) as small as 5 μm in diameter. The holes with a diameter $d < 30 \mu\text{m}$ were drilled by Micro Lasertec Deutschland GmbH (Kirchhain, Germany). The pinholes were located at the center of the MEA. To investigate the effect on material properties, three different GDEs at the cathode (GDE 1, GDE 2, GDE 3), differing with regard to their Pt loading and morphology were used. Figure 4.2 exemplarily shows the morphologies of GDE 1 and 2, where the electrode, the MPL and the carbon fiber substrate are visible. The different GDE morphologies, with regard to the penetration depth of the MPL into the fiber substrate, the homogeneous distribution of the MPL and the crack formation of the MPL and electrode led to different GDE properties like permeability, or thermal conductivity (see table 4.1). Their Gurley numbers showed only a slight deviation. In addition experiments were performed, where only GDLs (GDL 1, GDL 2) without electrode at the cathode were used.

In the following all test systems are classified according to their anode/membrane/cathode type. For test system I that means GDL/PI/GDE and

Table 4.1: Summary of the different test systems, consisting of a membrane separating GDL 1 placed at the anode side and different GDEs/GDLs placed at the cathode side. Material parameters like Gurley number, Pt loading and thickness of the different components are listed. Pt loading listed for test system II and III are taken from the supplier's datasheet. *Actual Pt loading of the degraded electrodes of test system III can deviate from the begin-of-life Pt loading, which is listed in the table.

	Test system I			Test system II		Test system III
Anode	GDL 1			GDL 1		GDL 1
Pt loading / mg cm^{-2}				0.08		0.05*
Membrane	Polyimide foil			Nafion		Nafion (degraded)
Cathode	GDE 1	GDE 2	GDE 3	GDL 1	GDL 2	GDL 1
Gurley Number (Model 4118) $\sim 1/\text{permeability}$ $10^{-2} \text{ sec cm}^{-3}$	95 ± 4	60 ± 5	105 ± 26	219 ± 30	1783 ± 224	219 ± 30
Pt loading / mg cm^{-2}	0.58 ± 0.11	0.43 ± 0.03	0.21 ± 0.01	0.40		0.30*
Thickness at 125.2 kPa / μm	240 ± 4	208 ± 4	200 ± 4	223 ± 4	232 ± 4	223 ± 4

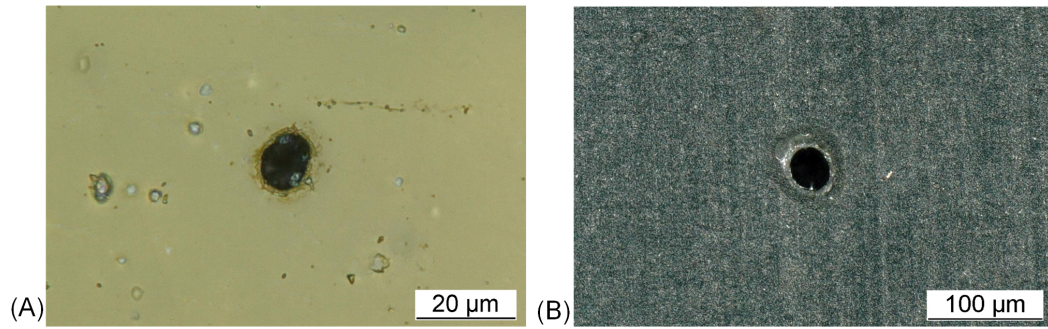


Figure 4.1: Optical micrographs of small pinholes laser drilled in (A) polyimide and (B) electrode Nafion assembly (top view on cathode). The pinhole diameter shown, are 10 μm and 40 μm , respectively.

GDL/PI/GDL. In test system II, electrodes were applied to a Nafion (Nf) membrane at anode and cathode. At the anode side the electrode, possessing a Pt loading of $0.08 \text{ mgPt cm}^{-2}$, was connected to GDL 1. At the cathode side two different GDLs (GDL 1 and GDL 2) were used in contact with the electrode with a Pt loading of $0.40 \text{ mgPt cm}^{-2}$. The Gurley numbers of GDL 1 and GDL 2 strongly differed

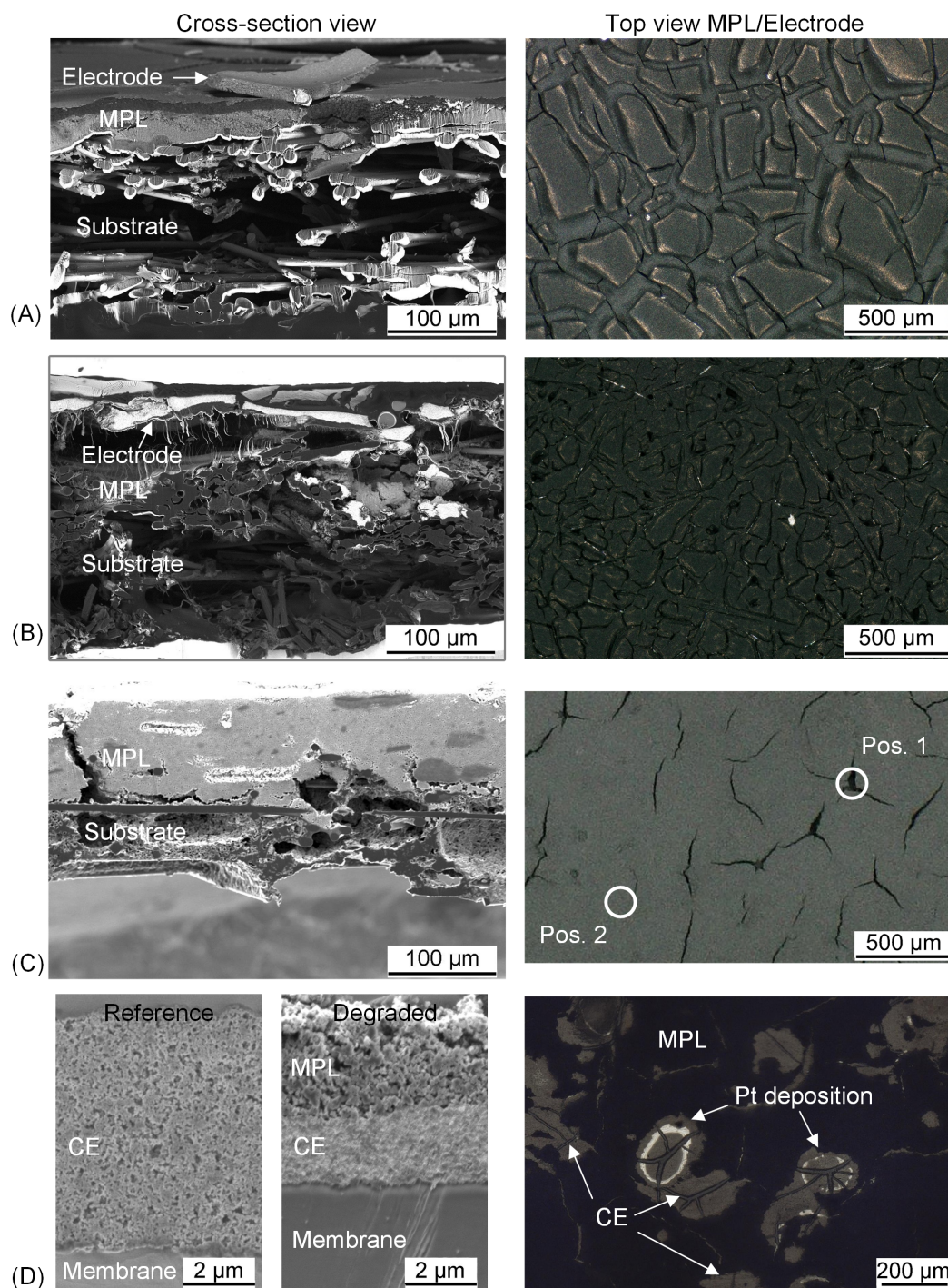


Figure 4.2: SEM micrographs of cross-sections (left) and optical micrographs showing the top view of the MPL/ electrode area (right) of GDE 1 (A), GDE 2 (B), GDL 1 (C), and the degraded cathode electrode (CE) of test system III (D).

(see table 4.1). Figure 4.2 (C) exemplarily shows the morphology of GDL 1. Circular shaped pinholes (see figure 4.1 (B)) with different diameters (approx. 40 μm , 100 μm , 200 μm , 500 μm) were laser drilled through both electrodes and the 15 μm thick Nafion membrane. Due to different material properties of the Nafion membrane compared to polyimide the smallest pinhole diameter, which could be fabricated was 40 μm . All pinholes were positioned in the center of the investigated MEA. In the following, test system II will be referred as GDL/E,Nf,E/GDL, wherein E indicates the electrodes applied at the anode and cathode side of the Nafion membrane.

In test system III, a degraded state-of-the-art electrode and Nafion membrane assembly was artificially perforated. The electrodes and the membrane were then assembled with two begin-of-life GDLs 1 at anode and cathode side. One 50 μm pinhole and two 100 μm pinholes were laser drilled in the degraded area. The original Nafion membrane thickness was specified as 15 μm and the original Pt loading was 0.05 mgPt cm^{-2} and 0.30 mgPt cm^{-2} on anode and cathode, respectively. Due to local fuel starvation, the cathode electrode and membrane had suffered from strong degradation as described in detail in chapter 6. Figure 4.2 (D) illustrates the severe thickness decrease and the complete porosity loss of the cathode electrode as well as MPL adhesion and Pt deposition on top of the degraded cathode electrode. This altered cathode electrode porosity can lead to a strong decrease in gas permeability towards electrochemical active sites. In addition, Pt deposition on top of the degraded cathode electrode (see figure 4.2 (D)) and Pt crystallite growth of up to 100 % compared to begin-of-life reference samples, as measured with X-ray diffraction, were found. This indicates a decrease in electrochemical active surface area (see chapter 6).

Finally, two state-of-the-art MEAs taken from two automotive mid-size stacks, were investigated with respect to pinhole formation.

4.2.3 Pinhole detection with infrared-thermography

For both pinhole detection with IR-thermography and He-detector a new cell hardware was designed. The basic principle is illustrated in figure 4.3 (A). Measurement gases (forming gas or He) were supplied via a connecting plate to a flowfield plate distributing the gases along a MEA being placed on top of the flow field plate. The gas pressure could be adjusted and controlled by a pressure reducing controller and a low pressure manometer. In this work, different pressures were established. In order to measure different MEA designs, the gas outlets of the connecting plate have to fit flowfield plates of different cell designs. To ensure gas tightness of the setup, flat sealings were applied on the flow field plate and the setup was compressed with the help of a clamping plate. For compression toggle clamps were used. Holes drilled in the clamping plate ensured direct access to the upside of the MEA. This was necessary to be able to image a hot spot on top of the MEA during pinhole detection with the IR-camera and to enable a scanning of the MEA surface

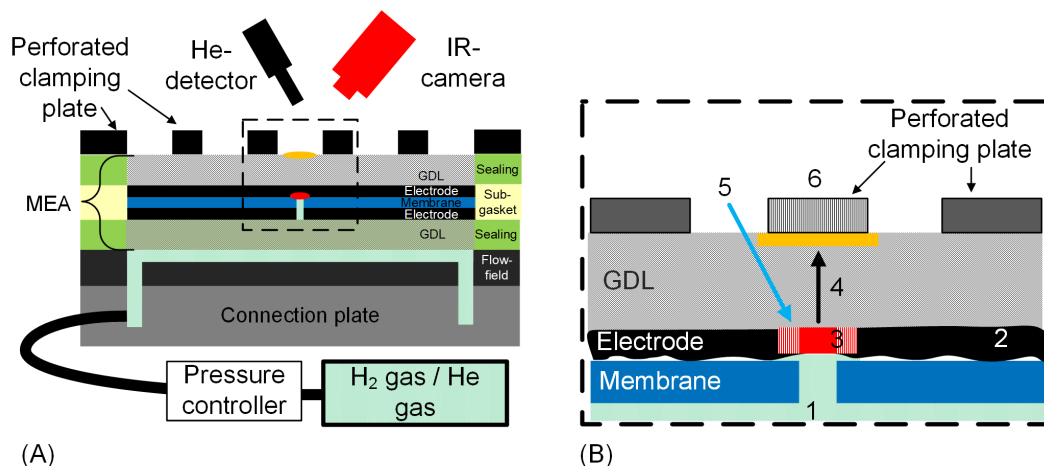


Figure 4.3: (A) Schematic drawing of the setup for IR-thermography and helium-gas detection methods. Dashed box illustrates position of image (B). (B) Magnification of pinhole area with numbers representing factors influencing the measured temperature rise for a pinhole of a specific size. 1) Forming gas pressure, 2) electrode properties, 3) hydrogen gas supply, 4) thermal conductivity of GDL, 5) oxygen gas supply, 6) positioning of clamping plate.

area with the He-detector. Perforation of the clamping plate was established by hexagonal ordered holes (diameter of holes = 10 mm), with centers located 11 mm apart from each other. The setup was colored black in order to suppress reflection of IR-radiation. During IR-thermography, forming gas (Mol-5% hydrogen, Mol-95% nitrogen) was supplied to the anode and different gas pressures ranging from 2 kPa to 38 kPa were established. Hydrogen permeated through the pinhole and reacted exothermically with oxygen at the catalyst sites. This reaction mainly takes place at the electrode facing the perforated clamping plate and leads to a local temperature rise ΔT at this electrode. If not specified otherwise, the cathode was facing the perforated clamping plate. The temperature rise stabilized within a few tens of seconds, depending on the cell size and the measurement setup used and was then captured by IR-imaging (Infra Tec VarioCAM hr). Thus, the pinhole was localized on the MEA. As can be seen in figure 4.4 (A), a quantification of the temperature rise was made by subtracting the average temperature of the MEA from the maximum temperature measured at the pinhole location. In general, a rise of the maximum temperature was accompanied by an increased area of the hot spot. Measurements were performed under ambient conditions.

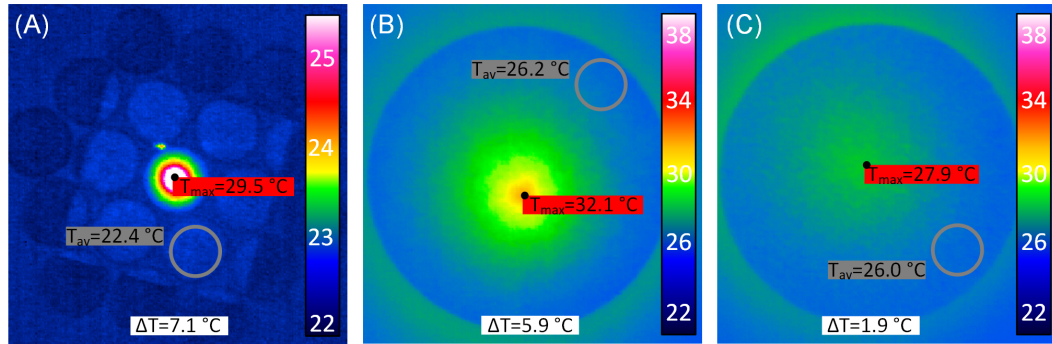


Figure 4.4: Top view IR-image of: (A) A perforated MEA (GDL1/PI/GDE1, pinhole diameter=200 μm , gas pressure= 2 kPa) showing a temperature increase at the GDL area above the pinhole due to exothermic reaction at catalytic sites. (B) GDE 1 and (C) GDE 2 both with the same local heat input by a metal rod at the backside (electrode area) to visualize the different thermal conductivities of the GDEs.

4.2.4 Pinhole detection with a helium-gas detector

The setup described in section 4.2.3 was used but He-gas was supplied to the anode and again different pressures ranging from 2 kPa to 38 kPa were established. For all measurements, the cathode was facing the perforated clamping plate. The MEA surface was scanned with two differently sized funnels (diameter: 15 mm; 40 mm; length: 1 mm; 2 mm) at the detector tip to find increased helium flows as compared to the background of non-perforated begin-of-life reference MEAs. The gas detector used (GL Science LD239) allowed a qualitative analysis of helium flow by displaying a qualitative intensity bar graph with a maximum intensity of eight. The minimum sensitivity of the sensor in the applied measurement mode was given by 0.005 ml min⁻¹ in atmosphere. Measurements were performed at ambient conditions.

4.2.5 Pinhole detection with the pressure drop method

A simple method to determine cross leaks in a MEA is to apply a pressure gradient between anode and cathode, stop the gas flow and measure the related change of the pressure at anode and cathode. For pressure drop measurements a commercial test station (Greenlight G100) and a 50 cm² cell-holder were used. The active area was mechanically compressed to 1.5 MPa. Cell and gas temperatures were set to 40 °C, and dry gases (< 10 % r.h.) were used to minimize gas crossover by gas diffusion through the membrane and maximize gas convection through the pinhole [146]. A differential pressure of 50 kPa between anode and cathode was established to promote convective gas crossover through the pinhole. After equilibration of the system, the pressure drop was measured over a time period of at least 6 min.

The analyzed volume within the cell holder and test station was estimated to be < 0.35 l. Before measuring the internal pressure drop, the external pressure drop was determined in order to take small external leakages into consideration. The internal pressure drop of MEAs was compared to reference values of non-perforated begin-of-life MEAs.

4.2.6 Pinhole detection with the hydrogen crossover method

Tests were performed on a 50 cm^2 cell setup with the help of a commercial test station (Greenlight G100). Again, a low gas temperature ($50\text{ }^{\circ}\text{C}$), a low relative gas humidity of 40 % r.h. and a differential pressure of 50 kPa between anode and cathode were established to minimize gas crossover by gas diffusion through the membrane and maximize gas convection through the pinhole. The hydrogen crossover current was calculated from current-voltage measurements in a potential range of 0.06 V to 0.80 V vs. standard hydrogen electrode. Measurements were performed using an electrochemical workstation (Zahner Zennium Pro) by applying a scan rate of 1 mV s^{-1} . Measured hydrogen crossover values were compared to reference values of non-perforated begin-of-life MEAs. The determination of the hydrogen crossover by measuring the current response of a linear potential sweep requires a proton conductive connection between the two electrodes, which is usually given by the proton conductive membrane. Since polyimide, as used in test system I is not proton conductive, test system I could not be used to investigate the hydrogen crossover method.

4.3 Results and discussion

4.3.1 Test of different pinhole detection methods

4.3.1.1 Infrared-thermography

IR-thermography was demonstrated to be a non-destructive technique. As exemplarily shown in figure 4.4 (A), a pinhole led to a temperature rise ΔT due to the exothermic reaction of hydrogen being supplied to the test setup and oxygen from the ambient air. The temperature rise ΔT was measured by an IR-camera and classified as detected if it was larger than the background noise of about $0.5\text{ }^{\circ}\text{C}$. For the example given in figure 4.4 (A), the perforated MEA of test system I showed a temperature increase of $\Delta T = 7.1\text{ }^{\circ}\text{C}$ at the pinhole (pinhole diameter = $200\text{ }\mu\text{m}$, gas pressure = 2 kPa).

IR-images were collected for different material systems with different pinholes sizes. The observed temperature rise ΔT was calculated for each image and the values were summarized in figure 4.5. For each measurement three samples were measured and averaged.

Considering test system I, pinholes with a diameter smaller than $50\text{ }\mu\text{m}$ were

detected when using GDL1/PI/GDE1 but could not be detected when using GDL1/PI/GDE2 and GDL1/PI/GDE3. As shown in figure 4.5, the minimal detectable pinhole size ranged from 10 μm to 100 μm depending on the GDE used. Other works reported the detection of pinholes with a size ranging from 75 μm to 305 μm [88, 94], which is both within the detection range determined in this work and supports the obtained detection dependence on the material system. For small pinholes ($d < 100 \mu\text{m}$) the temperature rise ΔT was increasing with pinhole diameter while for larger holes ($d > 100 \mu\text{m}$) the signal stagnated. This effect was however not observed for GDL1/PI/GDE3.

Figure 4.5 additionally illustrates that the Nafion based system II showed a comparable detection range for pinholes as observed for test system I. As for test system I, the detection limits depended on the material properties of the used GDL. Herein, the smallest pinhole diameter of 40 μm , which could be introduced in test system II, was easily detectable. A clear comparison of the different test systems was however difficult since both GDL properties (gas permeability, thermal conductivity) and electrode structure (Pt content, permeability) as well as the thermal contact between GDL and electrode were different.

The detection ranges were also validated on two state-of-the-art MEAs from automotive mid-size stacks. The first stack showed an internal leakage and a voltage drop of the MEA during begin-of-life characterization. Within the MEA seven pinholes all with a diameter of approximately 100 μm , as determined with optical microscopy, were detected by IR-thermography. Stack two was aged with automotive driving points for approximately 1300 hours. The MEA taken from stack two showed an increased fall-off of the open circuit voltage after stopping the gas supply. Within this MEA, two pinholes with diameters of approximately 10 μm and 20 μm were found with microscopic investigation. These pinholes could however not be detected with IR-thermography. By contrast, a region of severe membrane thinning was found by IR-thermography, whose thickness decrease was shown to be approximately 75 % by optical imaging of cross sections. Membrane thinning leads to an increased hydrogen crossover in the thinned membrane area, resulting in an increased exothermic reaction. The corresponding temperature increase could be observed by IR-thermography. It has to be mentioned, that GDLs of both MEAs were removed and assembled to the MEA again before applying the pinhole detection method, which could influence the measurement results. However, optical analysis did not show any damage of the electrodes or membrane due to the GDL removal.

4.3.1.1.1 Influence of MEA components and test hardware

As illustrated in figure 4.3 (B) there are several factors influencing the measured temperature rise ΔT for a pinhole of a specific size, including applied gas pressure (1), electrode properties (2), hydrogen supply to the pinhole (3), thermal conductivity of the GDL (4), and oxygen supply to the pinhole (5). In addition, also the design and positioning of the cell hardware (6) can have an influence on the mea-

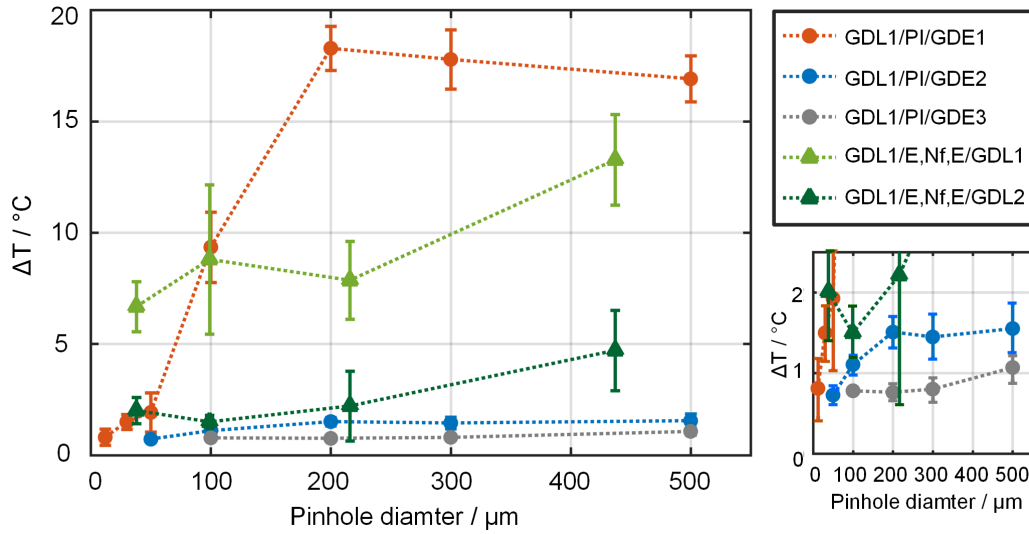


Figure 4.5: Temperature rise ΔT as a function of pinhole diameter, showing an increase of ΔT with increasing pinhole diameter and a strong dependence on the material system. Measurements were performed at 22 kPa gas pressure. A magnification of the lower ΔT range is given by the right inlet. Error bars show the scattering of samples of the same type.

sured temperature rise ΔT . A selection of these influencing factors is discussed in the following.

