

FRAUNHOFER-INSTITUT FÜR SOLARE ENERGIESYSTEME

Dietmar Gerteisen

Investigation of dominant loss mechanisms in low-temperature polymer electrolyte membrane fuel cells



FRAUNHOFER VERLAG

Fraunhofer Institute for Solar Energy Systems ISE

Investigation of dominant loss mechanisms in low-temperature polymer electrolyte membrane fuel cells

Dietmar Gerteisen

Contact: Fraunhofer Institute for Solar Energy Systems ISE Heidenhofstraße 2 79110 Freiburg Phone +49 (0) 761/4588-5150 Fax +49 (0) 761/4588-9342 E-Mail info@ise.fraunhofer.de URL www.ise.fraunhofer.de

Bibliographic information published by Die Deutsche Bibliothek

Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliografic data is available in the Internet at http://dnb.d-nb.de. ISBN: 978-3-8396-0192-1

D 325

Zugl.: Konstanz, Univ., Diss., 2009

Printing and Bindery: Mediendienstleistungen des Fraunhofer-Informationszentrum Raum und Bau IRB, Stuttgart

Printed on acid-free and chlorine-free bleached paper.

© by FRAUNHOFER VERLAG, 2010

Fraunhofer Information-Centre for Regional Planning and Building Construction IRB P.O. Box 80 04 69, D-70504 Stuttgart Nobelstrasse 12, D-70569 Stuttgart Phone +49 (0) 711 970-2500 Fax +49 (0) 711 970-2508 E-Mail verlag@fraunhofer.de URL http://verlag.fraunhofer.de

All rights reserved; no part of this publication may be translated, reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the written permission of the publisher.

Many of the designations used by manufacturers and sellers to distinguish their products are claimed as trademarks. The quotation of those designations in whatever way does not imply the conclusion that the use of those designations is legal without the consent of the owner of the trademark.

Investigation of dominant loss mechanisms in low-temperature polymer electrolyte membrane fuel cells

DISSERTATION

zur Erlangung des akademischen Grades des Doktors der Naturwissenschaften (Dr. rer. nat.) an der Universität Konstanz Fakultät für Physik

> vorgelegt von DIETMAR GERTEISEN

angefertigt am Fraunhofer-Institut für Solare Energiesysteme ISE Freiburg im Breisgau

Tag der mündlichen Prüfung: 23. Juli 2009 Referent: Referentin:

Prof. Dr. Gerhard Willeke Prof. Dr. Elke Scheer

Zusammenfassung

Diese Arbeit befasst sich mit der Analyse der dominierenden Verlustmechanismen in der Direkt-Methanol-Brennstoffzelle (DMFC) und der mit Wasserstoff betriebenen Polymer-Elektrolyt-Membran-Brennstoffzelle (PEFC) mittels experimenteller Charakterisierung und mathematischer Modellierung. Aufgrund der unterschiedlichen Brennstoffe, welche in den beiden Brennstoffzellentypen Verwendung finden, sind deren leistungsbestimmende Verlustmechanismen unterschiedlicher Natur.

Alle in dieser Arbeit verwendeten in-situ Charakterisierungstechniken basieren auf einer neuartigen Testzelle mit integrierten Referenzelektroden, welche wegen der technisch schwierigen Umsetzung bislang nicht standardmäßig in der Brennstoffzellenforschung eingesetzt wird. Im ersten Teil der Arbeit wird ein neues Konzept zur Umsetzung einer Referenzelektrodenanordnung in der Brennstoffzelle mit Hilfe der Laserablation vorgestellt. Ein Laserstrahl wird zur Verdampfung einer kleinen Aussparung der Elektrodenfläche auf der Membranelektrodeneinheit (MEA) genutzt, um die somit entstehende Referenzelektrode von der Arbeits-/Gegenelektrode zu isolieren. Diese Methode erlaubt eine beidseitig simultane Ablation der Elektroden (Anode/ Kathode) zur elektrischen Isolierung, da die Membran für den Laserstrahl transparent ist. Dadurch kann eine glatte Elektroden-Misalignment) realisiert werden. Es wurde eine Testzelle entwickelt, welche zusammen mit der ablatierten MEA die Separierung der Gesamtzellverluste in Kathoden-, Anoden- und Membranüberspannung sowohl in PEFCs als auch DMFCs ermöglicht.

Die Minderung des Kathodenpotentials in der DMFC aufgrund von Mischpotentialbildung infolge von Methanolcrossover kann durch die Verwendung eines selektiven Kathodenkatalysators für die Sauerstoffreduktionsreaktion (ORR) verhindert werden. Die Methanoltoleranz eines mit Selen modifizierten Ruthenium-basierten Katalysators (RuSe_x), wurde mithilfe von Polarisationskurvenmessung, elektrochemischer Impedanzspektroskopie und Stromabschaltmessungen (CI) unter realen Brennstoffzellenbedingungen untersucht. Die ORR-Selektivität des RuSe_x-Katalysators konnte indirekt über CI-Messungen nachgewiesen werden, doch zeigt RuSe_x eindeutig eine geringere katalytische Aktivität als ein Standard Platinkatalysator. Mit Hilfe der Referenzelektrodenkonfiguration konnte ein ausgeprägtes Unterschwingverhalten der Relaxationskurve der Anodenpolarisation bei CI-Messungen beobachtet werden, das bislang in der Literatur nicht diskutiert wurde. Zur Interpretation dieses Phänomens wurde ein eindimensionales, zeitabhängiges DMFC-Modell mit detailliertem Reaktionsmechanismus entwickelt. Im Unterschied zu den bislang veröffentlichten Modellen wurde angenommen, dass Sauerstoff durch die Membran permeieren kann, was eine parasitäre ORR auf der Anode zur Folge hat. Die Simulationen zeigen, dass die komplexe Kopplung zwischen dem bifunktionalen Mechanismus der Methanoloxidation, der Oberflächenbedeckung von Platin durch Kohlenstoffmonoxid und der parasitären ORR für den zeitlichen Verlauf des Anodenpotentials nach CI verantwortlich ist. Die Simulationen zeigen auch, dass die geringe Offenklemmenspannung einer DMFC großteils aus der hohen Anodenüberspannung resultieren und nicht von dem verminderten Kathodenpotential.

Um einen tieferen Einblick in den komplexen Wasserhaushalt einer PEFCs zu geben, wurde die Methode der inversen Modellierung angewandt. Es wurde ein eindimensionales, mehrphasiges, dynamisches PEFC-Modell entwickelt, welches räumlich die Gasdiffusionsschicht, Kathodenkatalysatorschicht und die Membran beschreibt. Die Struktur der porösen Elektrode wurde durch einen Agglomeratansatz abgebildet, mit der Annahme von Wasserfilmbildung in Gegenwart von flüssigem Wasser. Um den Effekt der Ionomeraustrocknung als auch der Flutung poröser Medien zu erfassen, wurde das Wasser in drei Phasen modelliert: dampfförmig, flüssig und im Ionomer gelöst. Die Anode wurde durch eine räumlich reduzierte Grenzfläche als Cauchy-Randbedingung modelliert, welche dem funktionalen Zusammenhang der Einlassgasfeuchte und dem Ionomerwassergehalt Rechnung trägt. Motiviert durch ESEM Aufnahmen von mikroskopischen Wassertropfen auf GDL-Fasern und deren Kontaktwinkel wurde eine irreduzible Sättigung eingeführt. Basierend auf der Annahme eines stetigen Kapillardrucks zwischen Katalysatorschicht und Gasdiffusionsschicht wurde ein Sättigungssprung an der Grenzfläche modelliert. Das Modell ist bei unterschiedlichen Feuchtebedingungen an dynamischen Strom-Spannungskennlinien validiert, welche alle ein ausgeprägtes Hystereseverhalten im Bereich der Massentransportlimitierung zeigen. Das zeitliche Verhalten des Sättigungsprofils zeigt deutlich einen unzureichenden Austrag von flüssigem Wasser, was zu Porenflutung und somit zu einer Sauerstofftransportlimitierung im Bereich großer Stromdichten führt. Simulierte Stromantworten auf Spannungssprünge (Chronoamperometrie) wurden mit Messdaten verglichen und analysiert.