4.3.1.1.2 Gas pressure

As shown in figure 4.6 (A), temperature rise ΔT was found to increase with advancing forming gas pressure for pinholes in a diameter range of 10 μm to 100 μm of test systems I and II. For each measurement point three samples were measured and averaged. This could be explained by a higher hydrogen supply at the electrode with increasing gas pressure. For larger pinholes (diameter 200 μm and 500 μm), the temperature rise ΔT of GDL1/PI/GDE1 and GDL1/PI/GDE2 was found to stagnate above a specific pressure. For instance, using GDL1/PI/GDE1, the temperature rise stopped increasing above 22 kPa for a 500 μm pinhole, reaching a value of $\Delta T = 18^{\circ}\text{C}$. This could be caused by several reasons including limitation due to thermal conduction through the GDL, or limitation of oxygen and hydrogen supply to the active sites of the electrode.

The gas pressure was only one of several factor influencing the measured temperature rise ΔT . A comparison of measured temperature rise ΔT above pinholes in the diameter range of 30 μm to 50 μm of GDL1/PI/GDE1, GDL1/E,Nf,E/GDL1 and GDL1/E,Nf,E/GDL2 at a specific gas pressure showed strongly deviating temperature rises among the systems (see figure 4.6 (A)). Possible explanations for the increased temperature rise ΔT of GDL1/E,Nf,E/GDL1 might be an increased ther-

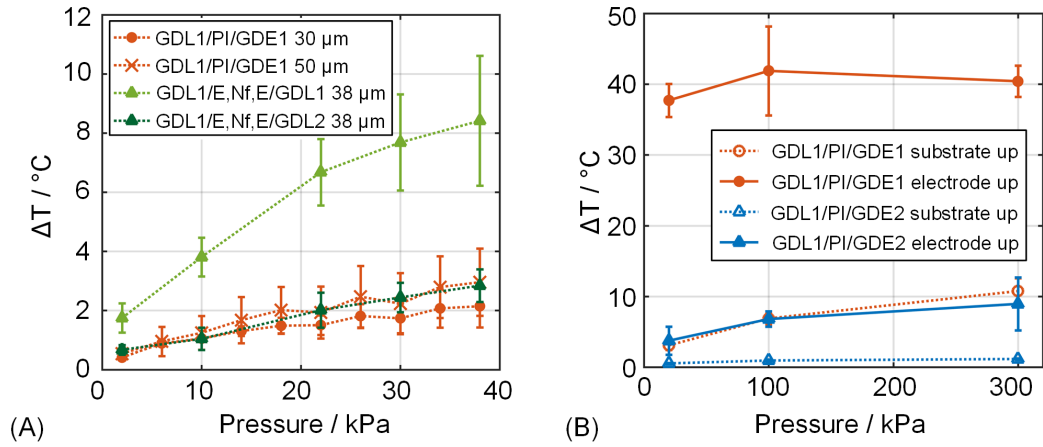


Figure 4.6: Dependence of the temperature rise ΔT on: (A) Applied forming gas pressure for test system I and II with pinhole diameters ranging from 30 μm to 50 μm . (B) Effect of orientation of GDE 1 and 2 in test system I, possessing a pinhole diameter of 100 μm (solid: electrode facing pinhole, dashed: substrate facing pinhole). Error bars show the scattering of samples of the same type.

mal conductivity of GDL 1 or an increasing amount of reacting gas molecules at the active sites, which will be discussed in the following.

4.3.1.1.3 Pt loading of electrode

The relevance of Pt loading on measured temperature rise ΔT and thus on the detectability of pinholes was shown by two experiments with test system I and II. Comparing measurements with GDL1/PI/GDE2 and GDL1/PI/GDE3 of test system I (see figure 4.5), an increase of the Pt loading resulted in an increase of the temperature rise ΔT . This dependence was shown for four pinhole sizes (100 μm , 200 μm , 300 μm , 500 μm) at ten different pressures (ranging from 2 kPa to 38 kPa). It has to be mentioned here that besides the Pt loading also the deviating permeability of GDE 2 and 3 could contribute to the observed change in the temperature rise ΔT .

The dependence of the temperature rise ΔT on the Pt loading was supported, when measuring the temperature rise ΔT on both sides of the electrode Nafion assembly of test system II. For the comparative measurement, the orientation of the electrode Nafion assembly was changed, that for the anodic measurement the anode side was facing the ambient air at the perforated clamping plate, while for the cathodic measurement the cathode side was facing the ambient air at the perforated clamping plate. The exothermic reaction takes mainly place at the electrode facing the perforated clamping plate, where hydrogen flowing through the pinhole and ambient air come into contact. Therefore, a difference of Pt loading could be investigated with

the described experiment, wherein the cathode possessed a larger Pt loading than the anode. For cathodic measurements the minimum pinhole diameter of 40 μm , which could be fabricated, was easily detectable, while for anodic measurements only pinholes larger than 200 μm could be detected. This indicated a strong dependence on the Pt content.

For test system III, the degraded MEA, it was found that artificial pinholes with a diameter of 100 μm could not be detected with IR-thermography, while for a perforated begin-of-life MEA pinholes with a diameter of 50 μm were easily detectable. Possible explanations might be the decreased electrochemical active area and the reduced cathode porosity within the degraded MEA. A decreased electroactive amount of Pt can reduce the amount of reacting gas molecules and thus the heat formation. This finding agrees with results of Moor et al. [87] observing a decreased temperature rise for advanced degraded MEAs compared to initially degraded MEAs. In addition, the porosity loss of the cathode electrode led to a reduced diffusion of reaction gases (hydrogen and oxygen) to the electroactive sites within the electrode, which also decreased the heat formation.

4.3.1.1.4 Thermal conductivity of GDLs

To qualitatively investigate the influence of the thermal conductivity of the GDL/ GDE, different GDLs/ GDEs were placed on top of a heated metal rod with a tip diameter of approximately 0.7 mm. Heat was not generated by exothermal reaction of hydrogen and oxygen at the electrode but was introduced by the tip of the metal rod. Therefore, the influence of gas pressure, gas supply and Pt loading was excluded. The different thermal conductivities of the GDEs/ GDLs resulted in a different thermal conduction of the heat from the MPL/ electrode side to the substrate side of the GDEs/ GDLs. Thus, for the same heat impact at the MPL/ electrode side, different temperature rises at the substrate side were measured. For instance, a tip temperature of approximately 40 $^{\circ}\text{C}$ led to a temperature rise of $\Delta T=5.9^{\circ}\text{C}$ and $\Delta T=1.9^{\circ}\text{C}$ on top of GDE 1 and 2, respectively (see figure 4.4 (B) and (C)). Therefore, it was concluded that thermal conductivity of the GDL had a strong influence on the detectability of pinholes. Herein, a high through-plane thermal conductivity led to a stronger local enhancement of ΔT .

4.3.1.1.5 Oxygen and hydrogen supply to active sites

Gas supply limitations of hydrogen and oxygen to the active sites of the electrodes, which reduce the amount of reacting gas molecules, were also assumed to have an influence on the measured ΔT . The oxygen gas supply was mainly limited by the permeation properties of the GDL, which was determined by the microporous structure of the MPL. This property could not only deviate for different GDL types (see e.g. GDL 1 and 2 in table 4.1), but could also be altered for degraded samples. The hydrogen gas supply is not only determined by the applied pressure, the pinhole size and the electrode porosity, but also by the contact area between pinhole

and electrode. As indicated in figure 4.3 (B) (3), a rough electrode area or an uneven MPL/ electrode interface increased the electrode surface area being supplied with hydrogen by introducing additional voids between MPL and electrode. For instance, the MPL of test system III was strongly adhering to the electrode area, which could result in a decreased amount of active electrode sites being exposed to both reaction gases. This could possibly contribute to the decreased pinhole detectability compared to begin-of-life reference samples.

In order to evaluate the influence of hydrogen and oxygen gas supply towards the active areas, the GDE of test system I was turned upside down, meaning that the GDL substrate and not the electrode is directly facing the pinhole. Thus, the oxygen supply towards the active sites was strongly enhanced due to the exclusion of oxygen permeation through the GDL/ MPL material. In addition, a larger electrode area was supplied by hydrogen by distributing the hydrogen through the porous structure of the GDL/ MPL. This configuration resulted in an increase of ΔT by up to 40 °C for GDL1/PI/GDE1 (see figure 4.6 (B)), demonstrating the influence of the gas supply to the active sites on the measured ΔT . For each measurement three samples were measured and averaged. The avoidance of thermal conduction through the GDL could maximally explain a rise of ΔT by approximately 15 °C.

A further increase of ΔT was obtained when blowing air towards the electrode, thus additionally showing the dependence of measured temperature rise on oxygen permeation towards the pinhole site. Although the influence of hydrogen and oxygen gas supply could not be separated in this experiment, it was shown that permeation properties of the GDL and the roughness of the pinhole/ electrode or pinhole/ MPL interface could lead to different temperature rises ΔT .

4.3.1.1.6 Hardware positioning

Finally, also the hardware design and positioning, especially of the perforated clamping plate (see figure 4.3 (B) (6)), was demonstrated to have an influence on the measured temperature rise ΔT . For instance, using GDL1/PI/GDE1, the minimum detectable pinhole diameter was increased from 10 μm to 50 μm when placing the pinhole below a bulk part of the perforated clamping plate.

4.3.1.2 Helium-gas detector

Similarly to IR-thermography, the method was found to be nondestructive. Figure 4.7 shows the helium flow rate above a 5 μm and 10 μm pinhole of test system I measured with two different GDL/ GDE types. Values were compared to the helium flow rate above a non-perforated begin-of-life reference MEA of test system I and II. Within the measurement accuracy of the sensor, the helium flow rate above a non-perforated polyimide foil (test system I) was found to be zero and independent on the applied pressure. The helium flow rate above the non-perforated Nafion based begin-of-life reference MEA of test system II was found to be around one to two intensity bars, which was increasing with increasing gas pressure.

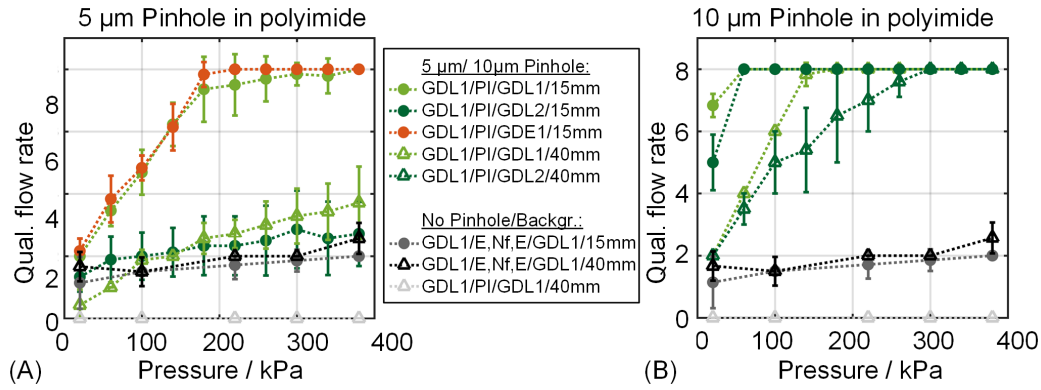


Figure 4.7: Qualitative helium flow rate as a function of applied gas pressure for a 5 μm (A) and 10 μm (B) pinhole in test system I. Background flow through a non-perforated MEA of test system I (polyimide membrane) and test system II (Nafion membrane) is shown for comparison. Funnel sizes (15 mm or 40 mm) are indicated in the legend. Error bars show the scattering of samples of the same type.

A pinhole was detected when the measured helium flow rate was increased by at least two intensity bars compared to the background of the non-perforated Nafion based begin-of-life reference MEA. Similarly to the non-perforated Nafion based MEA, the helium flow rate above the perforated MEAs of test system I and II were found to increase with increasing gas pressure. The detectability of pinholes depended on both the funnel size used and the GDL permeability. As shown in figure 4.7 (A), 5 μm pinholes were detected for GDL1/PI/GDE1 and GDL1/PI/GDL1, when using the 15 mm funnel but were not detected when using the 40 mm funnel. This was explained by the increased scanning area of the 40 mm funnel. The measured total diffusive He-crossover including background crossover was increased for the 40 mm funnel, while the convective crossover through the pinhole remains constant. Using GDL1/PI/GDL2 the measured helium flow rate above the 5 μm pinhole was not enough to detect the pinhole for both funnels, which could be explained by the strongly decreased gas permeability of GDL 2 compared to GDL 1 and GDE 1 (see table 4.1). Pinholes with a diameter of 10 μm and larger were however detected with both 15 mm and 40 mm funnel and for GDL1/PI/GDL1 and GDL1/PI/GDL2 (see figure 4.7 (B)). At this point, it has to be emphasized again that measured values were only qualitative and no quantitative comparison could be made. The obtained sensitivity is in good accordance with findings of Kreitmeier et al [146]. Using a mass spectrometer, they showed that the convective helium crossover through a 10 μm pinhole is comparable to the diffusive crossover through a 1 cm^2 sized and 25 μm thick Nafion membrane at an applied temperature of 80 $^{\circ}\text{C}$, a relative humidity of 0 % r.h. and a differential gas pressure of 10 kPa. As for IR-thermography, the detection ranges were also validated on two state-

of-the-art MEAs from automotive mid-size stacks. All pinholes, being observed by optical imaging, with diameters ranging from 10 μm to 100 μm on both MEAs were detected. In addition, the increased helium crossover above the region of membrane thinning was measured. These results support the detection limits determined with test system I and II.

Besides the influence of material properties like GDL permeability, also a dependence of the detectability on the hardware and its positioning was found. For instance, using GDL1/PI/GDL1 the helium flow of a 5 μm pinhole could not be detected anymore, when being placed below a bulk part of the clamping plate. For increasing pinhole diameter this effect was reduced. Pinholes with a diameter of 10 μm and larger could be detected with both funnels for GDL1/PI/GDL1, GDL1/PI/GDL2 and GDL1/PI/GDE1, independently of the positioning of the pinhole with respect to the perforated clamping plate.

4.3.1.3 Pressure drop method

Within the pressure drop method, a MEA was considered to be defective if an internal pressure drop between anode and cathode of 0.2 kPa min^{-1} was reached. With the measurement setup used, pinholes with a diameter of 200 μm and larger could be detected. This means that only large membrane defects were detected, which is in accordance with literature mostly applying the method as first test for leakage detection [87, 88]. In few cases, pinholes with smaller diameter were detected. This was likely due to the heterogeneous structure of the MPL. For instance, it is assumed that gas permeation and thus measured pressure drop can be strongly enhanced for pinholes being placed below a MPL crack (see Pos. 1 in figure 4.2 (C)) compared to pinholes being placed below a bulk-part of the MPL (see Pos. 2 in figure 4.2 (C)). Thus, our results indicated that the detection limit is dependent on local GDL properties. Similarly, Kreitmeier et al. [146] found a decreased gas crossover through a perforated membrane, when placing a GDE on top it.

4.3.1.4 Hydrogen crossover method

Comparing measured hydrogen crossover current of defective MEAs to begin-of-life MEAs enables the detection of membrane defects. As illustrated in figure 4.8 it was demonstrated, that the application of a differential pressure between anode and cathode results in an increase in the hydrogen crossover current difference between a perforated and a non-perforated catalyst coated membrane compared to measurements without differential pressure. This pressure dependence of the hydrogen crossover current is in accordance with He-gas crossover measurements of Kreitmeier et al. [146]. They showed that an increasing differential pressure resulted in a significant increase of convective He-gas flow through pinholes, while the diffusive convection through the membrane was only slightly increased. This correlation was used to optimize hydrogen crossover measurements for pinhole detection. Applying a differential pressure of 50 kPa, pinholes with an approximate

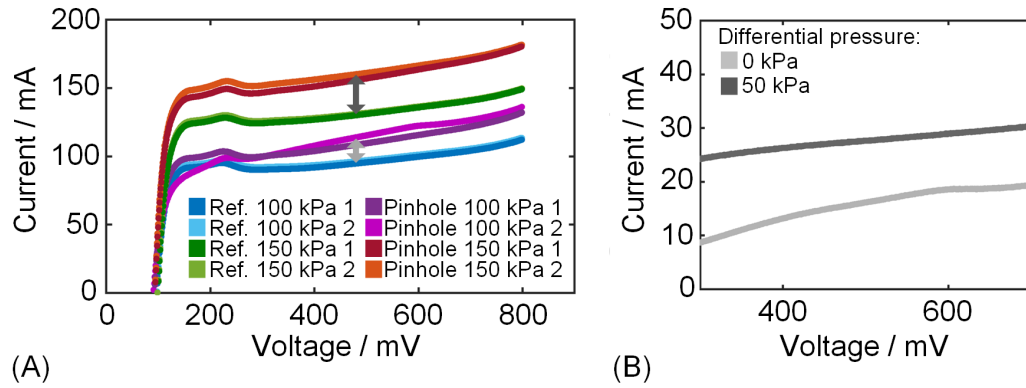


Figure 4.8: (A) Oxidation current of crossover hydrogen of perforated (Pinhole) and non-perforated (Ref.) MEAs with different differential pressures between anode and cathode as a function of applied potential. The pressure of cathode is 100 kPa and the pressure of the anode is listed in the diagram. The increase of the hydrogen oxidation current for a perforated MEA compared to non-perforated MEA is enhanced when applying a differential pressure between anode and cathode. (C) Increase of hydrogen oxidation current of a perforated MEA compared to non-perforated MEA at two differential pressures between anode and cathode as a function of applied potential.

diameter range of 40 μm to 50 μm in two different Nafion based MEAs of test system II (GDL1/E,Nf,E/GDL1) showed an average increase in hydrogen crossover current of about 10 % - 20 % compared to non-perforated begin-of-life reference MEAs and were thus considered to be detectable. Hydrogen crossover current of GDL1/E,Nf,E/GDL1 possessing a pinhole with a diameter of 100 μm were measured to increase by about 90 % compared to non-perforated begin-of-life reference MEAs. Since a pinhole diameter of 40 μm , which was the smallest size that could be fabricated, was easily detected, it was concluded that the detection limit of the method is below this value. This detection limit was found to be below pinhole diameters detected in literature, which range from 80 μm to 600 μm [91, 95, 96]. It has to be mentioned here, that the detection limit may be strongly influenced by the state of the electrode. As described by Kreitmeier et al., a decreased catalytic activity of the electrode, e.g. due to degradation effects, can strongly decrease the measured crossover current [146]. In addition, it is assumed that not only the catalytic activity of the electrode but also the hydrogen supply towards the catalytic sites influence the measured crossover current. Hydrogen distribution towards the catalytic sites was given by both the electrode porosity, the shape of the pinhole and the GDL/ electrode interface forming differently sized voids, which can especially be altered for degraded samples.

4.3.2 Comparison of the methods

A comparison of the methods as listed in table 4.2 showed different detection limits and detection dependencies on material properties as well as different handling characteristics and pinhole localization abilities. This illustrates, that each method is suited for a specific analysis. In the following the characteristics of the different methods are discussed.

Pinhole detection with IR-thermography enables a fast localization of all pinholes on a MEA by evaluating the hot spots in the IR-image. The method is strongly dependent on the electrode and GDL properties, which is especially relevant for degraded samples. This makes the definition of a clear detection limit ($d = 10\ \mu\text{m}$ to $100\ \mu\text{m}$ as determined in this work) and a calibration of pinhole size to measured temperature rise ΔT difficult. Furthermore, the positioning of the pinhole below bulk parts of the perforated clamping plate was found to have a strong influence on the detectability of small pinholes. This problem can of course be avoided by repositioning of the clamping plate, which is however a time-consuming process. Detection limits can be further improved by removing the GDL and thus eliminating the thermal conductivity and oxygen supply limitation of the GDL. The removal of the GDL is in most cases a destructive process. In addition, due to the lack of the mechanically and thermally stabilizing GDL, a destruction of the sample during the measurement cannot be excluded. Besides pinhole detection, the method can also be used for the detection of membrane thinning, by comparing the average MEA temperature of the degraded sample to a begin-of-life reference sample [92, 94]. Due to increased hydrogen crossover through a thinned membrane, an increased temperature resulting from increased exothermal reaction can be measured. It should be mentioned, that the measured temperature rise ΔT above a pinhole, calculated as the difference between maximum MEA temperature above the pinhole and average temperature of the surrounding MEA, is altered by membrane thinning. Thus, a comparison of temperature rises above a pinhole for MEAs with membranes of different thickness is difficult. As an additional tool short-cut measurements can be performed with the IR-thermography setup by applying an electrical potential between anode flow-field and perforated cathode clamping plate, wherein current flow at the short circuit leads to a local temperature rise [278]. In summary, IR-thermography is a fast method for pinhole localization. The detectable pinhole size, depends however strongly on the material properties of the MEA components, which is in particular relevant for degraded samples possessing altered and mostly unknown material properties.

Pinhole detection with He-gas detector was shown to be able to detect pinholes with a diameter of $5\ \mu\text{m}$, the smallest size, which could be fabricated. The detection limit were found to depend on the size of the used funnel. By scanning the MEA, pinholes can be localized on the MEA. The method possesses a dependence on gas permeability of the material system as well as on the positioning of the perforated clamping plate. Due to the manual scanning process, the measurement of

a whole automotive size MEA is time consuming in particular when compared to IR-thermography. In this context, an automation of the scanning process would be beneficial. Helium flow rate above the membrane can also be used as an indicator for membrane thinning. Increased background helium flow rate due to membrane thinning can however decrease the detectability of pinholes. In summary, it was found that the He-gas detector method is a very sensitive tool for detection and localization of small pinholes, which, however, when not automatized, requires an increased measuring time compared to other methods.

Both pressure drop and hydrogen crossover measurements possess the advantage of being directly implementable at the fuel cell test station and are thus a relatively quick option for pinhole detection. However, with both methods no localization of the pinholes on the MEA could be obtained. In addition, it was not possible to distinguish between one large pinhole or several small pinholes or severe membrane thinning.

Pinhole detection via pressure drop enables the reproducible detection of pinholes of 200 μm diameter and larger, which is similar to the detection range of relaxometry as shown by Moor et al. [87]. The method is strongly dependent on the local MPL properties in the proximity of the pinhole enabling the detection of smaller pinholes under specific conditions. It has to be mentioned here, that the method is also strongly dependent on the test station hardware, which determines the analyzed volume. With increasing analyzed volume the sensitivity of the method is decreasing, since at a constant volume flow through the pinhole, the internal pressure drop of the analyzed volume is decreased. By increasing the differential pressure, the detectability of the method can be improved. In summary, it is found that the pressure drop method is a very fast and easy implementable method for detection of large membrane defects, which is however not sensitive enough for reliable detection of small pinholes ($d < 200 \mu\text{m}$).

In case of hydrogen crossover measurements an electrochemical workstation is required in addition to the fuel cell test station. Hydrogen crossover measurements were found to detect pinholes of diameters as small as 40 μm , which was the minimum pinhole size, which could be fabricated in test system II. Electrode and GDL properties can have an influence on the measured hydrogen crossover current and thus the sensitivity of the method. Determination of pinhole size from measured hydrogen crossover current is difficult due to the dependence of the measured crossover current on the proximity of the pinhole to the gas outlets [91] and the fact, that total gas crossover will be underestimated by the methodology [146]. In summary, hydrogen crossover measurements were found to be a fast tool to detect pinholes with a diameter range of a few tens of micrometer.

Table 4.2.: Comparison of the four pinhole detection methods.

Method	Detection limit	Advantage	Disadvantage	Recommended application
IR-thermography	10 μm - 100 μm	- Pinhole localization - Short-cut detection possible - Fast method	Detection limit strongly dependent on electrode properties, GDL properties, and the positioning of the clamping plate	Fast localization of large pinholes or application for well-defined material systems (e.g. quality control after manufacturing)
Helium-gas detection	5 μm / 10 μm (dependent on funnel size)	- Pinhole localization - High sensitivity	- Slow manual scanning of MEA (automation possible) - Detection limit dependent on GDL permeability and positioning of clamping plate	Localization of small pinholes
Pressure drop	200 μm	- Fast method - Implementable at the fuel cell test station	- No pinhole localization - Detection limit dependent on GDL permeability - Low sensitivity	Fast and easy detection of large pinholes
Hydrogen crossover	< 40 μm (smallest diameter, which could be fabricated)	- Fast method - Implementable at the fuel cell test station	- No pinhole localization - Detection limit dependent on GDL permeability and electrode properties	Fast detection of mid-size pinholes

4.4 Conclusion

Four promising methods for pinhole detection, namely detection via IR-thermography, helium-gas detection, pressure drop and hydrogen crossover measurements, were investigated and compared by means of their detection limits and dependencies e.g. on the material system such as Pt loading and morphology of the carbon network. Pressure drop and hydrogen crossover measurements were found to be fast and relatively easy implementable methods with detectable pinhole diameters of approximately 100 μm and 40 μm for the investigated material and the used test station, respectively. Herein, detection limits of pressure drop and hydrogen crossover methods depended on material properties of the investigated MEA. Detection of reaction heat of crossover hydrogen by IR-thermography and detection of helium-gas concentration above a pinhole required an additional cell hardware with a perforated clamping plate. Detection by IR-thermography enabled a fast localization of pinholes. Detected pinhole sizes were strongly dependent on both electrode and GDL properties as well as on hardware positioning and varied between diameters of 10 μm and 100 μm for the investigated materials. For the material system used in this work, the use of a helium-gas detector enabled the localization of pinholes with a diameter of 5 μm (smallest pinhole size that could be fabricated), with the detection limit being dependent on GDL gas permeability and hardware positioning. Scanning of the whole MEA was more time consuming as for other methods. Due to the diversity of membrane degradation, different analysis task may arise ranging from fast screening of a general membrane failure to a sensitive localization of small pinholes. Therefore, a comparison of the different methods and a suggestion for their application was given. The detection of membrane defects of MEAs from two automotive stacks demonstrates the applicability of the IR-thermography and helium detection in an automotive failure analysis process. In total, an assembly of different pinhole detection methods was suggested for an appropriate pinhole analysis.

Chapter 5

Gas diffusion layer wettability determination by cyclic voltammetry for automotive fuel cells

This chapter is an extended version of a research article that was submitted in the journal *Fuel Cells* [279]. In brief, the following subjects are addressed. Fuel cell performance and durability are highly dependent on water management, wherefore wettability properties of the cell's gas diffusion layer are important. In this chapter, a method to determine the GDL wetted surface area is introduced, which is based on capacitance measurements by cyclic voltammetry with a pH-neutral, aqueous electrolyte, to an automotive size fuel cell failure analysis process and demonstrate its benefit. The electrolyte penetrates large pores of the GDL, wherefore, by contrast to most conventional methods, also inner parts of the GDL are measured. Tenside concentration of the electrolyte and penetration time, polytetrafluoroethylene treatment of the GDL and properties of the microporous layer highly influence the capacitance values. Thus, the method is sensitive to different GDL morphologies and surface modifications. Different degradation patterns for samples either artificially chemically and mechanically aged or after real-operation (e.g. prototype vehicle) were detected by the method. For a comprehensive understanding, the obtained results are compared to ex situ degradation analysis data. A comparison to static contact angle measurements, being a state-of-the-art method to determine GDL wettability, revealed a higher sensitivity of the introduced method to detect degradation, in particular of chemically aged and real-operation aged GDLs.

5.1 Literature review

For commercialization of fuel cell electric vehicles both a high efficiency and durability are of great importance, which depend on effective water management within the cell [36, 39, 83, 117]. Water formed by the electrochemical reaction or by condensation from humidified gases has to be removed from the CL to guarantee good gas supply to the active sites and to avoid electrode flooding. Electrode flooding both at anode and cathode can lead to performance loss and severe degradation [36, 39, 83, 156, 201, 280, 281]. On the other hand, membrane drying leading to both low performance due to a reduced proton conductivity and increased chemical membrane degradation [36, 39, 83, 155, 156, 201] has to be avoided. For optimized water management, wetting properties of GDLs play an important role [32, 39, 75, 83, 201, 282]. GDLs typically consist of a MPL being applied to a fiber substrate like carbon paper or carbon cloth. To improve water removal properties hydrophobic components like polytetrafluoroethylene (PTFE) are usually coated onto the GDL. Several methods exist to investigate the wetting behavior of water on the GDL surface [80], including dynamic and static contact angle measurements [80, 81], methods using capillary effects like the Washburn method [75–77], or methods using contact forces with a known liquid like the Wilhelmy method [78, 79]. In addition, in situ methods like electrochemical impedance spectroscopy or current density measurements can be used to obtain information on the transport of water within MEAs [80].

Another technique capable of determining the wettability of a GDL is cyclic voltammetry where typically an acidic electrolyte is used for the experiments. At the electrolyte/ GDL interface a Helmholtz double layer is forming. The corresponding capacitance measured with the CV experiment gives a value for the wetted GDL surface area and is thus an estimation of the GDL wettability. CV was used in several studies to determine wettability of different structures including carbon composites [283], carbon black and electrodes [284–286]. In addition, the method was also applied to carbon cloth materials [84–86]. For instance, Yu et al. [85] performed CV measurements to characterize GDLs after artificial electrochemical oxidation in acidic media and found an increasing CV current for electrooxidized GDLs. Their results were supported by decreasing contact angle values, indicating an increased wettability behavior. Similarly, Joo et al. [86] found increasing CV current for Pt-coated GDLs after potential cycling. Electrochemical oxidation is only one of several degradation mechanisms, which can occur for GDLs, an overview is given by Park et al. [181]. Numerous reasons starting from erosion by gas and fluid circulation [129, 183], electrochemical degradation like carbon corrosion resulting in changes of the GDL surface structure, formation of functional surface groups, PTFE loss [129, 185, 215, 287], degradation due to immersion in water or acidic media [183] and degradation due to compression [184, 190, 288] are described in literature.

In this chapter, CV measurements are adopted to determine GDL wettability and showed its benefit in a fuel cell degradation analysis process for automotive size PEMFCs. Instead of an acidic electrolyte as used in literature [84–86, 284–286], a pH-neutral aqueous electrolyte, improving handling and safety issues was used. Like that, a possible change of the GDL surface properties due to the acidic electrolyte was minimized. The influence of GDL's structural properties, tenside concentration of the electrolyte, and electrolyte penetration time were investigated. Various GDL types possessing different morphologies, as visualized by X-ray microscopy and scanning electron microscopy, were analyzed and shown to be distinguishable by our method. The benefit for failure analysis of automotive PEMFC was demonstrated by correlating the results of different artificially and real-operation degraded samples to ex situ degradation analysis and static contact angle measurements. Artificial chemical degradation of the GDLs was achieved by immersion into hydrogen peroxide (H_2O_2), as it was reported in literature that this leads to similar degradation concerning water management as long time operation of the MEA [201, 211]. Mechanical degradation was simulated by applying different compressive loads. Real operation samples, showing carbon corrosion degradation due to fuel starvation, were taken from a prototype vehicle as well as from a fuel cell test station operating at different automotive driving points.

5.2 Experimental details

5.2.1 Measurement setup

Cyclic voltammetry measurements were carried out with a three-electrode setup, as illustrated in figure 5.1. A gold wire and a saturated silver/silver chloride electrode (Ag/AgCl) were used as counter electrode and reference electrode, respectively. Reference electrode potential is given by 0.197 V vs reversible hydrogen electrode. The sample under investigation served as working electrode. Counter electrode and working electrode were attached with clip terminals. Samples were stamped out with the help of a stamping tool and put into a mask for proper placement of the working electrode in the measurement setup (see figure 5.1 A). A copper (Cu) plate was used for a good electrical contact of the working electrode. A solution of sodium chloride (0.1 mol l^{-1}) served as an electrolyte. In order to enable the electrolyte to penetrate the GDL and thus to wet its fiber substrate and MPL, the surface tension of the electrolyte had to be reduced. This was achieved by adding the tenside sodium lauryl sulfate (0.42 mol l^{-1}) to the electrolyte. For each measurement 60 ml of the electrolyte was filled in a reservoir, possessing a circular opening with a diameter of 1 cm. Herein, the opening was facing the substrate side of the GDL. Since the GDL thickness was much smaller than the diameter of this circular contacting area, we assumed the diameter of the area being penetrated by the electrolyte to be constant within the whole GDL. Therefore, the measured capacitance

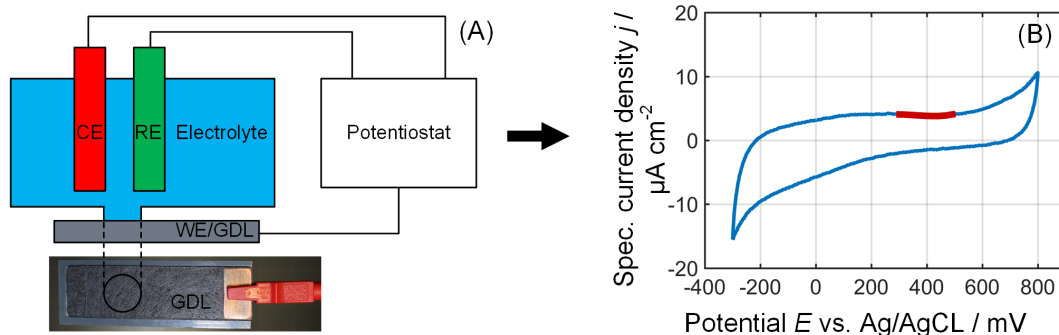


Figure 5.1: A) Schematic of the three-electrode setup for CV measurements, consisting of working electrode (WE), counter electrode (CE) and reference electrode (RE). A GDL, being placed in a mask with the substrate side facing the electrolyte, was used as a WE. An optical micrograph shows the GDL from top. (B) Example CV-curve, wherein the red line illustrates the specific capacitive current density used to calculate the specific capacitance.

is normalized to the circular contact area. For PTFE untreated GDL substrates the electrolyte visibly penetrated larger parts of the GDL. Since the exact penetrated area could not be measured, an estimation of a maximum and a minimum penetrated area was made for the normalization of the measured capacitance. The CV measurements were done with a potentiostat (Metrohm Autolab PGSTAT302N). If not otherwise specified, the measurement was started 10 min after filling the electrolyte into the cell. This exposure time prior to measurement is referred as penetration time in the following. Five CV cycles from -300 mV to 800 mV vs Ag/AgCl were recorded with the Software Nova (Vers. 1.11) (see figure 5.1 B). A scan rate of 200 mV s^{-1} and a step potential of 2.44 mV was applied. Due to the applied potential difference a double layer is formed at the interface between GDL and electrolyte. The associated capacitance was used as a measure for the wetted surface area. The specific capacitance of the GDL was calculated by dividing the mean capacitive current of the anodic trace in the range of 300 mV to 500 mV from the fifth cycle (see red line in figure 5.1 B) by the scan rate and normalizing it to the measured circular area. The potential range of 300 mV to 500 mV was chosen due to the stability of the capacitive current in this potential range for the investigated materials.

5.2.2 Investigated materials

Three different GDLs of SGL Carbon SE were analyzed, having a similar overall thickness and nominally the same PTFE treated fiber substrate (substrate 1) but different MPLs with approximately the same PTFE content. In addition to the GDLs themselves, the fiber substrates with PTFE-treatment (substrate 1) and with-

out PTFE treatment (substrate 1*) were also investigated individually to determine the effect of PTFE and the influence of the MPL.

Different degraded samples of GDL 1 and degraded fiber substrates with and without PTFE treatment were analyzed to prove the validity of the method. Samples of GDL 1 were mechanically aged by applying different compression forces to automotive MEAs being assembled in a short stack setup (stack static compressive forces up to 15 kN as well as cycling from 0 kN to 15 kN (10 times) and from 22 kN to 28 kN (10 times)). Due to the compression of the sealings, the applied compression force to the GDL will be smaller than the compression force being applied to the stack setup. Cycling under compressive load is supposed to simulate stack changes during operation, which are caused by humidity and temperature induced swelling and shrinkage of the stack components. The applied forces are typical compression forces occurring within the full size stack of the investigated automotive MEA design. The investigated GDLs had all the same size of approximately 260 cm². Samples of GDL 1 were additionally chemically aged by immersing the GDLs into a 30 % wt. H₂O₂ at 80 °C for different times. After chemical degradation samples were rinsed and immersed in distilled water for at least 24 h. This kind of artificial degradation was reported by Frisk et al. to show similar performance losses due to altered water management as GDLs being degraded during long term fuel cell operation [211] and was applied in several other studies [201, 215, 287, 289–292].

In a last step, GDLs degraded under real automotive conditions were investigated. GDLs of type 1 were taken from an automotive stack of a prototype vehicle. GDLs of type 2 were aged for approximately 100 hours in an automotive full size stack, and had suffered severe fuel starvation, as described in chapter 6. MEAs from both stacks showed carbon corrosion degradation.

5.2.3 Further analysis methods

Cross sections for scanning electron microscopy (SEM) imaging were prepared by a cryo cross section polisher (JEOL IB-19520CCP). SEM (FEI Quanta FEG 650) was applied to get morphological information in top and cross-section view. For imaging, back-scattered electrons or secondary electrons with an acceleration voltage of 10 kV were detected.

GDL and substrate thickness were measured at minimum 17 measurement points with a thickness gauge (Frank PTI 16502, tip diameter 5 mm, applied pressure 125.2 kPa). MPL crack density was determined by image threshold analysis (Imagic IMS (Vers. V19H2)) of optical micrographs (Keyence VHX-6000) as described in chapter 6. For each GDL, four images were used with a size of 11 mm x 11 mm. X-ray microscopy (XRM) of one 2 mm x 2 mm sample of each GDL was performed (ZEISS Xradia 620 Versa) by Dr. Stephan Diez to visualize the cross section and to determine the thickness of different layers. MPL thickness and penetration depth of each GDL was measured at 52 different positions with a spacing of at least 100 µm.

GDL and substrate thickness was measured at 10 XRM cross section images, with a spacing between the positions of the images of at least 200 μm . The areal weight was determined by measuring the weight of five samples with a defined area of 19 mm x 67 mm for each GDL and substrate with the help of an analytical balance (Satorius Cubis MSA).

The porosity of different samples was measured with mercury-porosimetry (Quantachrome Poremaster 60-GT) (performed by 3P Instruments GmbH & Co. KG). Each investigated sample had an geometric area of at least 11 cm^2 . Nitrogen sorption isotherms were recorded (Micromeritics ASAP 2020) to determine the surface area using Brunauer-Emmet-Teller (BET). Each investigated sample had an geometric area of at least 50 cm^2 . Inductively coupled plasma optical emission spectrometry (PerkinElmer Optima 8300) was applied in order to detect possible contamination with foreign ions.

The penetration properties of the electrolyte were studied by adding fluorescein (42 mmol l^{-1}) to the electrolyte and optical imaging of the GDL with ultraviolet light, after being exposed to the electrolyte for 10 min. In addition, Cu was plated on the GDL with the help of a two-electrode system (Cu-rod and GDL as counter/reference and working-electrode, respectively) and a potentiostat (Metrohm Autolab PGSTAT302N). A Cu-electrolyte (0.69 mol l^{-1}) in H_2SO_4 (0.24 mol l^{-1}) with the addition of tenside was used, with a similar surface tension than the standard electrolyte. For plating, a pulsed potential between 0 V (1 s) and 1.2 V (0.005 s) was applied between counter and working electrode for 1000 cycles. Mechanically cut cross-sections of plated GDLs were investigated with SEM. Finally, static contact angle measurements of distilled water degraded GDLs and begin-of-life reference GDLs were performed using the sessile drop method (Krüss DSA-100). Herein, the contact angle calculated from an ellipsoid fit of the water droplet of at least 15 measurement points at different positions of the investigated GDL were calculated and averaged.

The investigated GDL samples showed a high variance, leading to a strong scattering of the samples, exceeding the accuracy of the applied measuring techniques. Therefore, the uncertainty of the measurement values was specified as the scattering of the samples. An exception was made for the thickness gauge, where a measurement accuracy of 1 μm was included in the specified error.

5.3 Results and discussion

5.3.1 Influence of the morphology of gas diffusion layers

The sensitivity of the cyclic voltammetry method towards parameter changes and GDL characteristics was studied on begin-of-life samples. The GDL morphology was found to highly influence the measured specific capacitance.

The values for the areal weight are given in table 5.1 and it can be seen that they

are similar for all investigated GDLs. The contribution of the areal weight of the substrate with and without PTFE treatment ($35 \pm 1 \mu\text{g mm}^{-2}$ and $32 \pm 1 \mu\text{g mm}^{-2}$) was determined to be less than half of the GDL areal weight.

The different GDLs were studied by SEM and XRM to determine their morphologies. A three-dimensional reconstruction of GDL 1 ($1 \text{ mm} \times 1 \text{ mm} \times 0.23 \text{ mm}$) using XRM is illustrated in figure 5.2 A. The substrate of the GDL is shown on top and is formed by several carbon fibers creating a fiber network. The MPL of the GDL is displayed at the bottom and penetrates parts of the substrate forming a rough layer with several cracks. Figure 5.2 B exemplarily shows SEM micrographs of the MPL surface and XRM images of cross sections of GDL 1, 2 and 3, respectively.

The XRM and SEM images were used to determine the thickness of different layers and the MPL crack density, respectively (see table 5.1). Within the scattering of the samples, all GDLs showed similar thicknesses of approximately $230 \mu\text{m}$. From this total thickness, the thickness of the substrates amounts to a thickness around $185 \mu\text{m}$. The substrate of GDL 1 seems to be slightly larger, which might be due to local heterogeneities of the investigated GDLs. Similar thickness values of all GDLs were obtained using a thickness gauge and measuring at 20 different positions of each investigated GDL. The MPL thicknesses differ for the different GDLs, with increasing thickness from GDL 1 ($74 \pm 40 \mu\text{m}$) to GDL 2 ($90 \pm 34 \mu\text{m}$) and GDL 3 ($101 \pm 32 \mu\text{m}$). MPL penetration depth into the substrate showed values ranging from $0 \mu\text{m}$ to more than $100 \mu\text{m}$ for all investigated GDLs. The highest overall penetration depth was detected for GDL 2, where the penetration depth was larger than $40 \mu\text{m}$ for 61 % of the 52 investigated sample positions. GDL 1 and 3 showed a percentage of MPL penetration depth exceeding $40 \mu\text{m}$ of 37 % and 46 %, respectively, of all the investigated positions (more than 50). The threshold of $40 \mu\text{m}$ was chosen because this value roughly equals half of the total MPL thickness of GDL 1. In general, a large scattering of MPL layer thickness and penetration depth was observed, which is related to the porous morphology of the GDLs. In addition to the increased MPL penetration depth, GDL 2 showed an increased crack density ($9.4 \pm 1.8 \%$) as compared to GDL 1 ($4.0 \pm 1.7 \%$) and GDL 3 ($3.5 \pm 0.8 \%$), which might be correlated to the increased MPL penetration depth. Different penetration depths and crack densities could be due to different MPL deposition processes on the substrate for GDL 1, 2 and 3.

The different GDL characteristics can create different surface areas being penetrable by the electrolyte, leading to different specific capacitances (see figure 5.3). The specific capacitance of substrate 1 and 1* with and without PTFE treatment were measured to be $25 \pm 3 \mu\text{F cm}^{-2}$ and $188 \pm 65 \mu\text{F cm}^{-2}$, respectively. This shows that a PTFE treatment of the GDL substrate hinders the wetting of its surface. The values for the specific capacity of GDL 1, 2 and 3 were determined to be $25 \pm 5 \mu\text{F cm}^{-2}$, $35 \pm 4 \mu\text{F cm}^{-2}$ and $17 \pm 2 \mu\text{F cm}^{-2}$, respectively. These values show that the specific capacitance is affected by the type of MPL used, as GDL 1, 2 and 3 consist all of the same substrate 1 with the same PTFE treatment. Depending on the MPL type additional wetted surface area can be created due to the presences

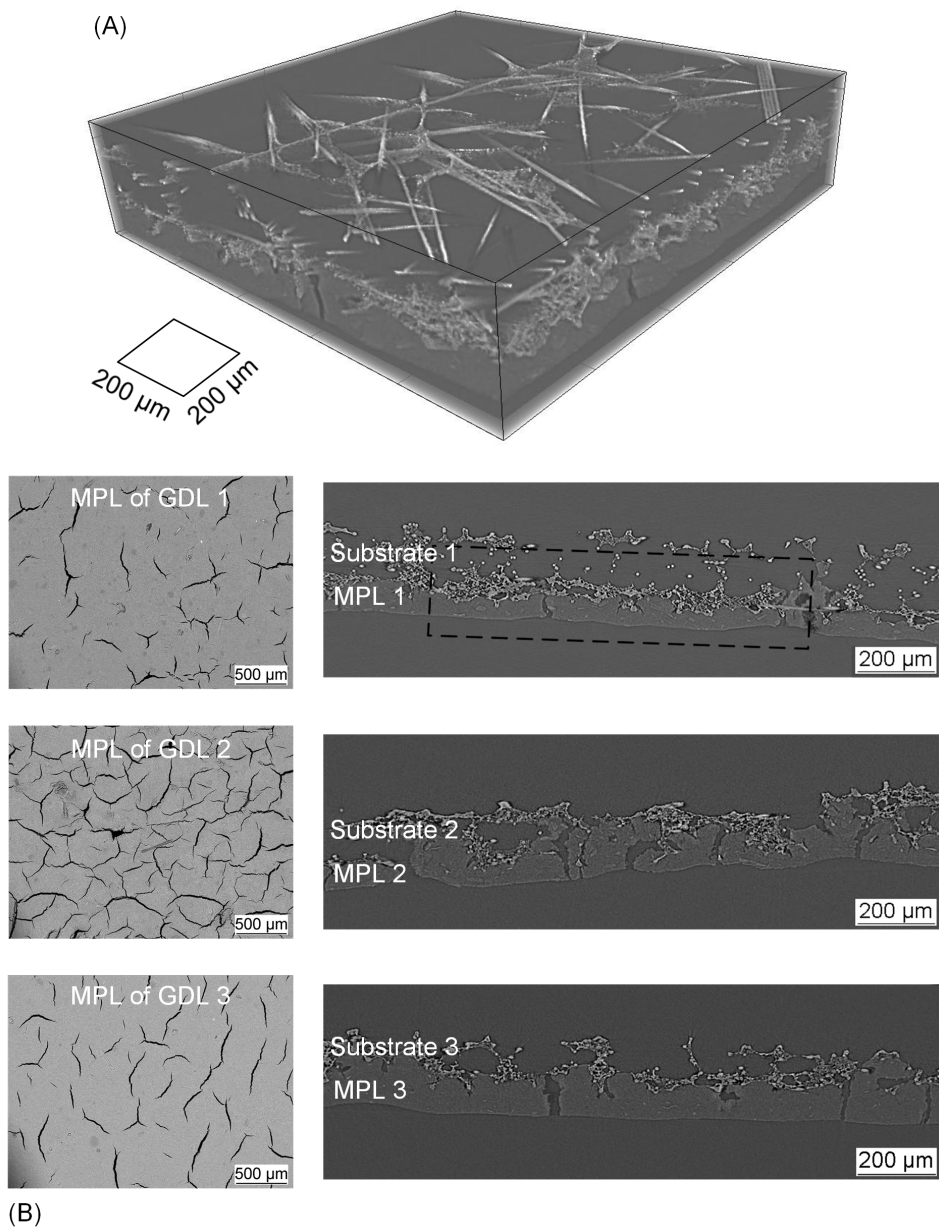


Figure 5.2: Morphologies of GDL 1, 2, and 3. (A) Reconstructed 3D XRM image of GDL 1 showing the fiber substrate on top of the MPL. (B) SEM micrographs of the MPL (left) and XRM cross section images of the GDL (right) of the three different GDL types. Dashed box in XRM image of GDL 1 shows the position of the 3D XRM image in (A). The GDLs differ in the crack density and the penetration depth of the MPL within the fiber substrate.