Zur Verbesserung des Wassertransports in flüssiger Phase wird in dieser Arbeit eine maßgeschneiderte GDL vorgestellt, welche den flüssigen Wassertransport von den Elektroden zum Gaskanal verbessert, und somit veringerte Massentransportverluste für Sauerstoff durch die porösen Medien aufweist. Die GDL wurde per Laserperforation im Hinblick auf die Gasverteilerstruktur systematisch modifiziert. Die perforierte GDL wurde mittels SEM charakterisiert. Das Verhalten der Zellleistung mit der eingebauten laserbehandelten GDL wurde in der Testzelle mit Referenzelektrodenanordnung mittels Voltammetrie und Chronoamperometrie bei unterschiedlichen Einlassgasfeuchten untersucht und mit Daten von Messungen mit einer nicht-modifizierten GDL verglichen. In allen Fällen kann aus den Kathodenüberspannungen auf eine verringerte Porenflutung zurückgeschlossen werden, was zu erhöhten Grenzstromdichten führt. Stromantworten von chronoamperometrischen Messungen zeigen eine

Verbesserung der Dynamik und Leistungsdichte der mit perforierter GDL bestückten Zelle. Die Laserperforationstechnik von GDLs wurde von einer Einzelzelle auf einen Brennstoffzellenstack für portable Anwendungen übertragen. Die experimentellen Ergebnisse zeigen auch hier anhand einer erhöhten Leistungsdichte und Stabilität des Stacks bei mittlerer und hoher Stromdichte einen verbesserten Wassertransport in den perforierten GDLs.

Abstract

This thesis deals with the analysis of dominant loss mechanisms in direct methanol fuel cells (DMFC) and hydrogen fed polymer electrolyte membrane fuel cells (PEFC) by means of experimental characterization and modeling work. Due to different fuels used in these two fuel cell types, the dominant loss mechanisms are different in their nature.

All in-situ characterization techniques that are used in this work are based on a novel test fuel cell with embedded reference electrodes, which up to now is not a standard setup in fuel cell research due to its sophisticated technical implementation. The first part of this work presents a new concept for realizing a reference electrode configuration in a polymer electrolyte membrane fuel cell by means of laser ablation. The laser beam is used to evaporate a small gap into the electrode surface of a catalyst coated membrane (CCM) to isolate the reference electrode from the working/counter electrode (WE/CE). This method enables the simultaneous ablation of the electrodes on both sides of the CCM because the membrane is transparent for the laser beam. Therefore, a smooth electrode edge without electrode misalignment of the WE to CE can be realized. A test fuel cell was constructed which enables, together with the ablated CCM, the separation of the total cell losses during operation into the cathode, anode and membrane overpotentials in PEFC as well as in DMFC mode.

The undesired deterioration of the cathode potential of a DMFC due to mixed potential formation caused by methanol crossover can be avoided by using an oxygen reduction reaction (ORR) selective cathode catalyst. The methanol tolerance of a selenium-modified ruthenium-based catalyst ($RuSe_x$) was investigated under real fuel cell conditions by polarization curves, electrochemical impedance spectroscopy (EIS) and current interrupt measurements (CI). The ORR-selectivity of this catalyst is indirectly proven by CI. The catalytic activity of $RuSe_x$ is much lower than a standard platinum catalyst. By means of the reference electrode configuration a pronounced undershoot of the relaxation curve of the anode potential is observed which has not been discussed in the literature so far.

For the interpretation of this phenomenon a one-dimensional, time-dependent DMFC model was developed which describes a detailed reaction mechanism. Deviant from the published models, oxygen crossover through the membrane and consequently a resulting parasitic ORR on the anode was assumed. Simulation results show that the complex coupling between the bi-functional mechanism of the methanol oxidation reaction on PtRu, the surface coverage of carbon monoxide on Pt and the parasitic ORR are responsible for the characteristics of the anode potential after CI. In addition,

the simulations reveal that the low open circuit voltage of a DMFC results mainly from high anode overpotentials and not from the deteriorated cathode potential.

To provide deeper insight into the complex water management of PEFCs, the method of inverse modeling is applied. A one-dimensional, multi-phase, transient PEFC model including gas diffusion layer (GDL), cathode catalyst layer and membrane is developed. The electrode is assumed to consist of a network of dispersed Pt/C forming spherically shaped agglomerated zones that are filled with electrolyte. In the presence of liquid water the agglomerates get covered by a water film. Water is modeled in all three phases: vapor, liquid and dissolved in the ionomer to capture the effect of dehydration of the ionomer as well as flooding of the porous media. The anode is modeled as a spatially reduced interface, implemented as Cauchy-type boundary condition, that accounts for a functional dependancy of the inlet gas humidity and the ionomer water content. Motivated by ESEM images of contact angles of microscopic water droplets on GDL fibers, the feature of immobile saturation is introduced. A step change of the saturation between the catalyst layer and the gas diffusion layer is modeled based on the assumption of a continuous capillary pressure at the interface. The model is validated against voltammetry experiments under various humidification conditions which all show hysteresis effects in the mass transport limited region. The transient saturation profiles clearly show that insufficient liquid water removal causes pore flooding, which is responsible for the oxygen mass transport limitation at high current density values. The simulated and measured current responses from chronoamperometry experiments are compared and analyzed.

In this work, a novel method to customize gas diffusion layers is presented that enhances liquid water transport from the electrode to the gas channels and therefore lowers mass transport losses of oxygen through the porous media. The GDL is systematically modified by laser-perforation with respect to the flow field design and characterized by SEM images. The performance of the laser-treated GDL was investigated in the novel test fuel cell with a reference electrode by voltammetry and chronoamperometry measurements and compared to corresponding data with a nonmodified GDL. Voltammetry experiments with different humidification levels of the inlet gases were conducted. In all cases, the cathode overpotential with the perforated GDL clearly shows reduced saturation which can be seen in a lower overpotential in the region limited by mass transport resulting in a higher limiting current density. The investigated current response of the chronoamperometry measurements shows a better dynamic and overall performance of the test cell with the perforated GDL. The laser-perforation technique of GDLs was transferred from the small test cell to a fuel cell stack for portable applications. The experimental results reveal that the perforation of the cathode GDLs improves the water transport in the porous media and thus the performance as well as the stability of the operating stack in the medium and high current density range.

Acknowledgements

Bedanken möchte ich mich in meiner Muttersprache, da ich mich zumindest auf dieser Seite der Arbeit nicht in dem engen Korsett meines bescheidenen Englisch-Vokabulars bewegen will.

Zuvorderst gilt mein Dank Prof. Dr. Gerhard Willeke für das in mich gesetzte Vertrauen, dass mir bei der Umsetzung dieser Arbeit entgegengebracht wurde und die Übernahme des ersten Gutachtens.

Prof. Dr. Elke Scheer danke ich für die freundliche Übernahme des Zweitreferats.

Meinem Abteilungsleiter Dr. Christopher Hebling will ich ganz besonders danken, da ich bei ihm vollstes Vertrauen genoß, was mir großen Freiraum in meiner Arbeit ließ. In einer ganz besonders schwierigen Zeit, abseits der täglichen Arbeit, hat mir Dr. Christopher Hebling durch sein Gegenkommen sehr geholfen.

Dr. Jürgen Schumacher hat mich überzeugt, in der Abteilung ENT meine Doktorarbeit zu schreiben und mir wichtige Tipps für das Doktorandenleben am ISE mit auf den Weg gegeben.

Für die Entwicklung der Testzelle profitierte ich sehr von dem Wissen von Dr. Alex Hakenjos. Er stand mir bei experimentellen Fragestellungen stets mit Rat und Tat zur Seite.

Zum Thema Wasserhaushalt hatte ich unzählige Gespräche mit Dr. Christoph Ziegler, welche letztendlich in einem komplexen mehrphasen PEFC-Modell fruchteten.

Bedanken möchte ich mich auch bei allen Mitautoren unserer gemeinsamen Veröffentlichungen: Dr. Christoph Ziegler, Tim Heilmann, Dr. Alex Hakenjos, Dr. Jürgen Schumacher, Dr. Michael Oszcipok, Robert Alink, Marc Walter, Steffen Eccarius.

Nicht vergessen will ich das Engagement und die Unterstützung von Marco Meyer, Michael Kornhaas and Christian Sadeler, deren Arbeit aus zeitlichen Gründen leider noch nicht in einer Publikation mündeten, aber sicherlich noch geschehen wird.

In einer Danksagung sollten auch nie die Kollegen fehlen, welche mit ihrer »Frohnatur«

für eine gute Arbeitsatmosphäre sorgen. Wollte ich nun all diejenigen aufzählen, so bräuchte ich noch mindestens die nächste Seite dafür. Deshalb beschränke ich mich an dieser Stelle (*hey Leute, ihr wart alle Spitze!*) auf Timo Kurz und Alex Hakenjos, die die letzten vier Jahre die Stimmung in unserm Büro hoch hielten.

Last but not least, einen ganz großen Dank an meine Freundin Melanie und an meine Familie. Diese Arbeit will ich meinem kleinen Kämpfer Mika widmen.

List of Abbreviations

ACL BP CCL CCM CE CI CV DMFC EIS FRA GDL HFR MOR MOR OCV PEFC PEMFC PEMFC PEMFC RE RHE RUSex WE	anode catalyst layer bipolar plate cathode catalyst layer catalyst coated membrane counter electrode current interrupt measurement cyclic voltammetry direct methanol fuel cell electrochemical impedance spectroscopy environmental scanning electron microscope frequency response analyzer gas diffusion layer high frequency resistance hydrogen oxidation reaction membrane electrode assembly micro porous layer methanol oxidation reaction open circuit voltage oxygen reduction reaction oxidant hydrogen fed polymer electrolyte membrane fuel cell polymer electrolyte membrane fuel cell platinum polytetrafluoroethylene reference electrode reductive relative humidity reversible hydrogen electrode selenium-modified ruthenium-based catalyst ruthenium scanning electron microscope working electrone
WE	working electrode

WTC water transport channel

List of Symbols

<i>a</i>	water activity
<i>b</i>	Tafel slope
<i>c</i>	concentration
C	heat capacity
C_{DL}	double layer capacity
<i>d</i>	water film thickness
<i>D</i>	diffusion coefficient
EW	equivalent weight
<i>F</i>	Faraday constant
<i>g</i>	molar free energy, lateral interaction parameter
\tilde{h}_{ql}	heat of vaporation/condensation
\check{H}	Henry constant
<i>i</i>	current density
<i>i</i> ₀	exchange current density
j	flux
j_{gen}^a	current generation per agglomerate
<i>k</i>	rate constant
K	permeability
L	layer thickness
<i>n</i>	number of transferred electrons
<i>p</i>	pressure
<i>q</i>	source/sink term
R	ideal gas constant
R_a	mean agglomerate radius
R_{Ω}	specific resistance
<i>s</i>	saturation
T	temperature
<i>U</i>	voltage
<i>V</i>	flow rate
Ζ	impedance
α	symmetry factor
α_{drag}	electro-osmotic drag coefficient

β	symmetry factor
Γ	active site density
$\Delta^{\#}G$	electrochemical free energy of activation
$\Delta s \dots$	molar entropy of reaction
η	overpotential
κ	thermal conductivity
λ	water content
Λ	agglomerate density
μ	liquid water viscosity
ν	molar volume, stoichiometry
ρ	density
σ	conductivity, surface tension
ε	volume fraction
Φ^e	potential of the electron conductor
Φ^p	potential of the proton conductor
$\Delta \Phi$	Galvanie potential
$\Delta\Phi^0$	reversible electrode potential
Ξ	geometry factor
θ	surface coverage, contact angle
Ω	transfer coefficient

Contents

Zu	Isam	menfassung	I
Ak	ostra	ct	V
Ac	cknov	vledgements	VII
Li	st of	Abbreviations	IX
Li	st of	Symbols	XI
1	Intro 1.1 1.2 1.3	oduction Background Motivation and Objectives Outline of this Thesis	1 1 2 3
2	Fun 2.1 2.2	damentals of a Polymer Electrolyte Membrane Fuel CellPEM Fuel Cell Components, their Properties and Functions2.1.1Bipolar Plate (BL)2.1.2Gas Diffusion Layer (GDL)2.1.3Catalyst Layer (CL)2.1.4Polymer Membrane2.2.1Butler-Volmer Equation2.2.2Reversible Electrode Potential2.2.3PEM Fuel Cell Loss Mechanism	5 6 7 7 8 9 10 13 14
3	Cha 3.1 3.2 3.3 3.4 3.5 3.6	racterization techniques Cathode and Anode Polarization Curve Potential Sweep Technique Electrochemical Impedance Spectroscopy Current interrupt method Chronoamperometry Imaging technique by Environmental Scapping Electron Microscopo	19 19 20 20 22 23 23

4	Dev 4.1 4.2 4.3 4.4 4.5	Development of a Fuel Cell with Reference Electrodes24.1 The Need and Challenge of Reference Electrodes24.2 Laser Ablation Technique24.3 Test Cell Design24.4 Proof of Concept34.5 Summarized achievements3		
5	Rea 5.1 5.2	ction Kinetics in a Direct Methanol Fuel CellProblem of Methanol Crossover and Mixed Potential	35 36 36 37 43 45 45 45 47 57 57 72 72	
6	Wata 6.1 6.2 6.3 6.4	er Management in Polymer Electrolyte Membrane Fuel CellMotivation and Literature Overview	79 . 79 . 81 . 86 . 89 . 92 . 112 . 113 . 124 . 126 . 130 . 130 . 132 . 134 . 142	
7	Sum	nmary of Results and Conclusion	151	
Bi	bliog	Iraphy	168	
Αυ	ithor [*]	's publications	169	



Chapter 1

Introduction

1.1 Background

A fuel cell is an electrochemical energy converter that produces electricity by a direct conversion of chemical energy within a redox reaction. The invention of fuel cells by Sir W.R. Grove and C.F. Schönbein dates back over a hundred years, but up to now fuel cell systems have not achieved a real technical breakthrough. Even though fuel cells are highly praised as clean energy converters with high efficiency, they have not yet really entered the market. So the question is raised "when" will they?

From the ecological point of view there is a strongly increasing demand for more efficient, non-polluting energy technologies. Fuel cells could be one of the answers because they have a substantial range of applications: stationary power generation systems, fuel cell powered vehicles and battery replacement devices.