Table 5.1: Properties of the investigated GDL samples. The errorbar is equivalent to the standard deviation.

	GDL 1	GDL 2	GDL 3
GDL thickness via thickness gauge / μm	224 ± 6	229 ± 3	229 ± 3
GDL thickness via XRM / μm	240 ± 13	224 ± 4	230 ± 7
Substrate thickness via XRM / μm	206 ± 15	184 ± 4	174 ± 8
MPL thickness via XRM / μm	74 ± 40	90 ± 34	101 ± 32
MPL penetration depth $> 40 \mu\text{m}$ via XRM / % of all investigated positions	37	61	46
MPL crack density via optical microscopy / % area fraction	4.0 ± 1.7	9.4 ± 1.8	3.5 ± 0.8
Areal weight / $\mu\text{g mm}^{-2}$	82 ± 1	81 ± 1	84 ± 1

of MPL pores and cracks. Likewise, the specific capacitance can be also reduced by blocking wetted surface area of the substrate. Although the MPL is penetrating large parts of the substrate for GDL 2, the large amount of cracks might increase the total wetted surface area, resulting in the increased specific capacitance compared to substrate 1. Similar to GDL 2, the MPL of GDL 3 is also penetrating large parts of the substrate, though showing a significantly smaller amount of cracks. Therefore, the overall wetted surface area seems to be reduced, resulting in a decreased specific capacitance of GDL 3 compared to substrate 1. With regard to GDL 1, blocking of wetted substrate area by MPL penetration and creation of additional surface area in MPL cracks might counterbalance each other leading to the same specific capacitance as substrate 1.

In addition to the MPL, also the PTFE treatment of the substrate was found to have a strong influence on the measured specific capacitance. As shown in figure 5.3, PTFE treatment of the fiber substrate (substrate 1* without PTFE treatment compared to substrate 1 with PTFE treatment) led to a strong decrease of the specific capacitance from $188 \pm 65 \mu\text{F cm}^{-2}$ to $24 \pm 3 \mu\text{F cm}^{-2}$, which is in accordance with the hydrophobic properties of PTFE.

Therefore, according to these results a comparison of the specific capacitance measured for different non-operated begin-of-life GDLs, can be used as an indicator for the morphology and surface structure of the GDLs under investigation.

5.3.2 Influence of electrolyte composition and penetration time

For interpretation of the measured specific capacitances, knowledge about penetration properties of the electrolyte is necessary. Adding fluorescein to the electrolyte revealed that the electrolyte penetrates the GDL, but did not wet the interface between MPL and catalyst coated membrane. This behavior was shown for begin-of-

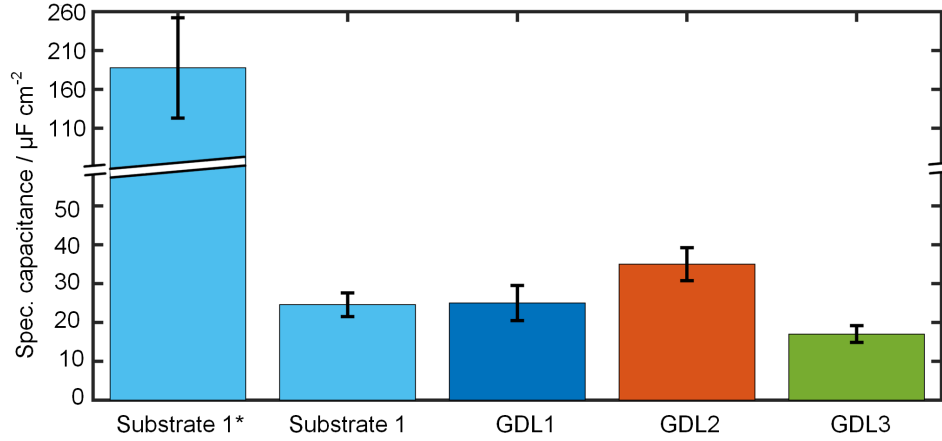


Figure 5.3: Specific capacitances of GDL 1, 2 and 3. All GDLs consist of substrate 1 with PTFE treatment and an MPL. Substrate 1* had no PTFE treatment.

life reference samples of GDL 1, 2 and 3 as well as for chemically and real degraded samples of GDL 1. Cu-plating from an electrolyte, with similar surface tension like the one used for CV measurements, to the GDL was performed to reveal areas of the GDL being penetrated by the electrolyte. SEM images showed plated Cu in pores of the substrate and MPL down to a size of a few micrometer (see figure 5.4), thus showing that the electrolyte is penetrating the MPL and the substrate. In addition, the surface area measured by BET, normalized to the circular area of the CV setup ($A = A_{BET} \cdot \text{specific weight} \cdot \text{measurement area}$), and the measured specific capacitance C_{spec} (also normalized to circular area) of GDL type 1, substrate type 1* (without PTFE treatment) and polished glassy carbon electrodes were compared (see table 5.2). The surface area of the glassy carbon electrode was assumed to be equal to the measurement area of the CV setup neglecting any surface roughness. Assuming a complete wetting of the glassy carbon surface area, the comparison shows that a large fraction of pores (especially micro- and mesopores in the MPL) were not wetted by the electrolyte during the penetration time used. It is assumed that both the hydrophobic GDL properties and air being captured in the GDL structure hindered a complete wetting of the GDL surface area.

Since a non-destructive disassembly of MEAs from stacks being degraded under real conditions could not be guaranteed, whole MEAs were measured instead of single GDLs. Thus, the influence of the anode and cathode CL on the measured specific capacitance value was investigated by a test system replacing the CCM within a MEA using a polyimide foil. Within the scope of measurement accuracy, no differences between specific capacitance values of GDL 1 + ACL, GDL 1 + CCL and GDL 1 + polyimide foil was obtained, which indicates that the CCM had only a negligible influence on the measured specific capacitance (see table 5.3). This result

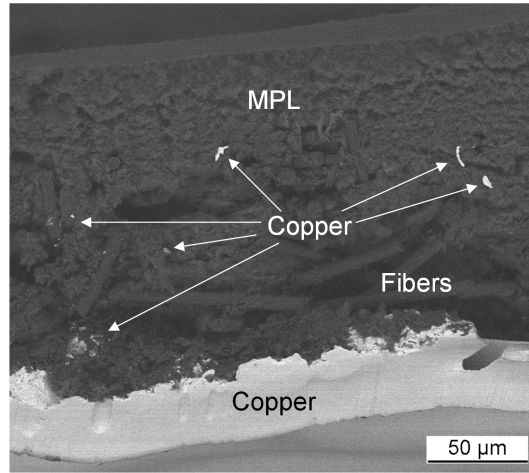


Figure 5.4: SEM image (BSE, 10kV) showing Cu being plated from the electrolyte to the GDL. Cu appears both at the GDL surface and within pores down to a size of a few micrometer.

Table 5.2: Comparison of normalized BET area and specific capacitance of GDL 1, Substrate 1* (without PTFE) and glassy carbon electrodes. ⁺ Area of glassy carbon electrodes is the geometric area neglecting surface roughness.

Sample	Normalized BET area A / cm^2	Specific capacitance / $\mu\text{F cm}^{-2}$
GDL 1	1303 ± 62	25 ± 5
Substrate 1	267 ± 8	188 ± 65
Glassy carbon	0.78^+	34 ± 1

is in accordance with the findings, that the electrolyte did not pass the GDL, and that accordingly the MPL/ CCM interface was not wetted.

As the determined specific capacitance strongly depends on the GDL area being penetrated by the electrolyte, values were highly dependent on both the tenside concentration of the electrolyte, and the exposure time of the sample to the electrolyte prior to the start of the measurement (penetration time). A linear increase of the specific capacitance was found with both penetration time and tenside concentration (see figure 5.5). Since the samples had a highly porous structure with hydrophobic character the electrolyte was supposed to slowly penetrate pores of the MPL and MPL/ substrate interface, replacing air in pores of the GDL. This finding is in accordance with results of Kangasniemi et al., reporting an increase in measured capacitance of carbon black electrodes with increasing penetration time of an acidic electrolyte [284]. In addition, a decrease of electrolyte surface tension

Table 5.3: Specific capacitance of GDLs with different CLs and polyimide foil facing the MPL area of the GDL. Within the scope of measurement no influence of the CL on the measured specific capacitance is found.

Sample	Specific capacitance / $\mu\text{F cm}^{-2}$
GDL 1 + polyimide foil	25.5 ± 1.0
GDL 1 + CCL	25.6 ± 0.9
GDL 1 + ACL	25.0 ± 1.1

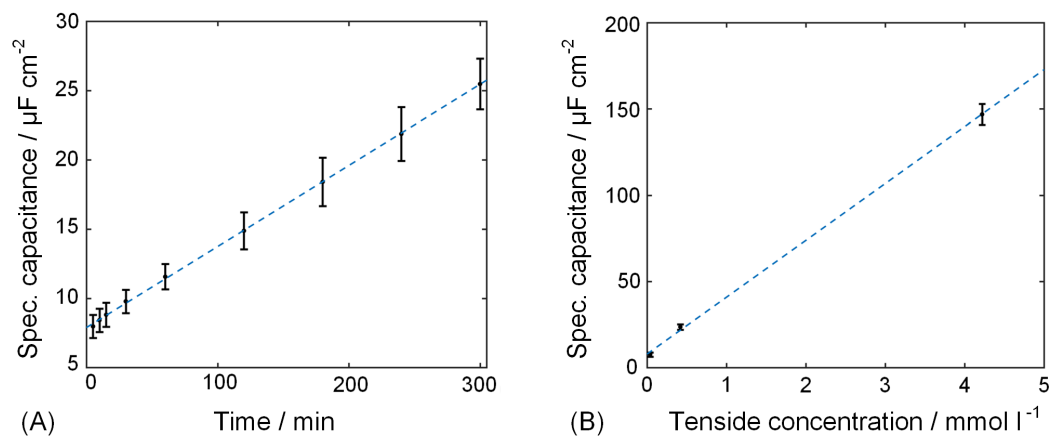


Figure 5.5: Specific capacitance of GDL 1 samples showing a linear increase with increasing penetration time (A) and tenside concentration (B).

by increasing the tenside concentration additionally facilitates the penetration into the GDL.

In general, a large scattering of measured specific capacitance values of degraded samples and non-operated begin-of-life reference samples (GDL or MEA) were found, which can be caused by air being captured in the GDL as well as the heterogeneous GDL morphology. Furthermore, it should be mentioned, that measured capacitance is only a semi-quantitative measure for the GDL hydrophobicity and wettability properties. Nevertheless, comparing degraded and begin-of-life reference GDLs with the same morphology enables the determination of changes in the hydrophobicity properties. Thus, the method was tested by measuring different artificially and real-operation aged samples and compared them to the begin-of-life samples as reference. Changes in the formation of the double layer and pseudocapacitances for degraded samples have herein to be taken into account.

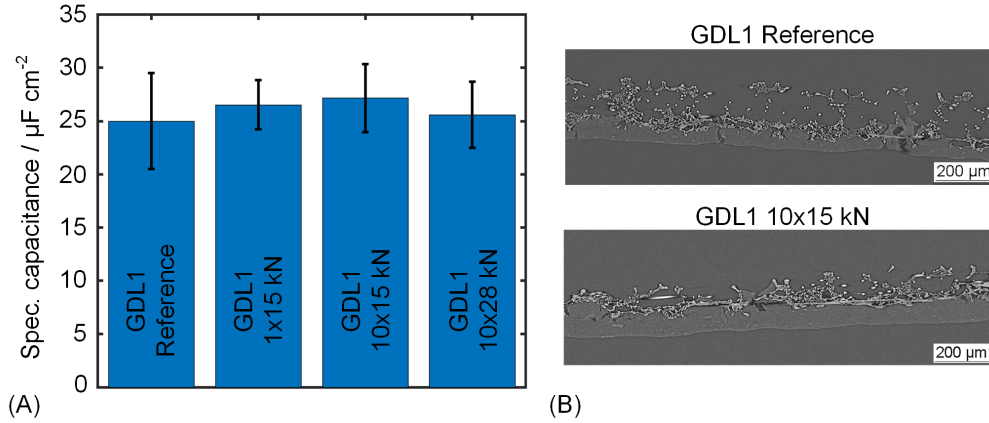


Figure 5.6: (A) Specific capacitance of mechanical degraded GDLs in terms of different applied clamping pressures compared to reference samples. (B) XRM images of GDL 1 cross sections before and after compression showing a collapse of the substrate after compression.

5.3.3 Method validation with mechanically degraded samples

Mechanical compression of the GDL was found to not significantly modify the wetted surface area as shown by the specific capacitance values in figure 5.6 (A). Different compression procedures applied to GDL 1 resulting in a reduced GDL thickness (reference: $224 \pm 6 \mu\text{m}$; compressed at 1x15 kN: $221 \pm 5 \mu\text{m}$; compressed at 10x15 kN: $217 \pm 6 \mu\text{m}$; compressed at 10x28 kN: $208 \pm 5 \mu\text{m}$) did not show a significant increase larger than the scattering of the reference. Compared to the reference specific capacitance of $25 \pm 5 \mu\text{F cm}^{-2}$, the specific capacitance of the compressed GDLs ranged from $27 \pm 2 \mu\text{F cm}^{-2}$, $27 \pm 3 \mu\text{F cm}^{-2}$, $26 \pm 3 \mu\text{F cm}^{-2}$ for a compression force of 1x15 kN, 10x15 kN and 10x28 kN, respectively. As shown by the XRM images in figure 5.6 (B), the compression leads to a densification of the substrate. Mercury-porosimetry and BET measurements of GDL 1 being cyclic compressed to 15 kN did not show a significant change in porosity and specific surface area, respectively, after compression (see figures 5.7 and 5.8). In addition, SEM images did not reveal any morphological changes of the fibers or the MPL after compression. Therefore, it is concluded, that GDL compression led to a compression of the fiber substrate but not to a significant change in substrate and MPL surface area being in contact with the electrolyte. Although compression can alter in-plane water transport in chemically degraded GDLs, as reported by Ince et al. [292], the macroscopic GDL morphology changes after compression, observed in this work, did not result in a significant increase in wetted surface area (see figure 5.6 (A)).

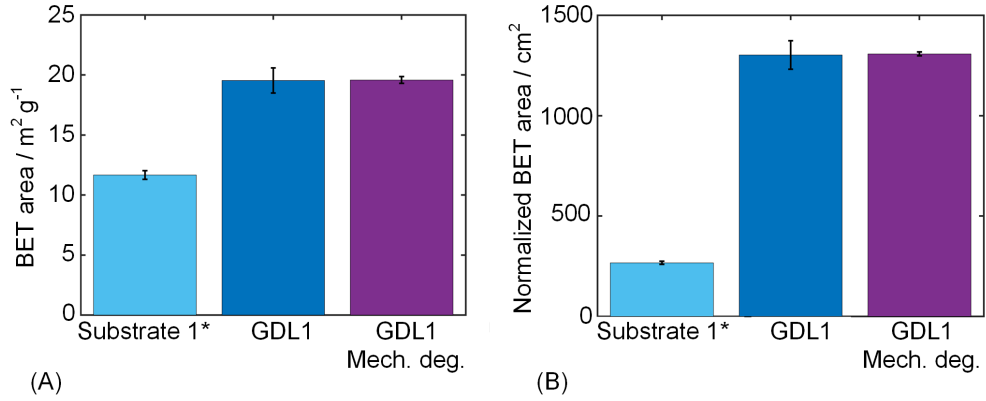


Figure 5.7: (A) BET surface area of substrate 1*, GDL 1 and GDL 1 being compressed ten times to 15 kN (Mech. deg.). (B) BET surface area normalized to the circular CV measurement area (0.78 cm^2) of substrate 1*, GDL 1 and compressed GDL 1 (Mech. deg.) (10x15 kN).

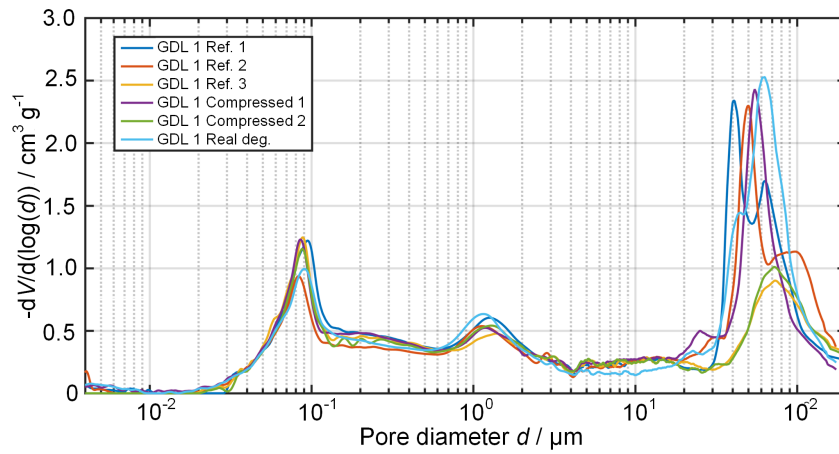


Figure 5.8: Pore size distribution determined by mercury-porosimetry for three reference GDL 1 (Ref. 1 – 3), two GDL 1 being ten times compressed to 15 kN (Mech. deg. 1 and 2), and one GDL 1 taken from the stack being operated in a prototype vehicle (Real deg.). The deviation of the pore size distributions of GDL 1 Ref. 3 and GDL 1 Compressed 2 in the diameter range of $100 \mu\text{m}$ is due to a different sample preparation.

5.3.4 Method validation with chemically degraded samples

GDL samples were chemically degraded by immersion in 30 % wt. H_2O_2 at 80 °C. Immersion of GDL 1 for 4 h, 15 h and 50 h resulted in a mass loss of 0.6 ± 0.2 %, 2.2 ± 0.4 % and 4.8 ± 2.8 %, respectively. Since H_2O_2 is accelerating carbon oxidation [82, 201, 289, 291], carbon corrosion is assumed to be the main reason for the observed mass loss. To separate the degradation of the different GDL components (MPL, substrate) and their impact on the capacitance change, also single fiber substrates with and without PTFE treatment were immersed in 30 % wt. H_2O_2 for 15 h, resulting in a mass loss of 0.5 ± 0.3 % and 0.6 ± 0.1 %, respectively. Figure 5.9 illustrates that immersed GDLs and substrates showed increased specific capacitances compared to reference samples, which corresponds to an increased wettability of the GDL. Wettability was increasing with increasing immersion time together with an increasing weight loss. Compared to the begin-of-life reference specific capacitance of $25 \pm 5 \mu\text{F cm}^{-2}$, the specific capacitance of the immersed GDLs were given by $35 \pm 4 \mu\text{F cm}^{-2}$, $1019 \pm 631 \mu\text{F cm}^{-2}$, $2115 \pm 410 \mu\text{F cm}^{-2}$ for an immersion time of 4 h, 15 h and 50 h, respectively. After immersion for 15 h the specific capacitance of the substrate 1 with PTFE treatment and substrate 1* without PTFE treatment showed an increased value of $30 \pm 3 \mu\text{F cm}^{-2}$ and $274 \pm 12 \mu\text{F cm}^{-2}$, compared to their reference values of $25 \pm 3 \mu\text{F cm}^{-2}$ and $188 \pm 65 \mu\text{F cm}^{-2}$, respectively. The wettability of substrate 1* without PTFE showed such a significant increase, that the wetted area during CV measurement was not limited to the circular measurement area, but was wetting larger parts of the sample. Therefore, specific capacitances shown in figure 5.9 were normalized to the mean area between total sample area (12.74 cm^2), resulting in a specific capacitance of $145 \pm 6 \mu\text{F cm}^{-2}$, and circular shaped measuring area (0.78 cm^2), resulting in a specific capacitance of $2371 \pm 102 \mu\text{F cm}^{-2}$. Specific capacitance normalized to total sample area and normalized to circular shaped measurement area are shown with dotted and dashed lines, respectively. The increased specific capacitance after immersion is in accordance with literature, showing increased capacitance of electro- or liquid-oxidized electrodes [284], carbon fibers [293–296] and GDLs [85, 284, 285]. The increase of capacitance and thus of the wetted surface area after carbon corrosion is also in accordance with findings of Zhang et al., showing increased mass transfer losses due to carbon corrosion of the MEA [297]. In addition, several studies are reporting increased water accumulation during fuel cell operation within GDLs being previously immersed in H_2O_2 as compared to reference samples [287, 289–291]. With regard to the degradation of single GDL components (fiber substrate and MPL), the comparison of immersed GDLs and immersed fiber substrates showed that the discrepancy between immersed and reference sample is significantly higher for GDLs with MPL (see figure 5.9). This indicates a strongly increased wettability of pores in the MPL and at the substrate/ MPL interface. The finding is in accordance with results of Liu et al. showing that during fuel cell operation, more water was accumulating in the MPL of GDLs being immersed in H_2O_2

as compared to untreated reference samples [287].

In order to investigate the reason for the observed capacitance increase after chemical degradation, different ex situ analysis methods were applied. SEM micrographs of a 50 h immersed GDL 1 showed small morphology changes such as small fiber damages like surface roughening (see figure 5.10 (A)) or fiber detachment from the MPL (see figure 5.10 (B)). The minor morphology changes found in this work after submerging in H_2O_2 are in accordance with findings of other studies, reporting structural changes of MPL and fibers in the nanoscale [201] and an increasing BET surface area [201]. Due to the small changes in the surface morphology compared to the large increase of the measured specific capacitance value, morphology changes are assumed to be only one of several effects leading to the observed capacitance increase.

In addition to morphology changes, literature also reports PTFE loss [85, 284] and the formation of functional groups on the GDL surface after electrooxidation in acidic media [85, 284, 285]. With its hydrophobic properties PTFE serves for good water removal, for which reason a decrease of PTFE contents will lead to an increased wetted surface area and thus to an increased specific capacitance. Additionally, an increase in surface oxygen groups was found to increase the measured capacitance of activated carbon fibers most probably due to increased hydrophilicity of the surface, the creation of excess double layer capacitance by changed electric charge density at the surface and additional pseudo-capacitances [118, 204, 284, 285, 293, 294, 296, 298–300]. With regard to literature, it is assumed that even small changes in PTFE content and surface functional groups of the degraded samples are able to influence the wettability behavior of the GDL.

In total, the combination of the different degradation phenomena of morphology changes, PTFE loss and the formation of hydrophilic surface groups will lead to the observed increase in wetted surface area. In particular, an increased wettability of the MPL and the MPL/ substrate interface was observed after chemical degradation.

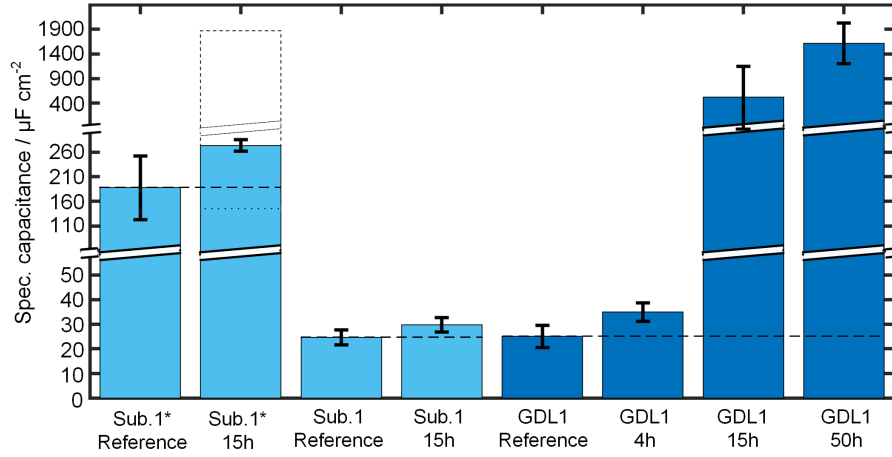


Figure 5.9: Specific capacitance of GDL 1 and substrate 1 with PTFE (Sub. 1) and without PTFE (Sub. 1*), being immersed in H_2O_2 for different times. For comparison values of begin-of-life reference samples are given. As described in the chapter, capacitance value of substrate 1* (without PTFE) was normalized to the mean area of total sample area and circular shaped CV measurement area.

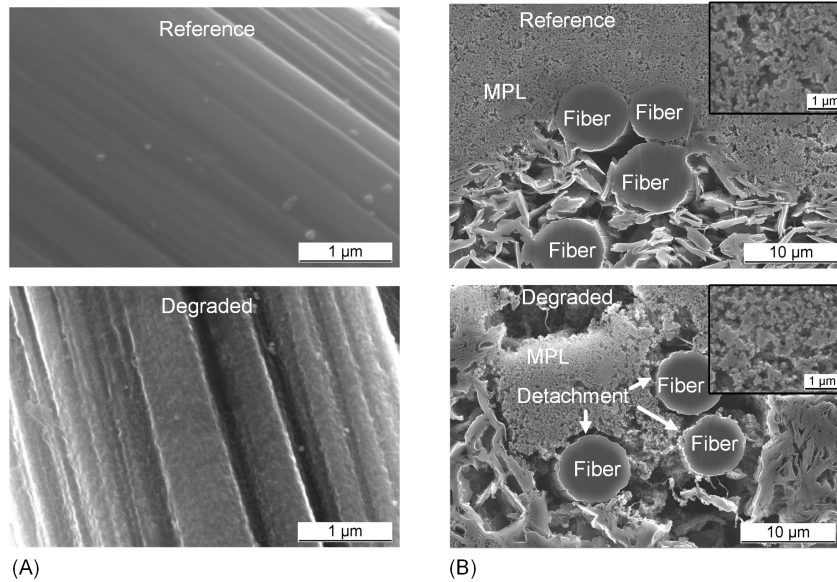


Figure 5.10: SEM micrographs (SE, 10 kV) of GDL 1. A comparison of a fiber of a reference (top) and 50 h immersed (bottom) GDL 1 shows minor fiber damage (A). Comparing cross-sections of the MPL of a reference (top) and a 50 h immersed (bottom) GDL 1, depicts a detachment of fibers from the MPL (B).

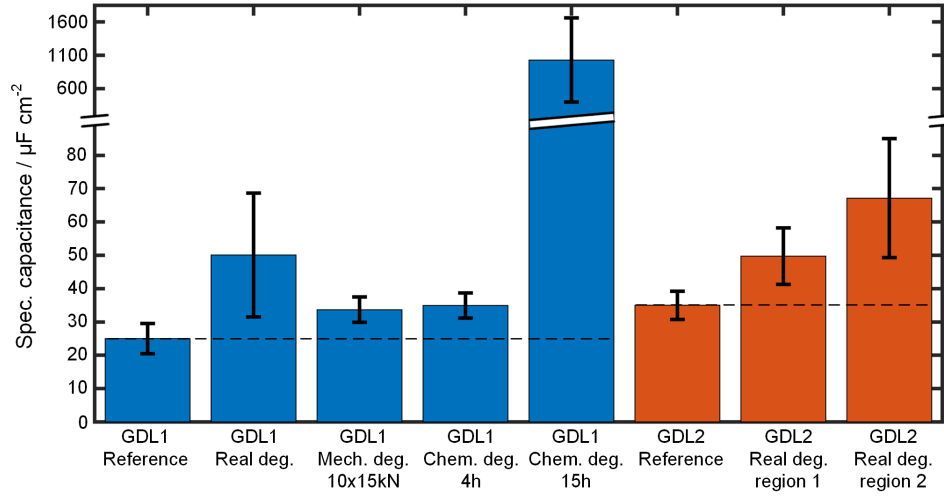


Figure 5.11: Specific capacitances of cathode GDLs of degraded MEAs taken from two automotive full size stacks (Real deg.) compared to reference GDLs and artificially mechanically (Mech. deg.) and chemically (Chem. deg.) degraded GDLs. Region 1 and 2 of stack two refer to regions of low and high carbon corrosion degradation at the CCM, respectively.

5.3.5 Application on gas diffusion layers of automotive stacks

Figure 5.11 shows measured specific capacitances of the cathode GDLs of MEAs of two automotive full size stacks. MEAs were measured instead of single GDLs since a nondestructive disassembly of the MEA could not be accomplished. As already shown, the CCM did not influence the measured specific capacitance value of the MEA. MEAs of both stacks showed an increased specific capacitance and thus increased wetted surface area compared to non-operated begin-of-life reference MEAs.

Considering stack one (GDL 1) being operated in a prototype fuel cell vehicle, the specific capacitance was measured to $50 \pm 19 \mu\text{F cm}^{-2}$ and thus increased significantly compared to non-operated reference MEAs, possessing a specific capacitance of $25 \pm 5 \mu\text{F cm}^{-2}$. According to the specific capacitance the degradation is more severe than mechanical compression degradation (specific capacitance for compression of 10x15 kN: $27 \pm 3 \mu\text{F cm}^{-2}$) or chemical degradation of 4 h H_2O_2 immersion (specific capacitance: $35 \pm 4 \mu\text{F cm}^{-2}$). The degradation is, however, less severe than for GDL 1 being chemically degraded for 15 h (specific capacitance: $1019 \pm 631 \mu\text{F cm}^{-2}$). This gives rise to the hypothesis of chemical degradation being the main degradation phenomena of stack one samples, while stack compression plays only a minor role. According to a degradation analysis performed on the MEAs (see figure 5.12), carbon corrosion degradation was found on the CCL such as layer thinning, porosity loss, and crack formation. However, no visible morphology change of the GDLs could be detected by SEM micrographs.

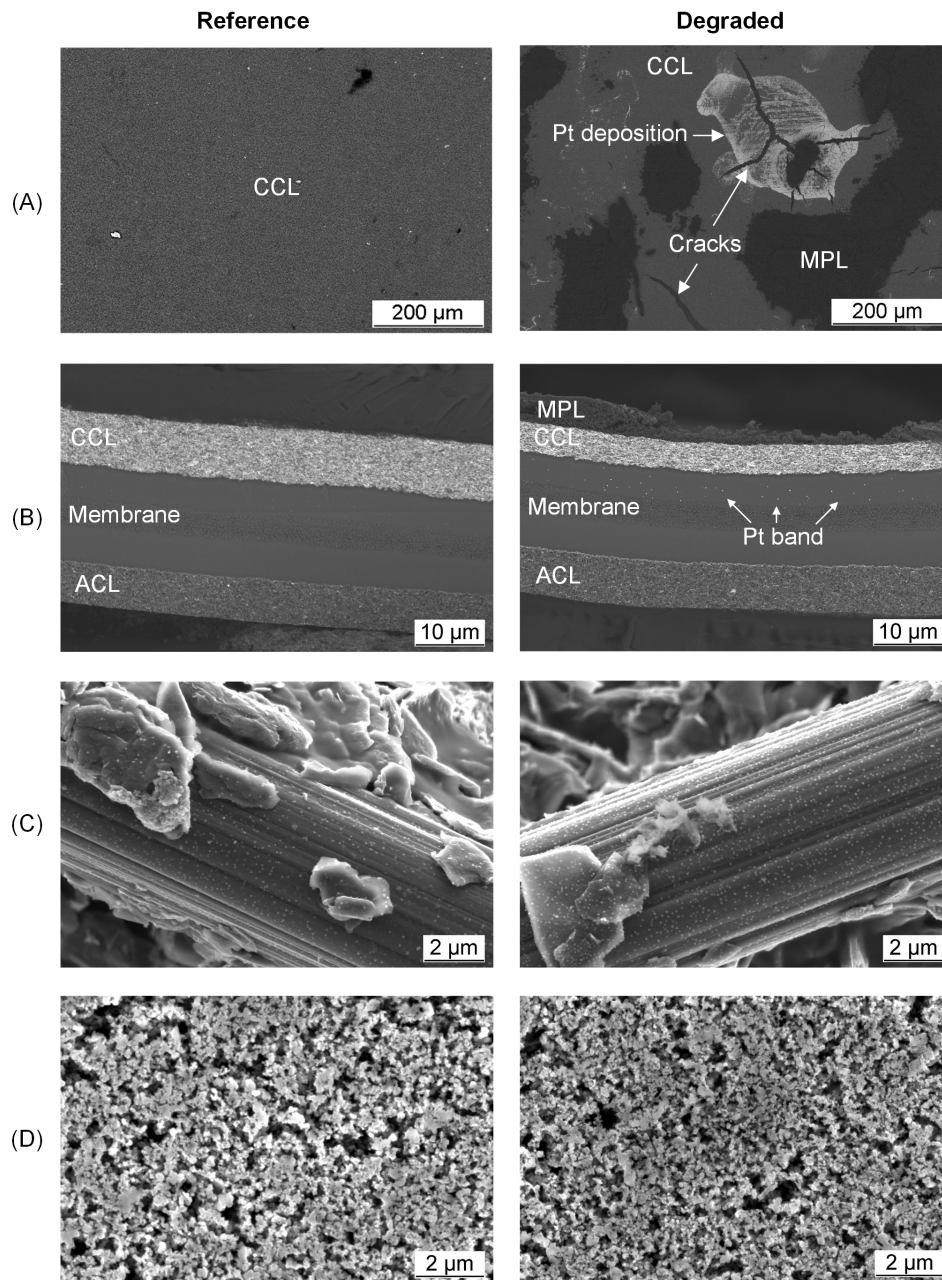


Figure 5.12: SEM images of reference CCMs (left) and CCMs taken from the stack of a prototype vehicle (right). (A) Top view (BSE, 5kV) of CCL and (B) CCM cross section (BSE, 5kV) showed different degradation phenomena including MPL (black) adhesion on the CCM (grey), Pt deposition on top of the CCL (white), CCL crack formation, CCL thinning and the formation of a Pt band close to the CCL (white dots). (C) and (D) show SEM images (SE, 5kV) of a carbon fiber and MPL cross section, respectively, where no degradation was observed.

Degradation on the nanoscale, being out of the resolution of SEM cannot be excluded. Within the scope of measurement accuracy, also mercury-porosimetry measurements did not show a significant increase in porosity (see figure 5.8). In addition, no contamination with foreign ions, like Fe or Cr, were determined with inductively coupled plasma optical emission spectrometry. Therefore, it is assumed that similar to chemically degraded samples, small morphology changes, PTFE loss and the formation of hydrophilic surface groups might cause the observed increase in wetted surface area.

With regard to stack two (GDL 2) being operated under severe fuel starvation conditions close to the anode outlet region of the MEA (region 2), as described in chapter 6, a significant increase of the specific capacitance of the cathode GDLs were found. Compared to region 1, close to the anode inlet, where a specific capacitance of $50 \pm 8 \mu\text{F cm}^{-2}$ was found, the specific capacitance in region 2, where increased fuel starvation degradation on the CCL by carbon corrosion was found, was increased to a value of $67 \pm 18 \mu\text{F cm}^{-2}$. This tendency is however within the scatter of the samples. The specific capacitance of the reference of GDL 2 was measured to $35 \pm 4 \mu\text{F cm}^{-2}$. As for MEAs of stack one, no carbon corrosion degradation of the GDLs could be visualized with SEM, changes in the nanometer scale can however not be excluded. An increase of the specific capacitance due to pseudocapacitances of contaminants in the MEA, was excluded by inductively coupled plasma optical emission spectrometry. As for stack one, it is therefore assumed that small morphology changes, surface oxide formation due to water accumulation and carbon corrosion as well as PTFE loss due to carbon corrosion to be responsible for the increased wettability properties.

5.3.6 Comparison to contact angle measurements

In order to evaluate the benefit of GDL wettability measurement by cyclic voltammetry, it was compared to static contact angle measurements, being a state-of-the-art method for determination of wettability properties. As illustrated in figure 5.13, both contact angle measurements at the GDL substrate and MPL as well as cyclic voltammetry detected altered wettability properties, for chemically and real-operation degraded samples of GDL 1. The reference contact angles of substrate and MPL side were measured to $148 \pm 2^\circ$ and $154 \pm 2^\circ$, respectively. Contact angles for GDLs being chemically degraded for 4 h and 5 h as well as being mechanically degraded (10x15 kN) and being real operation degraded (prototype vehicle) were determined to $146 \pm 1^\circ$, $147 \pm 2^\circ$, $148 \pm 2^\circ$ and $146 \pm 2^\circ$ on the substrate side and to $148 \pm 2^\circ$, $149 \pm 2^\circ$, $154 \pm 3^\circ$ and $152 \pm 2^\circ$ on the MPL side, respectively. For contact angle measurements of the MPL of real operation samples, GDLs were carefully removed from the MEA. No visible damage was found on the MPL after removal, which can however not completely be excluded. Cyclic voltammetry was found to be more sensitive to detect degradation in particular of long term chemically aged and real operated GDLs. Compared to the

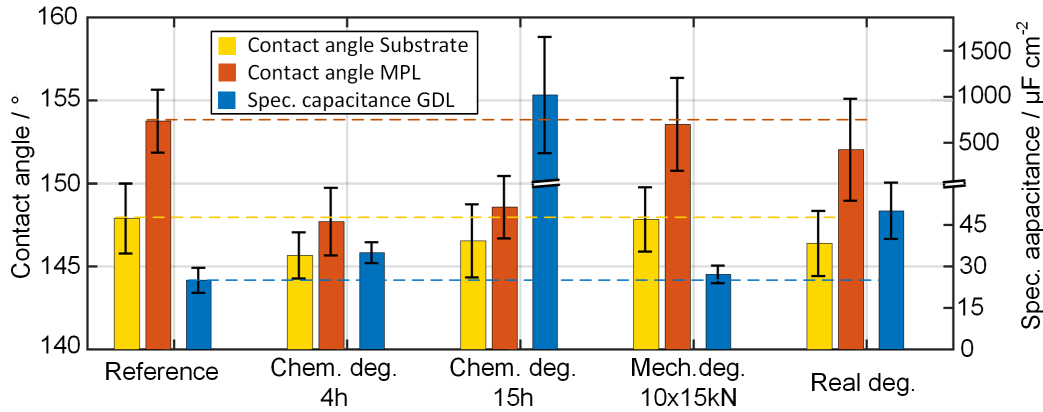


Figure 5.13: Static contact angle measurements of GDL 1 performed on substrate (yellow) and MPL (orange) side of differently mechanically (Mech. deg.), chemically (Chem. deg.) and real operation (Real deg.) degraded samples in comparison with measured specific capacitances by cyclic voltammetry (blue). In addition, values of a begin-of-life reference are given.

reference specific capacitance of $25 \pm \mu\text{F cm}^{-2}$, the specific capacitance of the GDLs being chemically degraded for 4 h and 5 h as well as being mechanically degraded (10x15 kN) and being real operation degraded (prototype vehicle) were determined to $35 \pm 4 \mu\text{F cm}^{-2}$, $1019 \pm 631 \mu\text{F cm}^{-2}$, $27 \pm \mu\text{F cm}^{-2}$ and $50 \pm 19 \mu\text{F cm}^{-2}$, respectively. This higher sensitivity is assumed to be due to the different measurement regions within the GDL. While contact angle measurements are only measuring the surface area on top of the substrate or MPL, cyclic voltammetry is able to additionally measure surface area within the GDL by the electrolyte penetrating into the inner parts of the GDL.

5.4 Conclusion

GDL wettability measurement by cyclic voltammetry was adopted for application in an automotive fuel cell failure analysis process. The specific capacitance of the GDL was used as a measure for the GDL's surface area being wetted with an electrolyte and thus gave information about the wettability properties of the GDL. Changes like an increase of the electrolyte tenside concentration and of the penetration time were found to increase the measured specific capacitance by increasing the number of GDL pores being in contact with the electrolyte. PTFE treatment of the fiber substrate, increasing entanglement of MPL and fiber substrate and decreasing crack density within the MPL, decreased the measured wetted surface area. The obtained results are in accordance to the ones obtained by SEM and XRM.

Thus, cyclic voltammetry can be used to identify differences in the GDL morphology and surface structure of automotive fuel cells. The method can be also used to determine structural changes of the GDL due to chemical, mechanical and real-operation degradation. Finally, the method was compared to static contact angle measurements and was found to be more sensitive to detect GDL degradation in particular of real-operation aged samples. In summary, the implemented method is a sensitive technique to measure changes of the wettability properties for both artificially and real-operation degraded samples, and is a suitable analysis technique in an automotive fuel cell analysis process.

Chapter 6

Local fuel starvation degradation of an automotive PEMFC full size stack

This chapter is based on a research article that was published in the special issue: 23rd EFCFACS of the journal Fuel Cells [301]. In brief, the following issue is addressed. An in-depth degradation analysis of two automotive full size stack is performed. Herein, the focus is put on defects at the CCL and their interrelation including inhomogeneous adhesion of the microporous layer on the CL, crack formation, CCL thinning and wrinkling of the catalyst coated membrane. In addition, linear and circular Pt depositions on top of the CCL are reported, which have to the best of our knowledge not been described in literature yet. For the latter, a degradation mechanism based on liquid water formation, local fuel starvation and current density distribution at the interface between microporous layer and CCL is postulated. Finally, a fast indication for stack degradation is suggested by correlating different degradation phenomena. This improved stack analysis approach allowed us to detect local differences in degradation on both cell and stack level. The obtained results are compared to GDL wettability changes of different cells of both stacks, which are determined with the method introduced in chapter 5.

6.1 Literature review

For the commercialization of fuel cell electric vehicles, a sufficient durability (> 5000 h) of the fuel cell stack is required [302]. Therefore, knowledge about full size stack degradation under realistic conditions is crucial. Several studies performed degradation analysis on lab-scale size single cells [101–104], on lab-

scale short- and mid-size-stacks [105–109] as well as on automotive size single cells [110] and on automotive size short- and midsize-stacks [111–113]. However only few studies exist which analyze the degradation of automotive full size stacks (> 350 cells, active area $\approx 300 \text{ cm}^2$). For instance, Ettingshausen et al. [114] and Pei et al. [115] investigated a full size stack of a prototype vehicle and a full size stack aged with an accelerated stress test, respectively. They both observed inhomogeneous degradation along the stack. In particular, they found local variations in the loss of electrochemical active surface area at different locations on single cells as well as on different cell locations within the stack [114, 115].

Nonetheless, none of them described degradation due to local fuel starvation, which is considered as a critical failure mode in automotive fuel cell applications [32, 36, 39]. The importance of this failure mode was emphasized by several studies experimentally investigating local fuel starvation on single cell level by simulating the degradation either by closing parts of the flow field channels [303, 304], impregnating the gas diffusion layer [305], reducing hydrogen stoichiometry [306, 307], supplying liquid water to the cell [308], or feeding air to the anode [196, 309]. Thinning and porosity loss of the CCL, an increase in the CCL's Pt particle size, and a loss of carbon at the CCL resulting in a performance loss of the cell were commonly found.

In this chapter both of the aforementioned highly relevant topics of automotive full size stack degradation analysis and local fuel starvation degradation obtained under realistic automotive conditions are addressed. The goal is to identify degradation phenomena with respect to their location on stack and cell level. Information about the distribution of degradation phenomena helps understanding different degradation process during fuel cell system operation and gives input to improve cell designs and operational strategies. Finally, a degradation mechanism for a novel degradation phenomena is postulated.

6.2 Experimental details

An automotive full size stack within the predevelopment stage was aged by applying conditions of different automotive driving points at a fuel cell test station for approximately 100 hours. The stack as illustrated in Figure 6.1 (A) consists of more than 350 cells with an approximate active area of 300 cm^2 each. Gases, which were supplied in counter flow from one end of the stack, flow in a U-shape from manifold inlet to outlet. Cells from eight different positions along the stack (region 1 to 8 in figure 6.1 (A)) were investigated thoroughly, in order to depict degradation inhomogeneities. Extensive degradation analysis was performed by a systematic failure analysis approach in which various techniques were employed to capture defects on multiple length scales. The location of degradation phenomena on the MEA was described using a location matrix as shown in figure 6.1 (B). Degradation analysis was initiated by photo documentation of bipolar plates, GDLs and CCMs.

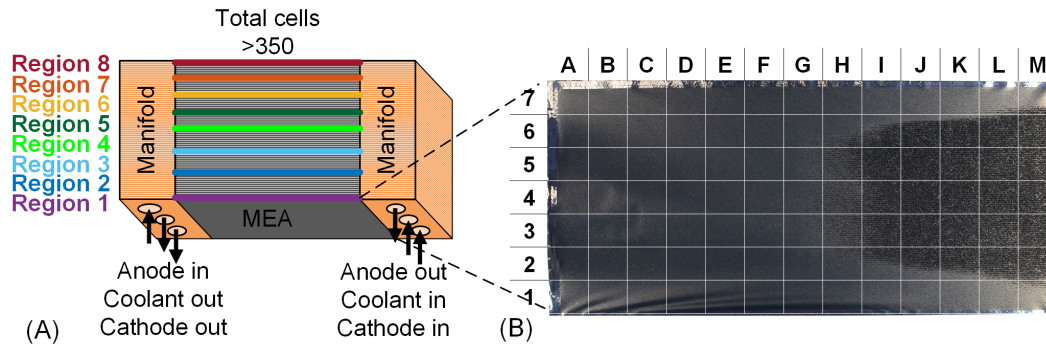


Figure 6.1: (A) Schematic of an automotive full size stack indicating the location of cells under investigation. (B) Location matrix of the MEA placed on top of the CCL. The CCL shows increased microporous layer adhesion (dark region from H6 to M2) at the anode outlet.

For CCM analysis, GDLs were carefully removed from the MEA.

Digital three-dimensional-light microscopy (Keyence VHX-6000) was used to investigate the morphology of GDLs and CCMs. Panorama images were taken to get an overview of the degradation phenomena distribution. In addition, single images with different magnifications and light settings were taken to analyze different degradation phenomena. In order to reveal local degradation development on a single cell, images of every single segment of the location matrix (see figure 6.1 (B)) were taken under the same conditions. A hole was artificially stamped into the MEA as a reference point to locally correlate degradation phenomena on GDLs, anode- and CCL. The Keyence VHX-6000 software was used to determine three-dimensions of different degradation phenomena.

Scanning electron microscopy (SEM, FEI Quanta FEG 650) was applied to get deeper morphological information. Back-scattered electrons with an acceleration voltage of 5 kV were used in most cases for imaging. Secondary electrons were only used to visualize surface topography with an acceleration voltage between 1 kV to 2 kV.

To monitor the development of degradation like crack formation and Pt deposition within the location matrix (see figure 6.1 (B)) BSE images possessing a higher contrast than optical images were taken on different cells of the stack, thus supporting information obtained from optical microscopy. Depending on the degradation phenomena investigated, 9 to 20 SEM images under the same conditions were taken on every of the 6 selected cells.

For a quantification of the aforementioned surface morphology changes, image analysis of optical and SEM images was performed by manually applying a contrast threshold with the software Imagic IMS (Vers. V18Q4) in order to distinguish different morphological compartments. Herein, the different components of each

sample are distinguished according to their brightness values. Every pixel of the image is evaluated and classified with a pre-set threshold range. Figure 6.2 shows two examples for such a threshold analysis. The micrographs are depicted on the left, the results of the analysis on the right. In figure 6.2 (A), MPL parts deposited on the CL appear as dark areas on the micrograph. As a result of the image analysis, all pixels within a certain threshold range are identified and marked in green, as seen on the right of figure 6.2 (A). By correlating the selected MPL area (color-coded in figure 6.2 (A)) to the total area of the image, the area ratio of MPL deposition on the CCL can be determined. The surface area ratio of MPL adhesion on the CL was calculated as: $\text{area of MPL in image} / \text{total area of the image}$. The surface area ratio of cracks and Pt deposition was calculated as: $\text{area of cracks or Pt deposition in the image} / \text{area of MPL-free CL in the image}$. Regions of the CCL covered by the MPL were excluded from the analysis as no information about crack formation or Pt deposition were accessible within these regions. It should be mentioned that preferential formation of cracks or deposition of Pt in MPL-free areas of the CCL cannot be excluded. Following this hypothesis an overestimation of the surface area ratio of cracks and Pt deposition with our calculation approach cannot be excluded.