Legislative initiatives such as the imposed strict requirements of carbon dioxide emissions for new cars by the countries of the European Union have forced the industries to look for new environmentally-friendly power sources. In contrast to combustion engines, the efficiency of fuel cells does not depend on their size. Thus the application of fuel cells in the range of milliwatts to several hundred watts, e.g. battery replacement devices, is also justified and is seen as the »first market« for fuel cells because of less stringent demands on system costs, even though impact on the energy economy is not large.

Different types of fuel cells exist and are classified by the operating temperature, the electrolyte and the fuel/oxidant used. This work addresses low-temperature polymer electrolyte membrane fuel cells (PEMFCs) for portable applications. As the name implies, this fuel cell type uses a proton-conducting polymer membrane as electrolyte and operates below the boiling point of water. Oxygen, usually from air, is used as oxidant on the cathode side. The anode is typically fed with hydrogen or with methanol, whereas ethanol as fuel has attracted much interest in recent years.

Image in chapter headings: William Grove's prototype fuel cell [Philos. Mag., Ser. 3, 14:127, 1839]

1.2 Motivation and Objectives

Hydrogen PEM (PEFC) and direct methanol (DMFC) fuel cell systems using air as oxidant are the most suitable for portable applications because of the low operating temperature, the carbon dioxide tolerance of the electrolyte, the high power density and the high energy conversion efficiency. In this market, fuel cells have to be competitive with batteries by having longer operating time and faster re-filling. Thus, the recent research and development targets are to increase performance, reliability and long-term stability while reducing the costs at the same time.

The investigation of loss mechanisms during operation of low-temperature PEM fuel cells such as DMFCs and PEFCs is a challenging task due to the following aspects: (a) Several processes that are highly coupled to each other are involved in the current generation, beginning with the reactant feed, through to the redox reactions, and the product removal; (b) Electrochemical reactions typically show non-linear characteristics on the applied voltage with complex reaction pathways; (c) The cell consists of several layers of different materials with different properties and length scales. For the most part their interface conditions are not well understood; (d) The fuel cell operates in two-phase flow regime; (e) Without disturbing the fuel cell operation by additional measurement devices, only the current-voltage characteristics can be drawn on for analyzing the loss mechanisms. This strongly limits the informative value. All of the mentioned aspects highlight the need for a tight coupling among experimental characterization and inverse modeling to improve the knowledge of the occurring processes and their interactions for increasing fuel cell efficiency.

The aim of this thesis is to improve the understanding of the present processes inside certain fuel cell components, their interfacial conditions and their complex mutual couplings which determine the performance and reliability. Therefore, dynamic characterization techniques are applied for getting answers on specific questions in the field of

reaction mechanism in a DMFC and

▷ two-phase transport in a PEFC.

In both fields the experiments are supported by modeling and simulation work for data interpretation. The obtained findings on the investigated cell level can be transferred to the stack level for improving fuel cell systems.

<u>Reaction mechanism in a DMFC:</u> A DMFC system is an attractive power source because of the high energy density of methanol, its availability and the possibility of rapid re-filling. The latter advantage results from the fact that methanol is a liquid fuel, which in turn, would lead to a relatively simple installation of a fuel infrastructure. To realize a real competitor to a battery or even to a methanol-reforming system combined with a PEFC, the power density and fuel utilization have to be increased. Therefore, a solution has to be found for one of the main performance losses of DMFCs, namely the fuel crossover through the membrane. The permeated methanol oxidizes on the cathode electrode leading to a lowered fuel efficiency and cell voltage. This problem could be avoided by identifying methanol-tolerant cathode catalysts that only catalyze the desired oxygen reduction reaction (ORR) but not the parasitic methanol oxidation reaction on the cathode side. The investigation of a promising ORR-selective catalyst based on ruthenium modified with selenium ($RuSe_x$) is one topic of this thesis. Since this catalyst is free of platinum, which is a very expensive noble metal, a cost reduction could be achieved by using $RuSe_x$.

<u>Water management in a PEFC:</u> The faster kinetics of the hydrogen oxidation compared to the methanol oxidation in conjunction with insignificant hydrogen crossover results in a much higher power density of the PEFC. One challenge of a PEFC system is to avoid the dehydration of the polymer membrane to ensure a proper protonic conductivity which forces the operating temperature below 100°C. This temperature limit dictates the operation of the fuel cell in the range where water also exists in liquid phase. Liquid water in the gas diffusion media and electrode can cause mass transport limitations of the reactants, especially at high current densities. Thus, water accumulation has to be avoided. The impact and transport of liquid water in the porous media, its coupling with the protonic conductivity of the membrane and kinetics are discussed in the second part of this work. The aim is to provide a better water management strategy and improved component design for an enhanced fuel cell performance and reliability by obtaining a better understanding of the complex interaction of water with other processes occurring within the fuel cell.

1.3 Outline of this Thesis

Chapter 2 provides a theoretical background to the fundamentals of a PEM fuel cell. All relevant fuel cell components, their properties and functions are discussed. A brief description of the basic principles of the electrochemistry in a PEM fuel cell is given. In Chapter 3 the applied characterization techniques used in this thesis are illustrated in a compact form. The development of a novel fuel cell with embedded reference electrode is presented in Chapter 4. A proof of concept of the laser ablation technique for isolating reference electrodes from a catalyst coated membrane is given. By means of this new developed test fuel cell the complex kinetics of a DMFC anode can get separated from the cathode processes, presented in Chapter 5. The measured dynamic behavior of the anode polarization is analyzed by a newly developed mathematical model that accounts for mixed potential formation and catalyst poisoning. Chapter 6 highlights the problem of water management in a PEFC. By means of dynamic measurements and imaging techniques the two phase flow in porous media is investigated, supported by a sophisticated multi-phase model. The improved understanding of the liquid water transport leads to a new GDL design, tested in single cell and stack experiments. Chapter 7 concludes this work.



Chapter 2

Fundamentals of a Polymer Electrolyte Membrane Fuel Cell

PEM fuel cells use a proton conducting polymer membrane as electrolyte. The membrane is squeezed between two porous electrodes (catalyst layers). The electrodes consist of a network of carbon supported catalyst for the electron transport (solid matrix), partly filled with ionomer for the proton transport. This network together with the reactants form a three-phase boundary where the reaction takes place. The unit of anode catalyst layer (ACL), membrane and cathode catalyst layer (CCL) is called membrane-electrode assembly (MEA)¹. The MEA is sandwiched between porous, electrically conductive gas diffusion layers (GDLs), typically made out of carbon cloth or carbon paper. The GDL provides a good lateral delivery of the reactants to the CL and removal of products towards the channel of the flow plates, which form the outer layers of a single cell. Single cells are connected in series to a fuel cell stack, that makes the anode flow plate with structured channels on one side to the cathode flow plate with structured channels on the other side. From the electrical point of view, this plate is on the one hand the "positive" cathode and on the other hand the "negative" anode and therefore called bipolar plate (BP).

A schematic diagram of the fuel cell configuration and basic operating principles of a hydrogen PEM fuel cell (PEFC) and a direct methanol fuel cell (DMFC) are shown in Fig. 2.1.

A short overview about the fundamentals of a PEM fuel cell is given in the following.

¹Since the catalyst layers are often brought onto the GDL and then hot-pressed with the membrane (5-layer MEA), the 3-layer structure of directly prepared CLs on the membrane is often called catalyst coated membrane (CCM).



Figure 2.1: Schematic of a PEM fuel cell. The cathode and anode reactions are given for a hydrogen PEFC and a DMFC. At high current density or high liquid water saturation of the GDL the shading of the catalyst layer by the rib area causes mass transport limitation, here illustrated for the cathode side.