Figure 6.2 (B) shows the selection of different layers of a CCM cross section by a threshold analysis, which is used to determine the average thickness of each layer in the image. Here, a certain range for the intensity is defined for each component, that should be identified on the micrograph. After selecting every single layer by manually setting a contrast threshold, roughly 60 single thickness measurements in a distance of 1 μm were automatically performed and averaged. Cross sections of the active layers were prepared by a cryo cross section polisher (JEOL IB-19520CCP) and are imaged with SEM (BSE, 5 kV).

Energy dispersive X-ray spectroscopy (Oxford X-Max 50, 5-10 kV) was performed to identify different materials on and within the CCM during SEM measurements. Finally, X-ray diffraction (Bruker D8 Advance 2010) was applied to investigate the Pt crystallite size changes. For qualitative comparison, Pt crystallite size was determined with Rietveld refinement under the fundamental parameter approach with the help of the software Bruker AXS Topas (Vers. 6).

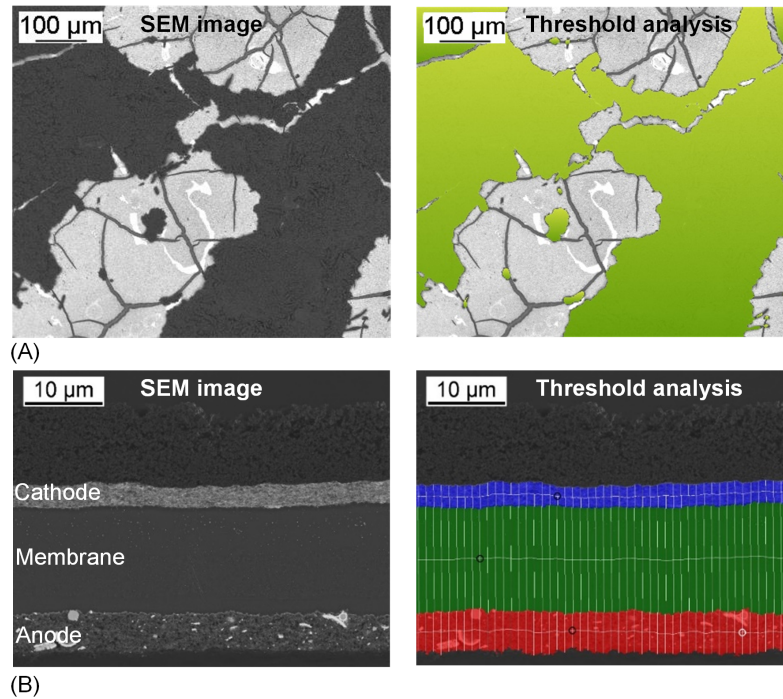


Figure 6.2: Examples of threshold analyses (right) to quantify information of SEM images (left). Quantification of the surface MPL deposition on the CCL (A) and of the thickness of single CCM layers (B) are shown. The selection of different components or layers is color coded. Selected deposited MPL is colored light green in (A). For the CCM shown in (B), the CCL, membrane and ACL are colored blue, green and red, respectively.

6.3 Results and discussion

6.3.1 Structural changes of membrane electrode assemblies after stack operation

The investigation of the degradation revealed distinct failure phenomena that were analyzed with respect to their appearance and distribution on the active area and at different stack positions to obtain a comprehensive image.

The GDLs of all investigated samples (15 MEAs at 8 different stack positions (see figure 6.1 (A)) showed increased adhesion towards the CCM compared to begin-of-life samples, resulting in MPL adhering to the CL after MEA disassembly. It needs to be mentioned that the GDL was not laminated onto the CCM during MEA production. On the ACL, only minor MPL adhesion with a surface area ratio smaller 2 % was observed. By contrast, a strong MPL adhesion on the CCL (see figure 6.3 (A)) was found, having surface area ratios of up to 88 % in a single segment

of the location matrix. Optical microscopy revealed that adhesion of the MPL on the CCL was inhomogeneous and increased towards the anode outlet region (see figure 6.1 (B)). Scanning electron microscopy images of CCM cross sections in the region of strong MPL adhesion showed a merging of the CCL and MPL at their interface.

Furthermore, cracks were visible in light and SEM micrographs (see figure 6.3 (B)). The occurrence of cracks on the CCL strongly correlated with the regions of MPL adhered to the CCL. Different typical crack shapes were found ranging from small crack networks, to linear cracks with radial side cracks, star like cracks as well as circular cracks. Six selected cells within region 1, 6 and 8 (see figure 6.1 (A)) showed that the crack size and crack surface area ratio at the CCL increase towards the anode outlet region, as analysed with image analysis. By contrast, only minor cracks at the ACL and no cracks on begin-of-life samples (see figure 6.3 (E)) were detected.

Besides cracks, the formation of a circular and a linear pattern, which appeared bright in BSE micrographs (see figure 6.3 (B)), were observed. Herein, circular deposition occurred both in a disc (filled ring) and ring like shape. The bright appearing features (see figure 6.3 (B) and 6.4) were analyzed by EDS measurements and were shown to consist of Pt. This Pt deposition on top of the CCL appeared within regions of strong MPL adhesion.

Optical panorama images showed accumulated occurrence of Pt deposition in distinct, but randomly distributed areas on the CCL close to the anode outlet. A threshold analysis of SEM images (taken from four cells of regions 6 and 8) showed a trend of increasing Pt deposition towards the anode outlet region. This result is supported by XRD measurements showing a decrease in peak width, which is typical for increasing crystallite sizes. Platinum crystallite growth towards the anode outlet region of the CCM was found. Compared to begin-of-life samples an increase in crystallite size by approximately 33 ± 3 % in the areas close to the anode inlet (values averaged of positions B2/ B6) and of 115 ± 4 % close to the anode outlet (values averaged of positions J3/ J5) for a strongly degraded cell in region 6 was found. For less degraded cells of region 7, an increase of Pt crystallite size by approximately 33 ± 2 % in the areas close to the anode inlet (values averaged of positions B3/ B5) and 54 ± 8 % close to the anode outlet (values averaged of positions K3/ K5) was found compared to begin-of-life samples.

Circular Pt deposition had a diameter range from a few tens of micrometers to a few hundred micrometers while having a depth range from a few micrometers to a few tens of micrometers. Linear Pt deposition possessed an average width and height of a few micrometers while having an average length of a few hundred micrometers.

Within its detection limits, SEM-EDS measurements of CCM cross-sections revealed that Pt concentration gradients did not exist in the proximity of the Pt deposition, neither in horizontal nor in vertical direction. Likewise no change in CL porosity was found in the vicinity of the circular Pt deposition. In addition, 83 % of 30 investigated circular Pt depositions on the CCM also showed Pt depositions

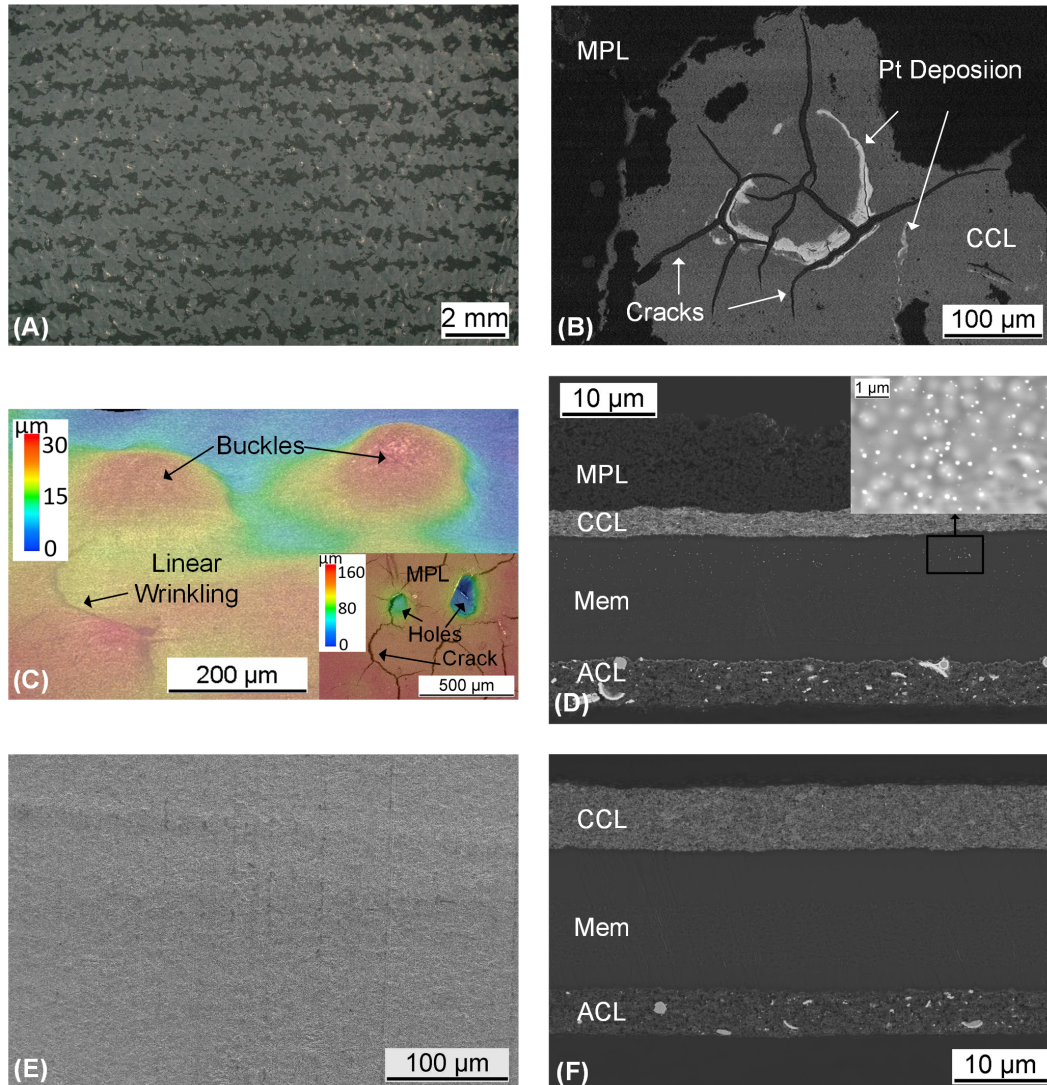


Figure 6.3: Assembly of different degradation phenomena observed on the CCM: (A) Optical microscopy image of a CCL (top view) showing MPL adhesion (black) on the CCL (grey). (B) SEM image of a CCL (top view) showing MPL adhesion (black), crack formation and circular and linear Pt deposition (white). (C) three-dimensional optical microscopy image showing buckling and linear wrinkling on the ACL. The inset shows corresponding holes and cracks in the MPL. (D) SEM image of CCM cross section showing CCL layer thinning and formation of a Pt band close to the CCL as compared to begin-of-life samples. (E) SEM image of a begin-of-life CCL (top view). (F) SEM image of a begin-of-life CCM cross section.

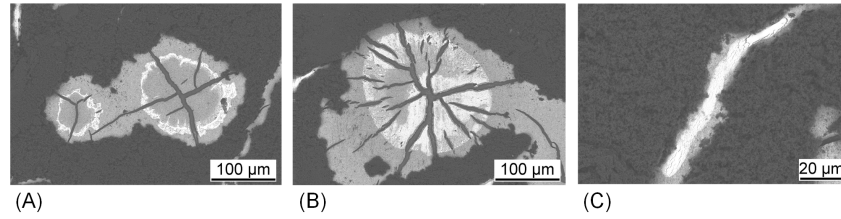


Figure 6.4: Different types of macroscopic Pt depositions on top of the CCL imaged by SEM. (A) Ring-like Pt deposition. (B) Disc-like Pt deposition. (C) Linear Pt deposition.

on the corresponding location of the MPL surface. The location of another 10 % of these Pt depositions correlated to holes in the MPL, where Pt deposition could not definitely be proven. No Pt deposition was found on the ACL and begin-of-life samples (see figure 6.3 (E)).

Degradation due to carbon corrosion was shown on cross sections of CCM samples taken at different locations from anode inlet to outlet. A gradual decrease of the CCL thickness towards the anode outlet region in all regions of the stack was observed (see later in figure 6.5 (B)). As shown in figure 6.3 (D), in the region close to the anode outlet a collapse of the porous CCL structure was detected compared to a begin-of-life sample (see figure 6.3 (F)). Within this region, a thickness decrease of up to 73 % (region 1, Position L4, 2 cells investigated), 72 % (region 6, Position L4, 2 cells investigated), and 64 % (region 8, Position L4, 2 cells investigated) were observed compared to begin-of-life samples. The ACL and membrane thickness remained constant within the measurement accuracy.

SEM-EDS measurements of CCM cross sections also showed the formation of a Pt band in the membrane close to the CCL, whose intensity extended towards the anode outlet region.

Additionally, circular and linear protrusions and extrusions of the CCM (see figure 6.3 (C)) were found on both the ACL and CCL. These circular and linear protrusions and extrusions, which will be referred to as buckling [310] and linear wrinkling, respectively, were observed to the same extent in terms of density and size distribution throughout all investigated single cells. Buckling exhibited a diameter range of a few tens of micrometers to a few hundred micrometers, while having a height range of a few micrometers to a few tens of micrometers. No differences of buckling at the anode and cathode were observed. Buckling was proven to be a wrinkling of the whole CCM by correlating location of protruding buckles at the CCL to extruding buckles at the ACL and vice versa. Buckling as a wrinkling of the whole CCM was also shown with cross section images. Linear wrinkling possessed an average width and height of a few micrometers while having an average length of a few hundred micrometers. No correlation between linear wrinkling on the ACL and CCL could be found. As shown in the inset of figure 6.3 (C), buckling and linear wrinkling were found to correlate to holes and cracks in the corresponding

MPL by comparing their shape, size and position. Additionally, it was discovered that 80 % of 38 circular Pt depositions of a single cell in region 6 correlated with geometric displacements like buckling and linear wrinkling. Herein, the dimensions of 93 % of 27 investigated Pt depositions were detected to be smaller than the dimensions of the corresponding buckle and linear wrinkling. No differences of buckling and linear wrinkling along a single cell and within different cells of the stack were observed.

6.3.2 Interpretation of structural changes

During operation MEAs undergo several relative humidity changes and can be exposed to harsh conditions like local fuel starvation, which can lead to the observed degradation phenomena. Especially, the observed degradation phenomena of CCL thinning, crack formation and Pt deposition indicate a rise of electrode potential at the cathode due to local fuel starvation [196, 303–305].

An elevated temperatures in the degraded area and carbon corrosion of the CL is expected to be responsible for the adhesion of MPL and CCL. Agglomeration of ionomer on top of the CCL due to carbon corrosion in combination with an increased mobility of the ionomer due to increased temperature could lead to ionomer migration into the MPL and thus leading to the observed adhesion effect. In addition, carbon corrosion during fuel starvation could lead to a roughening of the MPL and CCL surface, which could lead to a mechanical adhesion of the two layers.

Carbon corrosion is assumed to support crack formation at the CCL due to a weakening of the CCL structure, thus leading to the increased crack surface area ratio at the CCL compared to the ACL. Crack formation itself is assumed to be caused by tensions within the CL originating from membrane swelling, which occurs during cycling of the relative humidity [310]. This is also in accordance with the preferential formation of cracks in the vicinity of CCM buckles, where CCM expands during buckle formation.

The fact that Pt deposition is accumulated in distinct but randomly distributed areas close to the anode outlet of the CCL leads to the assumption of water accumulation at the CCL surface being a prerequisite for Pt deposition. This hypothesis is supported by the observed correlation of Pt deposition to geometric displacements like buckling and linear wrinkling, posing a possible location for water accumulation. In accordance with the results of Uchiyama et al. [310, 311], buckling and linear wrinkling is supposed to occur due to relative humidity cycling of the cell during operation. While Uchiyama et al. simulated low supporting MPL areas by introducing a perforated foil between CCM and GDL to artificially create buckles, in this work buckling was observed in a real system. Buckling formation is explained as follows: Due to relative humidity change the membrane swells and the CCM extends. At locations of low support due to holes or cracks in the MPL, the CCM releases the stress by wrinkling into these geometric displacements, thus

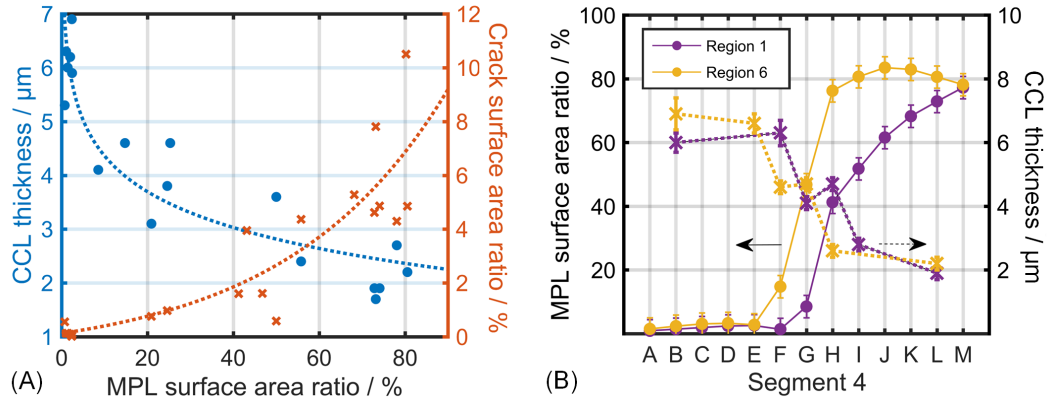


Figure 6.5: (A) Correlation of surface area ratio of adhered MPL, CCL layer thickness (blue) and crack surface area ratio (orange) of different segments of 6 cells within stack region 1, 6 and 8. (B) Spatially resolved correlation of surface area ratio of adhered MPL (solid) and CCL thickness (dashed) along row 4 (see figure 6.1 (B)) of a single cell of region 1 (purple) and region 6 (yellow) of the stack.

forming buckles and linear wrinkles. This hypothesis is in accordance with the position and shape of buckles and linear wrinkles to holes and cracks in the MPL. No correlation of linear wrinkles on the ACL and CCL was found. Therefore, linear wrinkling is a wrinkling effect of the single CL, which is in accordance with the results of Mehmood et al. [312].

6.3.3 Correlation of fuel starvation degradation phenomena

For a simplification of further stack analysis related to fuel starvation the degradation phenomena of MPL adhesion, CCL thinning and crack formation determined on different segments (along row 4) within 6 cells at stack position 1, 6 and 8 were correlated. Figure 6.5 (A) shows that an increase in MPL adhesion correlates with both an increase in crack surface area ratio as well as with a decrease in CCL thickness. In particular, figure 6.5 (B) shows strong CCL thinning in the transition region of low to high MPL adhesion of cells in region 1 and 7. In addition, a correlation in terms of an increase in both MPL adhesion and Pt deposition towards the anode outlet region was observed. Consequently, the degradation phenomena of MPL adhesion can be used as a first indicator for the degradation phenomena of CCL layer thinning, crack formation and to a certain extend for Pt deposition. The results therefore allow the conclusion that a fast indication of fuel starvation degradation along different cells of the stack can be made by analysing MPL adhesion on the single cells of the stack. It has to be mentioned that a transfer to different material systems and operation conditions still has to be proven.

6.3.4 Local development of degradation along single cells and within the stack

In order to investigate the influence of cell geometry as well as cell stacking on degradation the aforementioned correlation of different degradation phenomena was used to perform a simplified stack degradation analysis. The representative degradation phenomena of MPL adhesion was quantified by calculating the MPL surface area ratio (as described in the experimental section) at various positions within a single cell. Quantification was repeated for cells at eight different stack positions (regions 1 to 8 in Figure 6.1 (A)). Figures 6.6 (A) and (B) show the local development of the degradation along a single CCM at different stack positions. At least two specimens were taken for each location to analyze the degradation phenomena. An exception was made for region 2, where only one cell was investigated. A general trend of increased MPL adhesion towards the anode outlet (position M7) in both horizontal (position A-M) and vertical direction (position 1-7) was found. An exception was made for cells at the end of the stack (region 8), where a decrease of MPL adhesion towards the anode outlet after an initial increase of degradation was observed. This behavior might be due to a transport of excess hydrogen from the outlet manifold, which is also referred to as vacuum effect [55, 313, 314].

In addition, local differences in total cell degradation were found according to the cell position within the stack. As shown in figure 6.6 (C), increased degradation, by means of MPL covering the CCL, was found in the middle of the stack slightly shifted to the end of the stack (region 4 to 6, where region 4 depicts the middle of the stack). In addition, slightly stronger degradation was observed in the region close to the stack inlet (region 1) and at the end of the stack (region 8). The distribution of degradation along the stack was in accordance with in situ data, showing cell voltages (at a current density of 1.4 A cm^{-2}) within regions of increased degradation being lower compared to cell voltages within other regions of the stack (see figure 6.6 (C)).

Due to the complexity of the automotive fuel cell system and its operating points a clear reason for the inhomogeneous stack degradation could not be found. However, the occurrence of regions of stronger degradation within the stack could be explained by the stack and cell design as well as by self-worsening effects due to the mutual dependence of water accumulation and fuel starvation degradation. On the one hand, inhomogeneously incoming gas flow in different cells due to stack design and peripheral fuel cell system devices could have led to an increased local fuel starvation in distinct cells. On the other hand, fuel starvation could have been supported by water accumulation within the MEA by preventing hydrogen to access the active area. The observed degradation of buckling and linear wrinkling are supposed to support the accumulation of water [312] on both anode and cathode. In addition, degradation phenomena like crack formation on top of the CCL could also lead to an enhanced accumulation of water on the cathode side [312, 315].

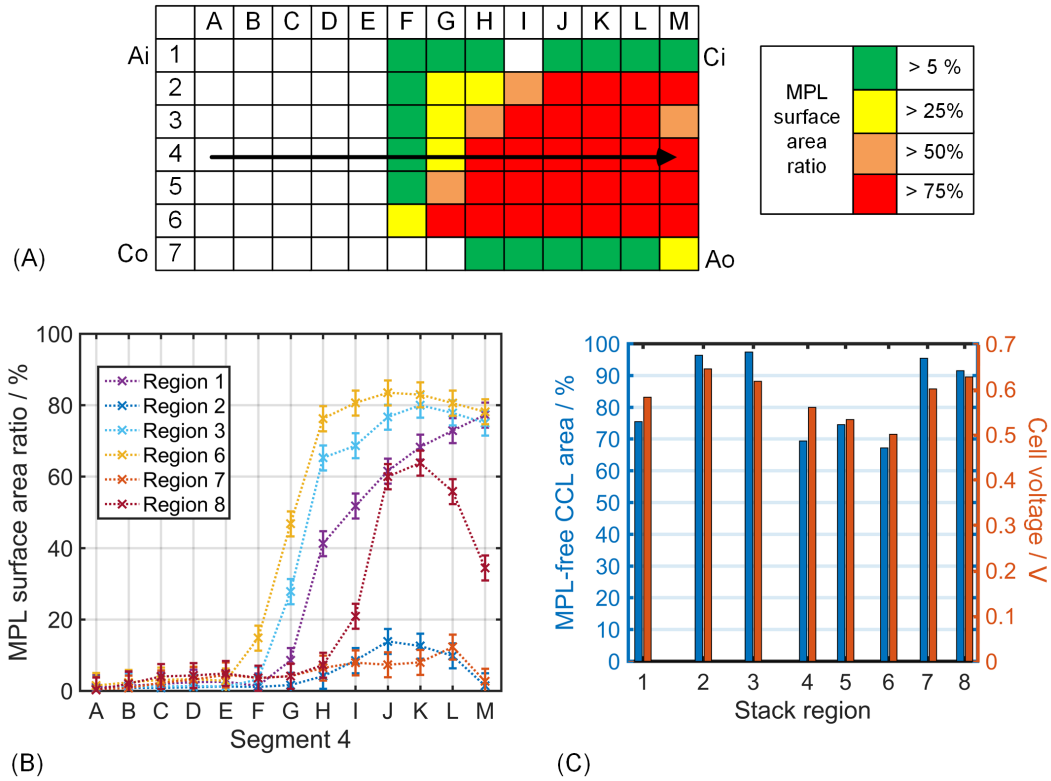


Figure 6.6: (A) Distribution of MPL adhesion on an exemplary cell of the stack, showing increasing degradation from anode inlet to anode outlet. Ai/Ci and Ao/Co indicate positions of anode/cathode inlet and outlet respectively. (B) Horizontal development of degradation from anode inlet to outlet region (as depicted by arrow in A) for different cells of the stack. Region 4 and 5 show similar results as region 6 and are excluded from the graph for reasons of clarity. (C) Left axis: MPL free area of the CCL as a measure for cell degradation at different stack positions. Increased degradation (lower MPL free area) in the middle of the stack slightly shifted to the end of the stack (regions 4 - 6) as well as at both ends of the stack (regions 1 and 8) were observed. Right axis: Cell voltage of different cells within the stack at 1.4 A/cm². Cells with increased degradation showed lower performance in terms of in situ measured cell voltage.