2.1 PEM Fuel Cell Components, their Properties and Functions

2.1.1 Bipolar Plate (BL)

The outer layer of a fuel cell is the current collector, or bipolar plate, for the case of a cell in a stack. As the name implies, the bipolar plate carries the electrons from the anode of a cell to the cathode of the adjacent cell. Additionally, a flow channel structure is embedded in the bipolar plate to deliver oxygen and fuel, respectively, over the cell area. Also, produced liquid water gets removed by the gas stream in the channels. By means of an elaborated flow field design, the appearance of inhomogeneities in reactant concentrations, humidity and temperature within the cell area can be reduced to a certain degree. Gas velocity as well as pressure loss in the flow channel strongly impact liquid water removal in the channel itself and in the subjacent GDL by gas shortening. The bipolar plates give the fuel cell mechanical stability and therefore assure for homogeneous contact pressure within the cell area. The bipolar plates are made out of metal or graphite compound. The material has to be gas tight, so that in a stack no reactants can permeate from the anode to the adjacent cathode or vice versa.

2.1.2 Gas Diffusion Layer (GDL)

The gas diffusion layer acts as gas diffuser and as electron carrier. In Fig. 2.1 it can be seen that large areas of the catalyst layer would be covered by the ribs of the flow field if no GDL is attached. This would lead to blocking of reactants to the catalyst layer under the ribs and therefore to huge dissipation of active area. With a GDL of sufficient thickness, reactants can flow by diffusion or convection, depending on the flow field design, to the shadowed area under the ribs. A second functionality of the GDL is to provide the electron pathway from the catalyst layer to the bipolar plates or vice versa. The GDL is typically made out of carbon cloth or carbon paper, impregnated by polytetrafluoroethylene (PTFE) to increase the hydrophobicity. A non-wetting surface of the GDL fibers is essential for a proper liquid water transport from the catalyst layer to the gas channel. The GDL also provides mechanical support for the flexible MEA, especially under the channel region.

2.1.3 Catalyst Layer (CL)

The heart of a fuel cell is the catalyst layer where the chemical energy of the reactants is converted into electrical energy. The catalyst layer forms a very complex structure and provides several functions: (1) the CL should provide a large active area (three-phase boundary) to minimize the activation overpotential for a given current density; (2) a catalyst is needed to improve the kinetics; (3) a sufficient reactant and educt pathway should be available. All three requirements should be met, provided that low costs are achieved. Therefore, a technical gas diffusion electrode for fuel cell applications is a highly porous structure of dispersed carbon supported catalyst, generally platinum-based. The carbon network is partially filled with ionomer, acting as binder in the layered structure and providing proton pathway. The porous CL with a thickness of generally $10 - 20 \,\mu m$ increases the active area for several orders of magnitude with regard to the geometrical area of length×width, which results in high current density values. A SEM image of a typical catalyst layer is shown in Fig. 2.2.

The CL shows mixed wettabilities, because the carbon support has a non-wetting surface, whereas the ionomer is strongly hydrophilic. For insufficient liquid water removal, the liquid water can cover the active sites, clog the void space and therefore hinders gas diffusion, which lowers the electrode performance.

Depending on the fuel, the CL can suffer from catalyst poisoning. For example, a small amount of carbon monoxide (CO) in the hydrogen stream, which is the case for reformat gas, or as intermediate species in the methanol oxidation reaction in DMFC application would lead to strong bonded CO on the catalyst sites, where the latter becomes inactive. This phenomenon is called catalyst poisoning.





2.1.4 Polymer Membrane

The membrane of a PEM fuel cell acts as separator of the anode and cathode compartment and as proton conducting electrolyte. The most well known polymer membrane is Nafion[®] (DuPont[™]), against which others are judged. The molecular structure based on polytetrafluoroethylene (PTFE), sulphonated by adding a side chain of sulphonic acid HSO_3 (see Fig. 2.3(a)). The HSO_3 group is ionically bonded (SO_3^-) on the PTFE backbone, and therefore called an ionomer. The presence of SO_3^- and H^+ ions leads to highly hydrophilic clusters within a generally hydrophobic structure. The hydrophilic regions can adsorb a large quantity of water due to interaction of water, having a dipole character, with the SO_3^- group. Within these hydrated regions the H^+ ions are relatively weakly bonded on the side chains, which leads Nafion[®] to a proton conductive material. The proton conductivity is a strong function of its hydration level [1], shown in Fig. 2.3(b) where the conductivity of Nafion[®] at different temperatures is plotted against the relative humidity of the environment in which the membrane is exposed. Nafion[®] exhibits high chemical and thermal stability, and is stable against chemical attack in strong bases, strong oxidizing and reducing environments at temperatures up to 125° C.

The separation of the reactants by the polymer membrane is sufficient in case of a hydrogen PEM fuel cell (PEFC), where the gas crossover reduces the open circuit potential at most about 200 mV. Problematical is the use of liquid methanol as fuel. Due to the similar physical/chemical properties of methanol and water, the uptake and permeation of methanol through the membrane is as high as for water, which results in strong performance losses due to mixed-potential formation. To prevent this problem, new membrane materials have to be developed which do not need the uptake of water for a good ionic conductivity and therefore can be of hydrophobic nature. This would inhibit the methanol diffusion through the membrane. A second alternative to prevent mixed potential on the electrode is the development of selective catalyst for





Figure 2.3: (a) Molecular structure of Nafion[®]. (b) Conductivity of Nafion[®] as a function of the relative humidity for three different temperatures, according to Springer et al [1].

2.2 Basic Principle of Electrochemistry in a PEM Fuel Cell

The principle of a PEM fuel cell based on redox reactions (electron transfer reactions) that are spatially separated by the electrolyte membrane. The catalyst layer donating electrons is defined as the anode and the cathode is the electron acceptor. A redox reaction of a half cell (cathode or anode) can be written as

$$\operatorname{Red} \leftrightarrow \operatorname{Ox} + n e^{-},$$
 (2.1)

where *Red* is the reductive and *Ox* is the oxidant. The number of electrons transferred between the electron conductor and the involved species in the redox reaction is denoted by n. The double-headed arrow, used in the redox equation, shows that the process is allowed in both directions. By applying a certain electrode potential this redox reaction can be forced towards an oxidation reaction or a reduction reaction. The relation is derived in the following subsection yielding the fundamental equation of electrochemistry, the Butler-Volmer equation.

2.2.1 Butler-Volmer Equation

The interfacial charge transfer flux at the electrode j^i depends on the rate constant k^i and the concentration c_i of the electroactive species at the site of electron transfer

$$j^i = \pm F \, k^i \, c_j \, . \tag{2.2}$$

The subscript j stands for the reductive and oxidant, respectively and the superscript i stands for oxidation and reduction, respectively. By convention [2], the charge transfer flux for the oxidation reaction is a positive quantity, whereas the charge transfer flux for the reduction reaction is defined as negative. F denotes the Faraday constant. The net charge flux at the phase boundary is the sum of the partial currents



(a) An activation barrier has to be overcome following the reaction path from reactant and product state, whereby the maxima of the free energy in between is called activated complex. (b) A catalyst modified the potential energy surface in such a way that the energy barrier is reduced.