Due to water diffusion from cathode to anode, water accumulation at the anode could also be increased by the aforementioned cathode degradation. This could have led to a self-worsening effect of fuel starvation degradation supporting further fuel starvation. Therefore, both an inhomogeneous incoming gas flow and the mutual dependence of water accumulation and fuel starvation can cause the observed inhomogeneous stack degradation.

6.3.5 Postulation of a degradation mechanism for circular and linear platinum deposition

It is well agreed that Pt agglomeration and particle growth is highly relevant for fuel cells and thus for stack performance loss [32, 122, 234]. Since circular and linear Pt deposition was observed throughout the stack and, to the best of our knowledge, has not been described in literature yet, an in-depth analysis of this degradation mechanism was performed.

As illustrated in figure 6.7, voids between MPL and CCL like buckling and linear wrinkling of the CCM as well as MPL cracks and holes are assumed to be the starting point of the degradation. At high current densities and/or high relative humidities of the supplied gases, these voids at the cathode are suspected to be filled with liquid water. Additionally, due to possible hydrogen starvation at the anode, the electrode potential U_c rises at the CCL according to the reverse current mechanism [196]. As a result of the increased cathode potential, Pt dissolves into water within the voids (see figure 6.7 (A)) [316, 317]. The dissolution of Pt ions in water is supported by the results of Xie et al. [235].

When starved anode regions are resupplied with hydrogen the potential U_c of the CCL decreases and reaches the reduction potential of dissolved Pt ions, thus leading to deposition of the dissolved Pt (see figure 6.7 (B)). In order to deposit Pt in the center of the macroscopic voids (diameter = a few ten to a few hundred micrometers, depth = a few to few tens of micrometers), electrons have to migrate a long distance in the order of tens of micrometers within the strongly degraded CCL possessing a severe decreased thickness of approximately two to three micrometers. The large electric resistance of the long path, that electrons have to move within the collapsed electrode leads to an increase in electric potential towards the center of the void. Since the change in protonic potential from the edge to the center of the void can be neglected, the increase in electric potential leads to an increase in the local cathode potential (see figure 6.7 (B)). Thus, dissolved Pt will preferentially deposit at the edge of the water filled void, where a lower cathode potential is present (see figure 6.7 (B)). In addition, dissolved Pt ions will migrate towards the edges of the macroscopic void, due to the established electric field, also leading to an increased Pt deposition at the edges of the void and thus explaining the formation of circular Pt deposition.

Another mechanism that could support the favored Pt deposition at the edges of the water-filled void is given by the cathode potential differences along the void during fuel starvation. According to the reverse current mechanism the potential increase at the cathode is caused by an oxygen reduction reaction at the starved anode and thus dependent on the oxygen diffusion from cathode to anode. The water droplet within the void having a thickness of several micrometers and having an oxygen diffusion coefficient in the range of fully hydrated polymer-electrolyte membranes possesses an additional diffusion resistance for oxygen diffusion from cathode to anode. Thus, the oxygen partial pressure at the anode and the corre-

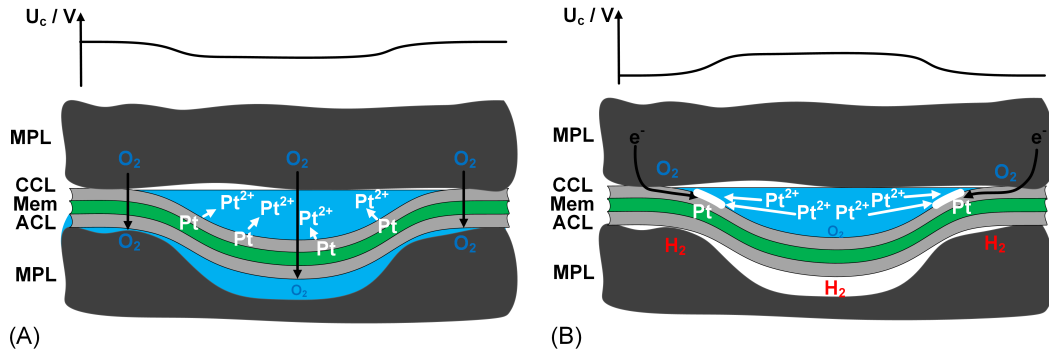


Figure 6.7: Schematic of the postulated formation mechanism of Pt deposition on top of the CCL. (A) Dissolution of Pt in water within a void (here: buckle) at elevated cathode potential due to local fuel starvation. (B) Pt deposition close to the contact area of MPL/CCL (high current density for Pt-ion reduction) at reduced cathode potential.

sponding local cathode potential in the center of the void is decreased. As a result, Pt dissolution at the edges of the water filled voids is enhanced leading to an increased Pt ion concentration in the water droplet in the proximity of the void's edges. This leads to an increased Pt deposition on top of the CCL compared to the center of the void, when the cathode potential drops below the Pt reduction potential during hydrogen resupply.

In case of linear Pt deposition the width of the linear voids (cracks: width = a few micrometers, length = a few hundred micrometers) is assumed to be not enough to create a sufficient increase in electric potential and/or decrease of oxygen partial pressure. Thus, a linear Pt deposition is formed.

6.3.6 In-depth analysis of the observed degradation phenomena

An in-depth analysis of the Pt deposition on top of the CCL was carried out in order to support the postulated degradation mechanism. In addition, a model experiment, simulating humidity cycles of single MEAs, was performed to prove the hypothesis of buckling and linear wrinkling being caused by humidity change induced swelling and shrinkage of the CCM.

Figure 6.8 shows SEM micrographs of Pt deposition on top of the CCL. A thin film was observed (see figure 6.8 (A)), which was shown by EDS mapping to consist of Pt (see figure 6.8 (B)). XPS measurements, which were acquired by Dr. Stefan Viehbeck, demonstrated that Pt occurred both as elemental Pt and as Pt-O₂ compound within the CL. This was observed for regions with and without Pt deposition. As indicated in table 6.1, the mapping of a CL in a region with Pt deposition showed, both an increase in Pt4f and O1s peaks when compared to a CL region without Pt deposition or to a region on the MPL. This demonstrated the accumu-

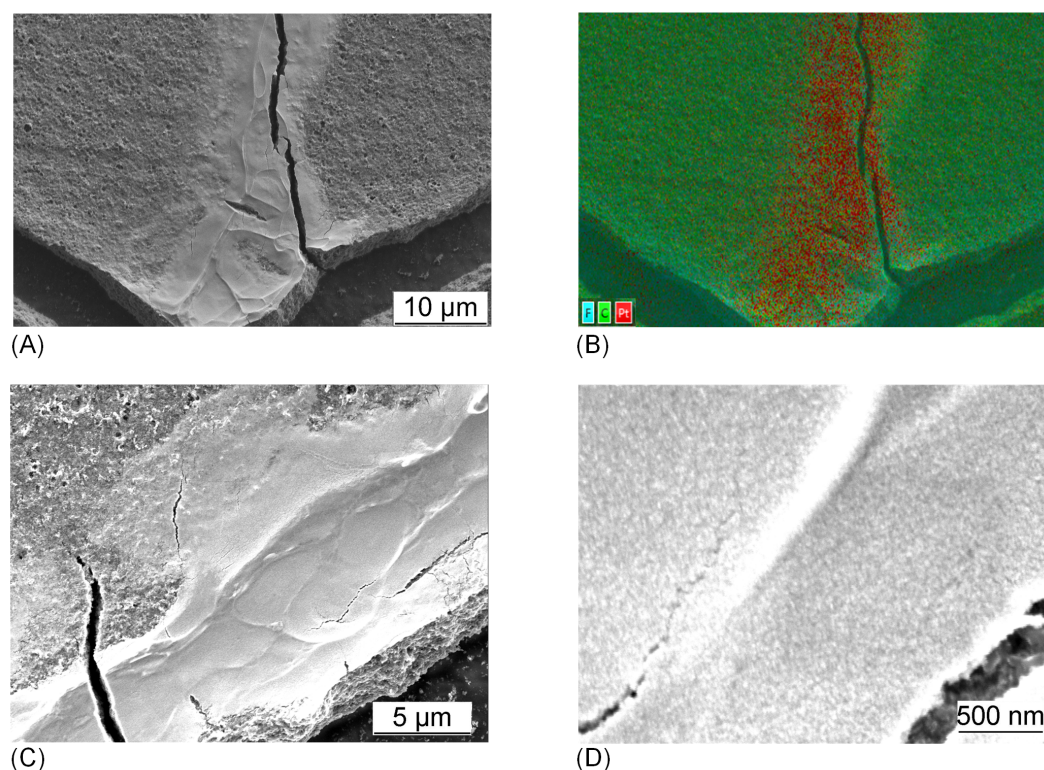


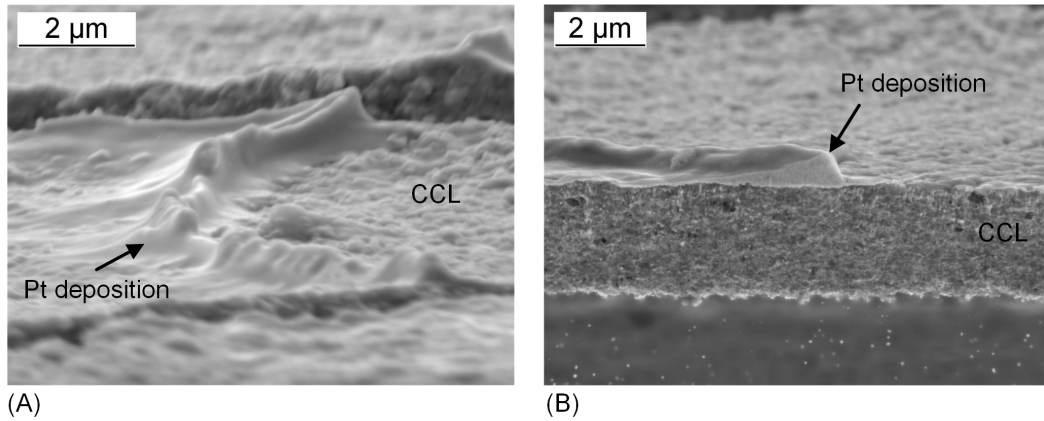
Figure 6.8: SEM micrographs (A, C, D) of Pt deposition with different magnifications. Pt was shown to form a film-like deposition with a rough surface. (B) EDS mapping of the region shown in (A).

lation of Pt and Pt-O₂ compound in the region of the Pt deposition. Higher magnification imaging (see figure 6.8 (C) and (D)) showed that the Pt film is formed of Pt particles and agglomerates. As illustrated in figure 6.9, Pt was found to form a meniscus-like deposition on top of the CCL. Within the degraded area of the MEA, a strongly decreased porosity of the CCL was found in addition to the Pt depositions, as shown in figure 6.10. This finding supported the hypothesis of local fuel starvation locally increasing the cell voltage according to the reverse current mechanism [196]. The cell voltage increase can lead to the observed severe carbon corrosion. An increasing loss of porosity towards the Pt deposition was not observed. In addition, no significant change of Pt loading towards the Pt deposition was detected by imaging the top of the CCL by EDS. It has to be mentioned here, that interaction volume of the electron beam within the sample might be too large for a sensitive spatial EDS analysis in the SEM.

The thickness of the CCL within the degraded region was found to differ in regions with MPL adhesion and buckle formation. Figure 6.11 (A) shows a decreased CCL thickness below MPL adhering to the CL. This effect might result from external

Table 6.1: Atomic concentration (at%) in different sample areas determined by XPS.

Sample area	C1s / at%	O1s / at%	F1s / at%	Pt4f / at%
MPL	69.8	1.1	29.0	0.1
CL	55.5	3.3	40.3	0.9
Pt deposition	47.4	4.8	46.8	1.0

**Figure 6.9:** SEM micrographs of Pt forming a meniscus-like deposition. (A) Top view on the CCL. (B) CCL cross section.

stack compression, wherein the compression force was introduced to the CL only at contact areas of MPL and CL. In addition, an increased CCL thickness towards the center of CCM buckles was observed (see figure 6.11 (B)). This is in accordance with the postulated degradation mechanism assuming a decreased potential at the center of the water filled buckles during fuel starvation. An increased potential will thus lead to increased carbon corrosion and therefore to a decreased CCL thickness.

For further investigation, TEM micrographs were performed by BMS Consulting (Burnaby, Canada). Samples were embedded in epoxy and cut into slices of approximately 100 nm by a microtome. Degraded samples were analysed from region L3/ L5 of the MEA location matrix (see figure 6.1 (B)). The TEM micrographs revealed that the meniscus-like Pt deposition consisted of an agglomeration of several small Pt particles in the nanometer scale rather than a single Pt crystal (see figure 6.12 (A), (B)). TEM micrographs were additionally used to investigate the Pt particle size distribution in the CCL. As depicted in figure 6.13, degraded samples showed an increased Pt particle size distribution as compared to a non-operated begin-of-life reference sample. The degraded samples were again taken from region L3/ L5 of the MEA location matrix (see figure 6.1 (B)). Figure 6.13 (C) shows the Pt particle size distribution, obtained from analyzing 200 Pt particles of two de-

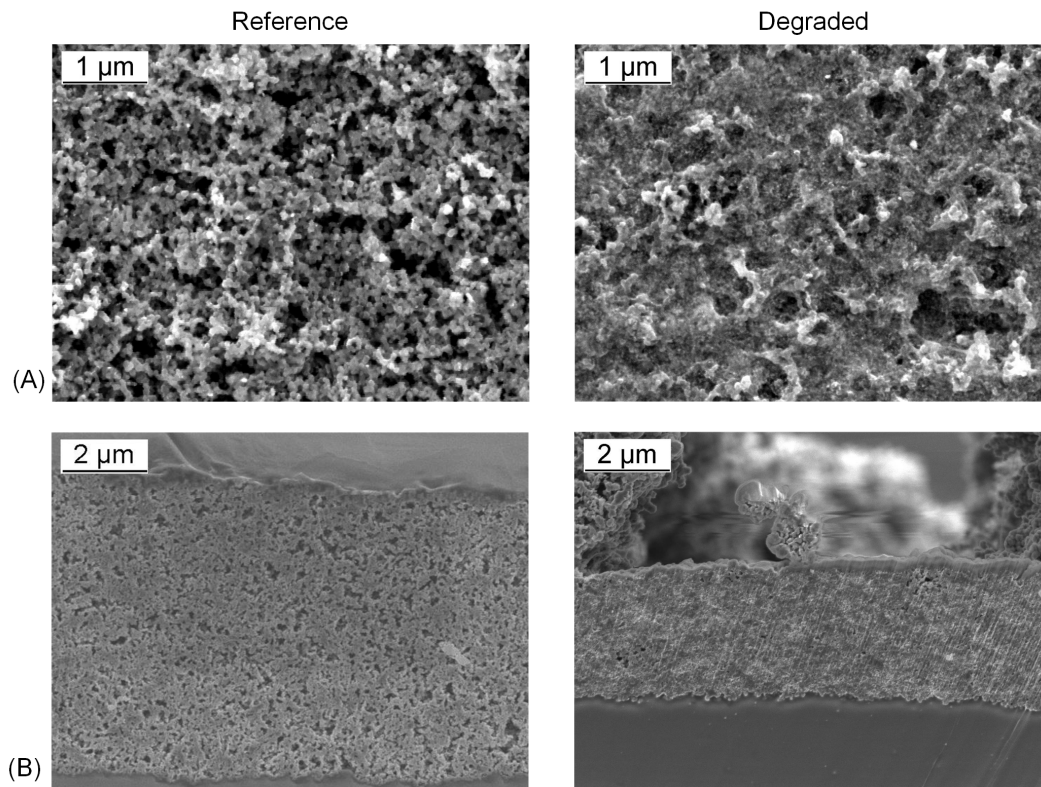


Figure 6.10: SEM micrographs showing decreased porosity of a degraded CCL (right) compared to a begin-of-life CCL (left) in both top view (A) and cross section view (B).

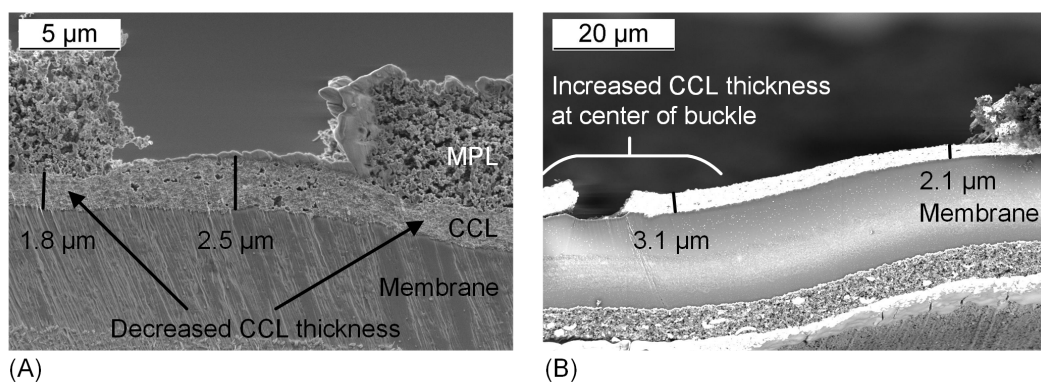


Figure 6.11: SEM micrographs of CCM cross sections showing decreased CCL thickness below MPL adhering to the CL (A) and increasing CCL thickness towards the center of CCM buckles (B).

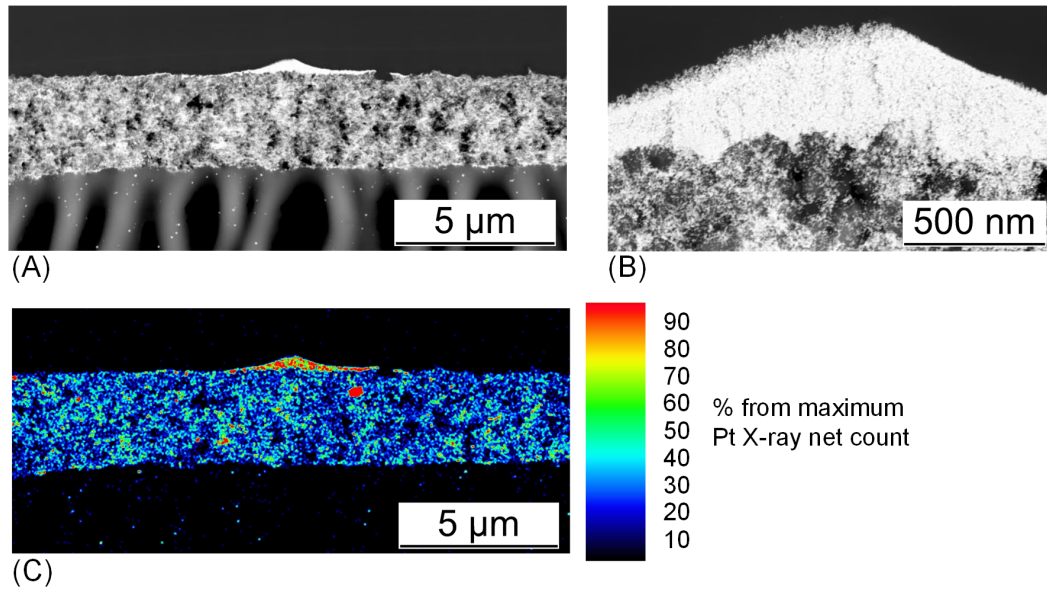


Figure 6.12: TEM micrographs showing a meniscus like Pt deposition on top of the CCL (A), consisting of Pt particles as shown with higher magnification imaging (B). EDS mapping showed no gradient in Pt loading of the CCL in the proximity of the Pt deposition (C).

graded and one begin-of-life reference CCLs. An increase in mean particle size by about 22 % is observed. This is less than the obtained increase in Pt crystallite size of approximately 115 % as obtained by XRD measurements on a similar degraded cell region. The deviation can be explained by the following. In case of the TEM investigation, the Pt particle size was calculated from the CL only, without taking the Pt deposition on top of it into account. By contrast, Pt size determination by XRD averages the Pt crystallite size in both the CL and within the Pt deposition. Nevertheless, the TEM and XRD results indicated a particle growth, which was especially pronounced in the Pt deposition on top of the CCL. This means, that the Pt particle size increase was dominated by Ostwald ripening and dissolution and redeposition rather than by Pt particle agglomeration. This supports the hypothesis of local fuel starvation and the corresponding potential rise to be responsible for the observed Pt particle growth and deposition.

TEM-EDS mapping, as exemplarily illustrated for one region in figure 6.12 (C), showed no gradient in Pt loading of the CCL in the proximity of the Pt deposition neither in in-plane nor in through-plane direction. A total region of approximately 40 μm around the Pt deposition was investigated. In particular, the Pt loading of the CL in the proximity of the Pt deposition did not deviate from the Pt loading of a non-operated reference sample. This led to the hypothesis, that Pt being dissolved

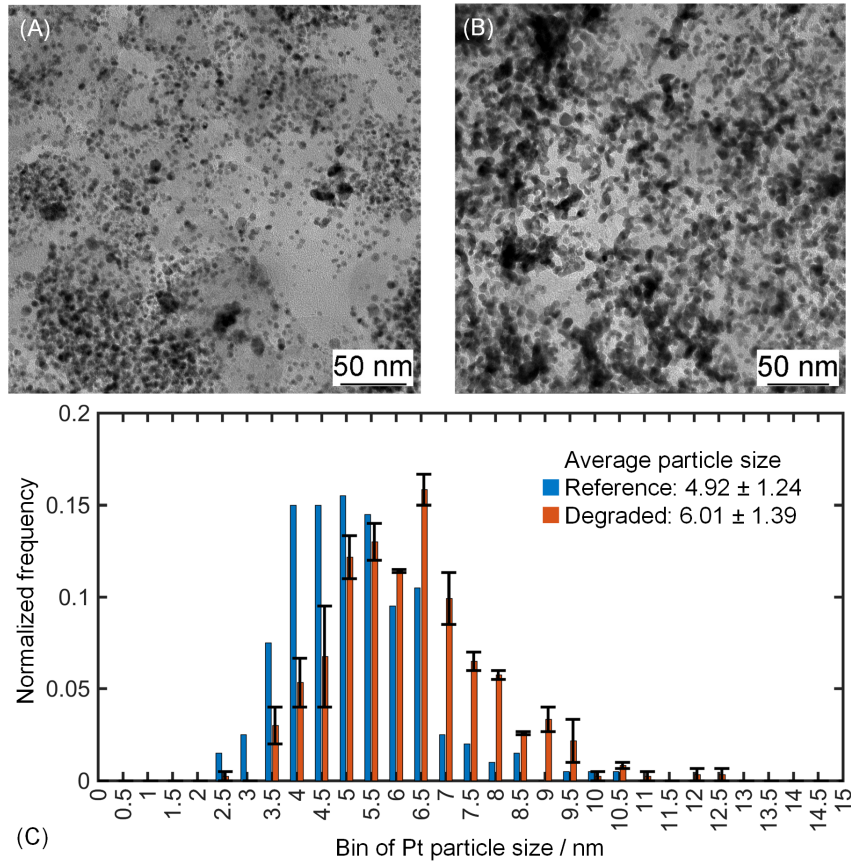


Figure 6.13: TEM micrographs showing Pt particles of a non-operated begin-of-life sample (A) and a sample taken from a full size stack operated under fuel starvation conditions at the test station (B). The particle size distribution of the different samples is given in (C).

in other regions of the cell might be transferred by liquid water to the deposition areas.