Figure 2.4: The potential energy surface determines the reaction path from the initial to the final state.

$$j = j^{Ox} + j^{Red} = F(k^{Ox} c_{Red} - k^{Red} c_{Ox}).$$
 (2.3)

It is an experimental fact that most rate constants vary with temperature T in the form of an Arrhenius equation

$$k^{i} = B^{i} \exp\left(-\frac{\Delta^{\#}G^{i}(\Delta\Phi)}{RT}\right) , \qquad (2.4)$$

where B^i is a constant in unit of $(m s^{-1})$, R the ideal gas constant and $\Delta^{\#}G^i$ the energy barrier that has to be overcome for the reaction. The idea of this energy barrier based on the activated complex theory, also known as transition state theory, illustrated in Fig. 2.4(a). As the reaction takes place, the molecules/atoms of the reactants have to change their position, their orientation, and have to desolvate and adsorb on the metal, etc. All these complex processes are expressed in terms of a multidimensional potential energy surface along generalized coordinates. The initial state corresponds to the reactant structure, the final state is the configuration of the product. Both states have to be local minima on the energy surface to remain as significant lifetimes. The reaction path connects two minima. The change in internal energy passing over an intermediate maximum (activated complex) is called the activation energy.

Figure 2.4(b) shows an example of a modified energy surface by the introduction of a catalyst, that changes the reaction path via an intermediate state and therefore reduces the height of the activation barrier.

In electrochemical reactions the activation energy is typically a function of the applied potential difference (electrode potential) between the potential of the solid matrix Φ^e and the potential of the proton conductor (electrolyte) Φ^p and therefore called the electrochemical free energy of activation $\Delta^{\#}G^i(\Delta\Phi)$, where

$$\Delta \Phi = \Phi^e - \Phi^p . \tag{2.5}$$

Inserting Eq. 2.4 into Eq. 2.3 yields

$$j = F B^{Ox} c_{\text{Red}} \exp\left(-\frac{\Delta^{\#} G^{Ox}(\Delta \Phi)}{RT}\right) - F B^{\text{Red}} c_{Ox} \exp\left(-\frac{\Delta^{\#} G^{\text{Red}}(\Delta \Phi)}{RT}\right) .$$
(2.6)

Equilibrium of the redox reaction is given for a net charge transfer of zero (j = 0). Depending on B^i and c_j , equilibrium is achieved for an electrode potential of $\Delta \Phi = \Delta \Phi^0$, which is called the reversible electrode potential. At reversible electrode potential the partial interfacial charge transfer are equal and defined as **exchange current density** i_0

$$i_0 = F B^{o_x} c_{\text{Red}} \exp\left(-\frac{\Delta^\# G^{o_x}(\Delta\Phi^0)}{RT}\right) = F B^{\text{Red}} c_{o_x} \exp\left(-\frac{\Delta^\# G^{\text{Red}}(\Delta\Phi^0)}{RT}\right) .$$
(2.7)

As a first approximation, a linear dependence of the free energy of activation $\Delta^{\#}G^{i}(\Delta\Phi)$ on the applied potential difference can be assumed

$$\Delta^{\#}G^{i}(\Delta\Phi) = \Delta^{\#}G^{i}(\Delta\Phi^{0}) + \beta^{i}nF(\Delta\Phi - \Delta\Phi^{0}), \qquad (2.8)$$

where the symmetry factors β^i describes the fraction of the change of free energy of



Figure 2.5: Free energy of activation diagram as function of the reaction coordinate. *Red* and *Ox* denotes the reductive and oxidant respectively, abbreviations are introduced for $\Delta^{\#}G^{i} = \Delta^{\#}G^{i}(\Delta\Phi)$, $\Delta^{\#}G^{i}_{0} = \Delta^{\#}G^{i}(\Delta\Phi^{0})$ and $\eta = \Delta\Phi - \Delta\Phi^{0}$.

activation to the total energy change $(nF(\Delta\Phi - \Delta\Phi^0))$ (see Fig. 2.5). The symmetry factors are assumed to be constants, taking values between 0 and 1. Substitution of Eqs. 2.8 into Eq. 2.6, whereas $\beta^{\text{Red}} = \alpha$ and $\beta^{\text{Ox}} = -(1 - \alpha)$, yields to the fundamental equation of electrode kinetics, the **Butler-Volmer equation**

$$j = FB^{o_{x}}c_{\text{Red}}\exp\left(-\frac{\Delta^{\#}G^{o_{x}}(\Delta\Phi^{0})}{RT}\right)\exp\left(\frac{(1-\alpha)nF(\Delta\Phi-\Delta\Phi^{0})}{RT}\right)$$
$$-FB^{\text{Red}}c_{o_{x}}\exp\left(-\frac{\Delta^{\#}G^{\text{Red}}(\Delta\Phi^{0})}{RT}\right)\exp\left(-\frac{\alpha nF(\Delta\Phi-\Delta\Phi^{0})}{RT}\right)$$
$$= i_{0}\left(\exp\left(\frac{(1-\alpha)nF(\Delta\Phi-\Delta\Phi^{0})}{RT}\right) - \exp\left(-\frac{\alpha nF(\Delta\Phi-\Delta\Phi^{0})}{RT}\right)\right)$$
$$\Rightarrow j = i_{0}\left(\exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) - \exp\left(-\frac{\alpha nF\eta}{RT}\right)\right), \qquad (2.9)$$

12

where the deviation between the applied electrode potential and the equilibrium (reversible) potential is called **overpotential**, sometimes also referred to as overvoltage²

$$\eta = \Delta \Phi - \Delta \Phi^0 . \tag{2.10}$$

2.2.2 Reversible Electrode Potential

After knowing the characteristic of the net charge flux with applied electrode potential, the reversible electrode potential is of note. The maximum energy that can be used from a redox reaction like Eq. 2.1 at constant pressure p and constant temperature T is given by the change of the molar free energy of the products and educts

$$\Delta g(T,p) = g_{\text{product}}(T,p) - g_{\text{educt}}(T,p) .$$
(2.11)

The electric energy W_{el} of *n* electrons passing the electrode of a Galvani potential of $\Delta \Phi$, which is given by $\Delta g(T, p)$, can be described as

$$W_{el} = \Delta g(T, p) = -nF\Delta\Phi .$$
(2.12)

Solving Eq. 2.12 for $\Delta \Phi$ yields the reversible electrode potential

$$\Delta \Phi^0 = \frac{-\Delta g(T, p)}{n F} . \tag{2.13}$$

The electrode potential is not a direct measurable quantity, since the protonic potential Φ^p has to be known. Therefore a second electrode in contact with the same electrolyte (same Φ^p), acting as a reference with a fixed potential, is necessary to measure the desired electrode potential. By definition, the reversible electrode potential of the redox reaction of hydrogen on a platinum surface at standard conditions³ is used as reference and its potential set to 0V

$$H_2 \leftrightarrow 2 H^+ + 2 e^- : \Delta \Phi^0_{H_2} = 0 V.$$
 (2.14)

The cell voltage at open circuit condition (OCV) of a chemical cell (fuel cell, battery) is the difference between the cathode and anode reversible electrode potential

$$\mathsf{OCV} = \Delta \Phi_c^0 - \Delta \Phi_a^0 . \tag{2.15}$$

The relevant electrode potentials (oxygen reduction and methanol oxidation) and the-

²Strictly speaking the overvoltage is the sum of the overpotentials of the two electrodes and the ohmic loss of the cell. In this thesis the term "overpotential" is used for the analysis of a certain electrode, even if ohmic losses are included in the data.