Finally, the correlation between humidity cycles and the formation of geometric CCM deformation like linear wrinkling and buckles was confirmed by a model experiment. Nine humidity cycles from 0 % r.h. to 120 % r.h. were performed for a 50 cm² MEA with a similar material system with the help of a commercial fuel cell test station (Greenlight G60). Figure 6.14 shows the formation of buckles and linear wrinkling on the CCM after humidity cycling, thus demonstrating humidity cycles causing the formation of geometric displacements of the CCM.

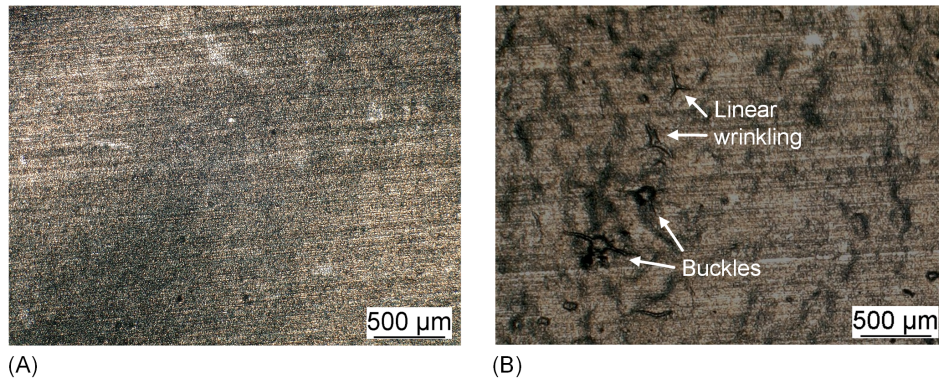


Figure 6.14: Optical micrographs of CCM before (A) and after (B) humidity cycling. Buckles and linear wrinkling were observed after the humidity cycling.

6.4 Distribution of gas diffusion layer degradation on single cell and stack level

In the previous sections the distribution of local fuel starvation degradation of an automotive stack on both single MEA and stack level was described. Fuel starvation can be caused by water accumulation, being correlated to water management properties within the electrode, GDL and flow field. Therefore the obtained results were compared to GDL wettability properties at different MEA and stack positions. The GDL wettability properties were determined by the method introduced in chapter 5. All GDLs taken from different regions of the MEA and of the stack possessed an increased specific capacitance as compared to reference samples (see figure 5.11 and 6.15). At first glance, no clear correlation between MPL adhesion, being a indicator for fuel starvation degradation, and specific capacitance at different positions on the MEA could be drawn (see figure 6.15 (A)). However, when averaging the region of low fuel starvation (segments A to E in figure 6.1 (B)) and the region of high fuel starvation (segments I to M in figure 6.1 (B)), as illustrated in figure 5.11, the tendency of increased specific capacitance in the region of increased fuel starvation degradation was observed on the MEA level.

On the stack level (see figure 6.15 (B)), both MPL adhesion and specific capacitance increased from the region 1 to 4. In addition, both measures decreased from region 4 to 6. Thus, MPL adhesion and specific capacitance showed a similar trend on stack level. The gas supply of the stack was herein located in region 1. Region 5 was an exception showing an increase in specific capacitance but a decrease in MPL adhesion. Under the assumption of local effects influencing the increase of specific capacitance in region 5, MPL adhesion being a measure for fuel starvation degradation and specific capacitance being a measure for GDL wettability properties seemed to be correlated to each other. Lower wettability promotes fuel

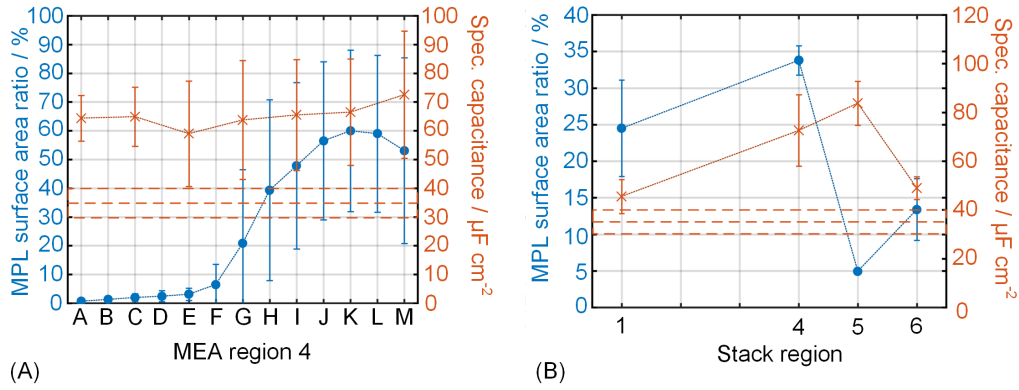


Figure 6.15: Correlation of MPL adhesion on the CCM (blue) as an indicator of fuel starvation degradation and specific capacitance (orange) as a measure for GDL wettability changes for samples taken from a full size stack being aged under severe fuel starvation conditions at the anode outlet. Mean value and standard deviation of specific capacitance of reference samples is given by the dashed orange lines. (A) Correlation at different regions on the MEA. (B) Correlation at different positions within the stack.

starvation degradation. On the other hand an increased cell voltage due to fuel starvation can accelerate GDL degradation resulting in reduced water management properties.

Similar results were obtained for a second automotive size full size stack being aged in a prototype vehicle. Stack analysis showed a correlation between reduced fuel starvation degradation and specific features of the bipolar plate enabling improved gas supply and water removal. To obtain information about the degradation's distribution, the introduced method to indicate fuel starvation degradation distribution by determining MPL adhesion was applied to this stack in the master thesis of Mert Dalkilic [318], which was supervised in this work. In order to reduce the effort to quantify the MPL adhesion on a single MEA, three main regions of the MEA were distinguished. Main region one, two and three covered the MEA area at the anode inlet, MEA center and anode outlet, respectively. Each main area was divided in 24 subsections. For a semi-quantification of the MPL adhesion the amount of subsections possessing MPL adhesion was counted and the MPL adhesion on two representative subsections was quantified using optical micrographs and image threshold analysis. The product of the number of subsections possessing MPL adhesion and the mean value of the quantified MPL adhesion gave a measure for the MPL adhesion of the whole main region. The distribution of MPL adhesion, being an indicator for fuel starvation degradation on single MEA and stack level of the prototype vehicle are shown in figure 6.16. The obtained results were also compared to specific capacitances measured at different MEA and stack positions.

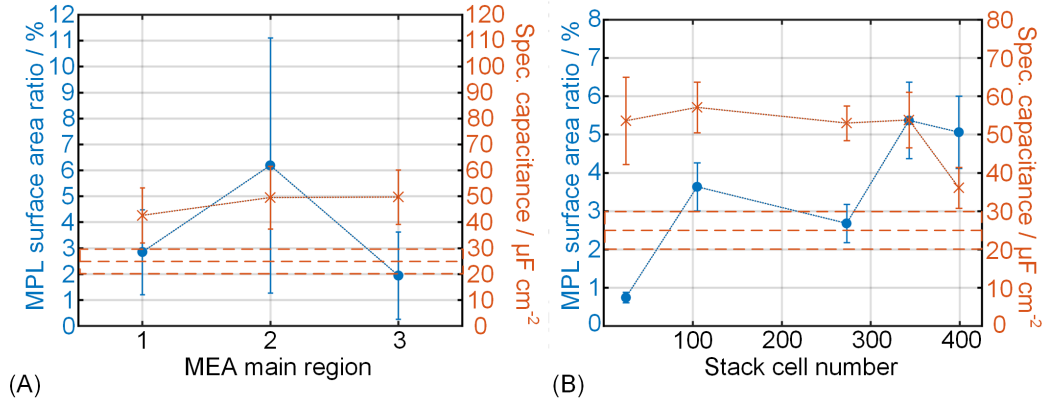


Figure 6.16: Comparison of MPL adhesion on the CCM (blue) and specific capacitance of the GDL (orange) on the MEA level (A) and at different positions within the stack (B). The mean value and standard deviation of the specific capacitance of reference samples is given by the dashed orange lines. MPL adhesion and specific capacitance serve as a measure for fuel starvation and GDL wettability changes, respectively. Samples are taken from a prototype vehicle stack.

While MPL adhesion and thus fuel starvation degradation increased at MEA main region two and to the end of the stack, no clear dependence of specific capacitance and thus GDL wettability properties on either stack and MEA position was found. Each region showed however increased specific capacitance values as compared to reference samples.

Both stacks showed a decrease of specific capacitance at the end of the stack (see figure 6.16 (B) and 6.15 (B)), with specific capacitance values being close to begin-of-life reference values. This indicates that changes in the gas supply and/ or in the water removal at the end of the stack reduce GDL degradation. Since for both stacks no significant correlation between fuel starvation degradation and GDL degradation could be drawn, other factors like gas supply distribution or local temperature effects were assumed to cause the observed distribution of fuel starvation degradation. Similarly, as already discussed in chapter 5 the degradation of GDL was assumed to be only partially caused by carbon corrosion degradation.

6.5 Conclusion

Different degradation phenomena were found on cells of an automotive full size stack operated under different automotive driving points. By correlating the observed degradation phenomena of crack formation, CCL thinning and Pt deposition, to the degradation of MPL adhesion, a fast indicator for degradation inhomogeneity was found.

geneities of fuel starvation degradation within single cells and between different cells of the stack were presented.

Buckling (wrinkling of the CCM) and linear wrinkling of the CL were observed continuously throughout the cell and stack, the other degradation phenomena were found to increase towards the anode outlet and exhibited different extent at different locations of the stack. An increased degradation in terms of MPL adhesion in the second half of the stack as well as a slightly increased degradation at both ends of the stack were detected. A potential rise at the CCL due to fuel starvation was most likely causing the degradation. Gas flow inhomogeneities and self-worsening effects due to the mutual dependence of water accumulation and fuel starvation were thought to be responsible for the different extents of degradation along the stack.

A degradation mechanism for the formation of Pt deposition was proposed: In brief, voids between MPL and CL being filled with liquid water were suggested to be the starting point of the Pt deposition. A potential rise according to the reverse current mechanism was suggested to lead to Pt dissolution in water filled voids. After the resupply of hydrogen and the corresponding decrease of potential, dissolved Pt deposits preferentially at the edge of water filled voids. This might be due to an increased cathode potential in the center of the void, which is caused by a high in-plane electron resistance of the degraded CCM. In addition, an increased Pt ion concentration at the edges of the water filled voids can explain the preferential Pt deposition. An in-depth analysis of the degradation was performed, with respect to shape and composition of the Pt deposition and with respect to the extend of carbon corrosion. Herein, the postulated degradation mechanism was supported by decreasing CCL thickness in the middle of buckles, which correlates to the hypothesized increased potential at the center of the buckle during fuel starvation. The correlation between humidity cycles and the formation of geometric displacements of the CCM were shown by a model experiment.

Since fuel starvation degradation can be caused by water accumulation within the GDL, the degradation was compared to altered GDL wettability properties. A comparison of the CCL fuel cell degradation and GDL hydrophobicity loss from samples taken from two automotive full size stacks being degraded in a prototype fuel cell vehicle and under fuel starvation conditions on a test station did not show a significant correlation neither on single cell nor on stack level. Therefore, other factors like gas supply distribution or local temperature effects within both stacks were assumed to cause the observed distribution of fuel starvation degradation.

Chapter 7

Summary and Outlook

The scope of this work was to improve an automotive failure analysis process by extending knowledge about failure phenomena by e.g. revealing failure mechanisms and by the adoption and development of analysis methods for automotive size PEMFC single cells and stacks. Knowledge about degradation mechanisms and the ability of their instrumental characterization enable directed improvements of the fuel cell material system and the operation strategy. In addition, directed actions for the prevention or suppression of the degradation mechanism can be taken during operation.

The work focused on degradation phenomena being crucial to fulfill life time targets of automotive fuel cells. In particular membrane defects, changes in wettability properties of gas diffusion layers, and fuel starvation degradation of the catalyst layers were addressed.

Firstly, membrane defects were studied in chapter 4 of this work. For an optimized failure analysis four promising methods for pinhole detection were investigated and compared by means of their detection limit and detectability dependencies e.g. on the material system. Model experiments with artificial pinholes showed that pressure drop and hydrogen crossover measurements are methods which can be implemented quick and relatively easy, with detectable pinhole diameters of approximately 200 μm and $< 50 \mu\text{m}$ for the investigated material and test station, respectively. Both methods depend on the properties of the material system like the GDL permeability. The pressure drop method is recommended for a first leak check of the cell, while the hydrogen crossover method can be applied for a more sensitive detection of pinholes. An additional cell hardware was constructed for pinhole detection via infrared-thermography and helium-gas detection. Both methods possess the advantage to enable a localization of the pinhole position on the MEA. Detection via infrared-thermography is a fast tool for pinhole localization, the minimal detectable pinhole size (here 10 μm to 100 μm)

is however strongly dependent on the material properties like the GDL's thermal conductivity and gas permeability or the electrochemical active area of the CL. Helium-gas detection was found to be able to detect pinholes as small as 5 μm in diameter and showed fewer dependence on MEA properties. A manual scan of the MEA is however more time consuming as compared to infrared-thermography. The application of infrared-thermography and helium-gas detection to real operated samples enabled the localization of several pinholes with a diameter of approximately 100 μm . Helium detection could additionally localize pinholes with a diameter of 10 μm on real degraded samples. Therefore, infrared-thermography is recommended for a fast localization of large pinholes, while the helium-gas detection is recommended for a localization of small pinholes. Concluding, an evaluation matrix of the different methods including a recommendation for their practical application was given.

In future works, a reduction of analysis time to detect membrane defects via infrared-thermography and helium-gas detection could be addressed by an improvement of the cell hardware. For instance, a stationary compression device with pressure cylinders for a homogeneous compression in combination with a connection plate for a fast exchange of MEAs under investigation is suggested. With regard to helium-gas detection, an automation of the scanning process is advised. Possible approaches are the assistance of a robotic arm that handles the sensor or the use of an electric driven table to move the whole MEA with respect to the fixed sensor. Although the robotic arm might be the more complex solution, it would additionally allow the automated application of different funnel sizes. For both, the infrared-thermography and helium-gas detection method, the measurement results are suggested to be directly fed, analyzed and documented in a data base which is able to automatically create an analysis report. Finally, a more comprehensive understanding of the failure mode could be achieved by a combination of the different methods. Again, an automatic gathering and comparison of the measurement results in a database would highly decrease the working time and improve the understanding of the failure phenomena. Machine learning for the correlation of different results from infrared-thermography, helium detection, pressure drop and hydrogen crossover method to ex situ characterization of membrane defects (e.g. defect size) by optical imaging, electron or X-ray microscopy could be applied for an improved failure analysis.

Secondly, in chapter 5, the analysis of GDL wettability, being a key factor for water management within a MEA and thus for cell performance and degradation, was discussed. Determination of GDL capacitance by cyclic voltammetry, as already successfully applied in literature using acidic electrolytes, was adopted for the application in an automotive fuel cell failure analysis process by substituting the electrolyte to a pH-neutral electrolyte. A detailed characterization of the method and its validation on artificially and real-operation aged samples was performed. In a first step, the dependence of the measured capacitance value on measurement settings like the tenside concentration of the electrolyte or the penetration time

was investigated. In addition, the correlation of GDL morphology to the measured capacitive value was drawn and interpreted. The method was found to not only measure the outermost parts of the GDL but also large pores in the MPL and at the substrate/ MPL interface. Electrolyte tenside concentration and penetration time before measurement were shown to highly influence the measurement result by altering the ratio of GDL pores being in contact with the electrolyte. With respect to morphological composition of the GDL, PTFE treatment of the fiber substrate as well as properties of the MPL were found to highly influence the measured wetted surface area. Thus, the introduced method was shown to indicate differences in GDL morphology and surface structure of non-operated begin-of-life samples. The validity of the method was demonstrated by measuring the capacitance increase of different mechanically and chemically degraded samples and their comparison to ex situ determined changes in morphological properties. While mechanical compression of the cell did not show a significant change in capacitance, an increase for chemically aged samples was found when compared to reference samples. PTFE loss and changing surface properties e.g. due to an increase of surface oxygen groups are suggested to cause the increased wettability of chemically degraded samples. Samples taken from two automotive stacks were shown to have increased GDL wettability properties after their operation. This has a negative impact on the cell performance and degradation as the produced water cannot be transported away from the active sites. The measurement results were again compared to ex situ degradation analysis results. Finally, a comparative study demonstrated, that the introduced method possesses a higher sensitivity as static contact angle measurements, in particular for real operation degraded samples.

Future works could focus on the dependence of the measured capacitance changes to the applied electrolyte tenside concentration or penetration time. As shown in this work, both parameters highly influence the ratio of the GDL being penetrated by the electrolyte. This indicates that different degradation mechanisms in MPL or substrate could be addressed with different penetration properties of the electrolyte. A setup enabling a direct, non-destructive measurement on the MEA would also be beneficial, in order to avoid cutting of the MEA samples. Furthermore, different positions on the MEA could be analyzed automatically. Finally, the question whether air being trapped within the GDL could hinder proper penetration of the electrolyte into the GDL can be addressed in future works. Depending on the pore structure of the substrate and MPL, air might be removed from the GDL to a different extend after being in contact with the electrolyte. This issue could be a reason for the high scattering of the reported results. Thus, a device enhancing air removal from the GDL, e.g. a vacuum pump being connected to the GDL, could improve the sensitivity and reproducibility of the method.

Thirdly, as described in chapter 6, the degradation of two automotive full size stacks, where one was operated in a prototype vehicle and one under severe fuel starvation conditions at a fuel cell test station, were analyzed. Herein, an in-depth

analysis of single degradation phenomena and their local development on single MEAs and at different positions within the stacks was performed. Both stacks showed similar degradation patterns including adhesion of parts of the MPL on the catalyst layer, buckling and wrinkling of the catalyst coated membrane, catalyst layer crack formation, Pt deposition on top of the cathode catalyst layer as well as catalyst layer thinning. Buckling and wrinkling of the catalyst coated membrane was found throughout the MEA and the stack with no regular pattern. They were correlated to humidity induced extension and shrinkage of the MEA at regions without support of the MPL, like MPL holes and cracks. With the help of a model experiment, the postulated degradation mechanism for buckle formation was verified.

The degradation patterns of the catalyst layer showed a dependence on the local gas supply within the MEA and stack. For stack one, taken from the prototype vehicle, a correlation between degradation and specific features of the bipolar plate enabling improved gas supply and water removal was found. Stack two, being aged under severe fuel starvation conditions at a fuel cell test station, showed strongly increased degradation towards the anode outlet region, where hydrogen gas supply was decreased. This gives evidence, that fuel starvation is the dominant driving force for the degradation of both stacks. To quantify different degradation patterns, an image threshold analysis was introduced. A correlation of different quantified degradation patterns being typical for fuel starvation degradation, showed that the quantified ratio of MPL adhering to the catalyst layer can be used as a fast indicator for fuel starvation degradation. Thus the analysis time was strongly decreased. With the help of the fast indicator method, the degradation distribution was investigated as a function of the cell position within the two full size stacks. Inhomogeneities in the gas supply within stack two were suggested to be the reason for the increased degradation in the second half of the stack. In addition, self-reinforcing effects due to the mutual dependence of water accumulation and fuel starvation were presumed to promote degradation at different stack positions. For further clarification, the obtained degradation distribution within the stack could be correlated to a detailed simulation of the gas supply within the stack in future works.

Finally, a focus was put on Pt depositions on top of the CCL. The Pt deposition was found to consist of elemental Pt and Pt-O₂. It was especially found in regions close to geometric displacements of the catalyst coated membrane or at the location of MPL defects like holes or cracks. These regions suffered from severe carbon corrosion. The extend of carbon corrosion was found to decrease towards the center of these geometric displacements. A degradation mechanism for the formation of linear and circular Pt depositions on top of the cathode catalyst layer, which were not reported in literature yet, was formulated. In brief, voids between MPL and catalyst layer are suggested to be the starting point of the Pt deposition. A potential rise according to the reverse current mechanism is suggested to lead to Pt dissolution in water filled voids. After the resupply of hydrogen and the corresponding

decrease of the potential, the dissolved Pt deposits preferentially at the edges of the water filled voids. This might be both due to an increased cathode potential in the center of the void due to high in-plane electron resistance of the degraded catalyst coated membrane and an increased Pt ion concentration at the edges of the water filled voids. Model experiments of MEAs of the same material system including relative humidity and potential cycling did not show Pt deposition. This gives evidence, that especially water accumulation at the interface of microporous layer and catalyst coated membrane, which was difficult to implement during the model potential cycles is important for the mechanism to work. Future works could focus on model experiments ensuring the accumulation of water in voids at the interface of microporous layer and catalyst coated membrane to finally prove the mechanism. This could be achieved by using GDLs with decreased wettability properties e.g. by a previous aging of the GDLs in hydrogen peroxide or by the inclusion of periods of excess water production during the model experiment. To reduce the analysis time, future work could also draw attention to the automation of the introduced method to indicate the distribution of fuel starvation degradation on stack level. For instance, an automatic imaging and image analysis of different MEAs in combination with a database, correlating the occurrence and extend of different degradation phenomena to the position on the MEA and to the cell numbering within the stack would highly increase analysis efficiency. Additionally, the obtained results could directly be compared to in situ and operando electrochemical characterizations of the fuel cell single cells and stacks and could be included in an automatically created analysis report.

In conclusion, the work demonstrated the importance of the development and the adoption of methods for the analysis of automotive PEMFC and PEMFC stacks. In addition the relevance of revealing the life-time limiting degradation phenomena for an improved fuel cell development were shown.

List of publications

Obermaier M., Bandarenka A. S. & Lohri-Tymozhynsky C., A comprehensive physical impedance model of polymer electrolyte fuel cell cathodes in oxygen-free atmosphere. *Scientific reports* **8**, 1-9 (2018).

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Obermaier M., Jozwiak K., Rauber M., Bauer A. & Scheu C., Comparative study of pinhole detection methods for automotive fuel cell degradation analysis. *Journal of Power Sources* **488**, 229405 (2021).

Obermaier M., Bauer A., Dalkilic M., Rauber M. & Scheu C., Gas Diffusion Layer Wettability Determination by Cyclic Voltammetry for Automotive Fuel Cells. *Fuel Cells* **21**, 221-233 (2021).

Obermaier M., Degradation Analysis of a PEMFCs of an automotive full size stack. 23rd EFCF Conference 2019 “Low-Temperature Fuel Cells, Electrolyzers, H₂-Processing Forum”, Lucerne, Switzerland.

Lochner T., Hallitzky L., Perchthaler M., Obermaier M., Sabawa J., Enz S. & Bandarenka A. S., Local degradation effects in automotive size membrane electrode assemblies under realistic operating conditions. *Applied Energy* **260**, 114291 (2020).

Du F., Dao T. A., Bauer A., Obermaier M., Schmidt T. J., Orfanidi, A., Understanding the performance losses from carbon corrosion experiments in PEMFCs: “Invasiveness” of in situ characterizations. *to be submitted*

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