³Standard condition: $T^0 = 25^{\circ}$ C, $p^0 = 1 bar$

	PEFC	DMFC
anode reaction	$H_2 \leftrightarrow 2H^+ + 2e^-$	$CH_3OH + H_2O \leftrightarrow CO_2 + 6H^+ + 6e^-$
$\Delta g_a / k Jmol^{-1}$	0	+9
$\Delta \Phi^0_a / V$	0	0.015
cathode reaction	$\frac{1}{2}O_2 + 2H^+ + 2e^- \leftrightarrow H_2O$	$\frac{3}{2}O_2 + 6H^+ + 6e^- \leftrightarrow 3H_2O$
$\Delta g_c / k Jmol^{-1}$	-237.3	-711.5
$\Delta \Phi_c^0 / V$	1.229	1.229
overall reaction	$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$	$CH_3OH + \frac{2}{3}O_2 \leftrightarrow CO_2 + 2H_2O$
$\Delta g / k Jmol^{-1}$	-237.3	-702.5
OCV/V	1.229	1.214

oretical open circuit voltages for this work are summarized in Table 2.1.

Since the Gibbs free energy is a function of the temperature T and pressure p, the theoretical OCV can be derived to

$$U_{oc}(p_i, ..., T) = U_{oc}(p_i^0, ..., T^0) + \frac{\Delta s}{2F}(T - T^0) - \frac{RT}{2F} \sum_i \nu_i \ln\left(\frac{p_i}{p_i^0}\right) , \qquad (2.16)$$

where Δs is the molar entropy of reaction, p_i the partial pressure of the educts and products respectively, and ν_i the stoichiometry factor (negative defined for educts).

2.2.3 PEM Fuel Cell Loss Mechanism

Activation Overpotential

In electrochemical systems, e.g. the oxygen reduction reaction on the cathode of a fuel cell, it is convenient to consider the limiting behavior of the Butler-Volmer equation (see Eq. 2.9) for large negative overpotential

$$j = -i_0 \exp\left(-\frac{\alpha n F \eta}{RT}\right) \quad \text{for} \quad -\eta \gg \frac{RT}{nF} ,$$
 (2.17)

and in case for a slow oxidation reaction, the limiting behavior for large positive overpotential

$$j = i_0 \exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) \quad \text{for} \quad \eta \gg \frac{RT}{nF}$$
 (2.18)

These relationships are often written in form of the Tafel equation

$$\eta = -\frac{RT\ln(10)}{\alpha nF} \lg \left(\frac{|j|}{i_0}\right) \quad \text{for} \quad -\eta \gg \frac{RT}{nF} ,$$

$$\eta = \frac{RT\ln(10)}{(1-\alpha)nF} \lg \left(\frac{|j|}{i_0}\right) \quad \text{for} \quad \eta \gg \frac{RT}{nF} , \qquad (2.19)$$

where

$$b^{i} = \frac{RT\ln(10)}{\beta^{i}nF} \tag{2.20}$$

is known as **Tafel slope**.

In case of a kinetic controlled reaction the polarization loss of the electrode under load is called activation overpotential $\eta = \eta_{act}$.

Concentration Overpotential

The derivation of the Tafel approximation from the limiting behavior of the Butler-Volmer equation (Eqs. 2.17 and 2.18) was done with the assumption of a constant exchange current density (kinetic controlled), which implies a constant concentration of the educts $c_{0,j}$. In general, a decline in concentration c_j with increasing current occur due to mass transport limitation. To take this into account, Eqs. 2.17 and 2.18 can be written as

$$j = \mp i_0 \frac{c_j}{c_{0,j}} \exp\left(\mp \frac{\beta^i n F \eta}{RT}\right) , \qquad (2.21)$$

$$\eta = \mp \frac{RT \ln(10)}{\beta^{i} nF} \left[\lg \left(\frac{|j|}{i_0} \right) + \lg \left(\frac{c_{0,j}}{c_j} \right) \right] .$$
(2.22)

A comparison of Eq. 2.22 with Eq. 2.19 leads to the expression of the concentration overpotential

$$\eta_{con} = \mp \frac{RT \ln(10)}{\beta^i n F} \lg \left(\frac{c_{0,j}}{c_j}\right) .$$
(2.23)

Reaction Overpotential

The intrinsic redox reaction can be hindered by chemical steps that must occur before the electron transfer reaction and thus determine the reaction rate. Such systems are known as 'preceding chemical reactions'

$$A \leftrightarrow Ox$$
, (2.24)

$$Ox + ne^- \leftrightarrow Red$$
. (2.25)

It is also possible that the product of a redox reaction has to react in a second chemical step to clean the active sites, which is known as 'following chemical reactions'

$$Ox + ne^- \leftrightarrow Red$$
, (2.26)

$$A + Red \leftrightarrow P$$
. (2.27)

If this first (reaction 2.24) and second step (reaction 2.27), respectively, is slow, it would determine the overall reaction rate. For a detail description of such systems, it is referred to Chapter 5, where the problematic is discussed in detail for a operating DMFC. These performance losses can be concluded as reaction overpotential η_r [2, 4].

Ohmic Overvoltage

Due to the finite conductivity of the fuel cell components (current collector, GDLs, CLs and membrane), as well as the non-negligible contact resistances between the layers, ohmic losses at high current densities has a strong attribute on fuel cell losses. These losses are called ohmic overvoltage and can be expressed by Ohm's law

$$\eta_{\Omega} = j R_{\Omega} , \qquad (2.28)$$

where R_{Ω} is the specific resistance in (Ωcm^2) .

Crossover and Mixed Potentials

Due to the finite leak-tightness of the polymer membrane for the electrochemical active species, it is possible that passed oxidant reacts on the anode side and fuel on the cathode side, respectively. This leads to internal parasitic current that suppresses the electrode potential despite a nominal zero charge flux at the external circuit. This phenomenon is called mixed potential and is discussed in detail in Chapter 5.

Cell Voltage Under Load

Summarizing all loss mechanisms the cell voltage under load can be calculated as follows:

$$U_{cell} = \Delta \Phi_c - \Delta \Phi_a - \eta_{\Omega}$$

= $\Delta \Phi_c^0 - \underbrace{\eta_{act,c} - \eta_{con,c} - \eta_{r,c}}_{\text{cathode losses}} - \Delta \Phi_a^0 - \underbrace{\eta_{act,a} - \eta_{con,a} - \eta_{r,a}}_{\text{anode losses}} - \eta_{\Omega} . \quad (2.29)$

Figure 2.6 illustrates the potential distribution along a cross-section of a fuel cell. Ohmic losses due to finite conductivity of the layers are visible by the potential gradients and the contact resistances by the steps between the interfaces. Activation, reaction and concentration overpotentials are integral parts of the reduced Galvani potential in the electrodes $\Delta \Phi_{a/c}$. The cell voltage is the difference between Φ_c^e at the outer surface of the cathode bipolar plate and Φ_a^e on the anode bipolar plate. The protonic potential is not measurable. Its value is determined by the cell current in such a way that the resulting overpotentials on both electrodes generate the same current which in term links the cathodic and anodic electronic potential.



Figure 2.6: Schematic potential distribution across the layers of a PEM fuel cell. On the cathode side the ohmic overvoltage due to contact resistance between the layers are labeled, on the anode side the ohmic losses due to finite conductivity are marked.

For analyzing the different losses within a fuel cell several characterization techniques are necessary which are discussed in the next chapter.


Chapter 3

Characterization techniques

In this chapter a short overview of the applied characterization techniques and measuring devices used in the thesis is given. Depending on the question that is addressed every experimental method has advantages or disadvantages. These are briefly discussed.

3.1 Cathode and Anode Polarization Curve

The most applied characterization technique for fuel cells is the measurement of steady-state voltage-current curves. Every operating point is held as long as equilibrium is reached and finally logged. This measurement technique is adequate if only the overall cell performance is of interest. The voltage-current curve can not provide any information about the dynamic behavior of the cell since the recorded data are measured at steady-state. If not only the overall cell performance but rather the electrode performance is of interest, it is essential to distinguish between the anode and cathode polarization by means of a reference electrode. Embedding a reference electrode in a fuel cell is not state-of-the-art. It involves several technical difficulties and challenges, which have to be overcome in order to avoid systematic errors. A detailed discussion about this issue is given Chapter 4, where a realization of a test fuel cell with integrated reference electrodes is presented.

In this work a Solartron 1286 is used as electrochemical interface which measures the current for an applied cell voltage (potentiostatic mode) and the voltage for an applied current load (galvanostatic mode), respectively. The distinct potential differences between working, counter and reference electrodes are measured with a datalogger from Agilent (HP 34970A).

3.2 Potential Sweep Technique

The potential sweep technique is a dynamic experiment where the cell voltage is swept between two values U_1 and U_2 at a known sweep rate ν , before halting the potential sweep. It is also possible to cycle the cell voltage between the two values, i.e. on reaching the cell voltage U_2 , the sweep is reversed. The entire cycled sweep can be repeated several times. The choice of the start and end voltage as well as the sweep rate determines which process can be identified. The potential sweep technique (also called cyclic voltammetry CV) is well known in half cell measurements used to investigate e.g. the active surface area, reaction kinetics and intermediates. In this thesis, the technique is applied to investigate membrane hydration/dehydration as well as flooding phenomena. Both processes cause a unsteady behavior of the cell performance, implying that steady-state measurements or electrochemical impedance spectroscopy can not be performed in the desired region.

3.3 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) is a powerful characterization tool to investigate electrochemical systems. The system performance is generally governed by a number of coupled processes each proceeding at a different rate, e.g. electrode reactions, double-layer charging, charge migration or diffusion processes. In the direct current case (DC), an overall resistance of the fuel cell can be assigned by the slope of the voltage-current curve. This resistance is the sum of all limiting processes occurring at the measured operation point. By means of EIS, these losses can be distinguished in case of specifiable relaxation time constants of the investigated processes.

EIS can be performed on every well-defined operating point along the voltage-current curve, as long as this point is stable during the measuring time. A schematic is shown in Fig. 3.1. A small harmonic excitation signal at a particular frequency ($i[t] = i^* \cos[\omega t]$, when operated in galvanostatic mode or $u[t] = u^* \cos[\omega t]$, when operated in potentiostatic control mode) is added to the DC operating point. A frequency response analyzer (FRA) determines the impedance of the cell ($Z[\omega]$) at the given frequency by the measured AC voltage across the cell and the AC current passing through the cell

$$Z[\omega] = \frac{\int_0^\infty u^* \cos[\omega t]}{\int_0^\infty i^* \cos[\omega t + \varphi]} .$$
(3.1)

When measuring only the oscillating potential drop across the electrode to be analyzed with respect to a reference electrode, the measured impedance contains only the losses of this electrode.

EIS bases on linear response theory, which means the system gives a linear response



Figure 3.1: Schematic of EIS measurement: a small harmonic excitation signal at a particular frequency is added to the DC operating point and the response is measured. The amplitude and phase of the response at different frequencies gives information about the excited process.



Figure 3.2: A typical Nyquist plot of an impedance spectrum. Characteristics are the intercept at high frequency (R_{Ω}) and the charge transfer loop (R_{CT}) .

to an excitation. Due to the fact that electrochemical systems are highly non-linear, the excitation has to be small to avoid distortion by higher harmonics, in this case about $10 \, mV$ [5]. For characterizing the concurrent processes in a fuel cell the impedance is measured for a number of frequencies in the range of interest.

One possible representation of an impedance spectrum is the Nyquist plot shown in Fig. 3.2. The impedance data are plotted in the complex plane (real and imaginary part of the impedance) for every measured frequency. The intercept with the abscissa at high frequencies (commonly about $10 \, kHz$ for fuel cells) is the sum of all ohmic resistances. Since the resistance of the electron conductive phases (BP, GDL, carbon in CL) and the contact resistance are small compared to the ionic conductive ionomer, the measured high frequency resistance (HFR) is primarily the membrane resistance. Thus, the HFR is a good quantity for the hydration level of the membrane. Depending on the dominating processes different loops are visible in the Nyquist plot. The first loop (high frequencies), which is always present in fuel cells, addresses the charge transfer process of the redox reaction. For thick electrodes with low conductivity a linear branch with an angle of 45° is also visible in the high frequency range due to the combined process of proton migration and double-layer charging [6]. Several loops in the low frequency range can appear in case of slow processes determining the current generation, which do not have to be essentially of capacitive nature. Diffusion processes and flooding events behave like a capacitance, while ad-/desorption processes of educts or intermediates generally show inductive behavior.

A Solartron 1250 is used as FRA for the impedance measurements in combination with a Solartron 1286 electrochemical interface.

3.4 Current interrupt method

The current interrupt method is usually used for determining the ohmic cell resistance. First, the cell is operated at a certain current as long as the cell reaches steady-state conditions. Then the load is abruptly switched off and the cell voltage is recorded. Instantaneously, the voltage increases to about the ohmic drop $(i \cdot R_{\Omega})$, therefore the resistance R_{Ω} can be extracted. The following voltage relaxation can be used to investigate double-layer charging and diffusion processes. Again, in case of polarized anode and cathode electrodes, a reference electrode is essential to separate the time-dependent voltage curve into the anode and cathode polarization relaxation curve. A KEPCO[®] load (BOP 20-5M) is used as electrochemical interface. The relaxation curves are recorded by a digital oscilloscope (TEKTRONIX[®] TDS 3014B).

3.5 Chronoamperometry

Chronoamperometry is a potential step experiment, where the cell voltage is stepped instantaneously from a value of U_1 to a value of U_2 , and the current-time response is recorded. Depending of the sample rate of the data acquisition, relaxation processes within the cell in the range of μs to min can be examined. Chronoamperometry is a strong tool for highlighting flooding effects which appear in a time-scale of seconds. The data are recorded by a fast measuring board from National InstrumentsTM (NI cRIO-9215).

3.6 Imaging technique by Environmental Scanning Electron Microscope (ESEM)

An ESEM is a scanning electron microscope that permits the imaging of wet systems without any prior special preparation by operating in low vacuum. The electron beam of a conventional SEM accumulates negative charge on insulating specimens and thus creates an electrical potential, which deflects the electron beam from the scanned point. To avoid this charging artifacts in the image, the specimen have to be coated by a conductive layer. An ESEM takes advantage of the gas molecules in the low vacuum of the specimen chamber. Some gas gets ionized by the electron beam and discharges on the specimen surface. Therefore, with the applied technique it is not necessary to make non-conductive samples conductive. Thus, the surface properties remain unchanged and dynamic measurements of mobile surfaces such as droplet growth and movement can be performed.

An ESEM (FEI Quanta[™] 400) was used for ex-situ examination of the wettability of fuel cell components such as gas diffusion layers. The condensation of the water can be forced by increasing the pressure in the sample chamber or by cooling down the sample with an integrated cryostatic sample holder (Emott HK102HT) until a saturated atmosphere is reached and water droplets grow on the GDL fibers. A detailed description of the ESEM and the cooling process is given in Alink et al. [7].



Chapter 4

Development of a Fuel Cell with Reference Electrodes

Analyzing loss mechanisms in a PEM fuel cell in operando is an ambitious task due to the complex coupling of different processes occurring in different layers. A large step is done if it would be possible to implement a reference electrode in a fuel cell, that is able to serve for steady state as well as for dynamic measurements. A solution of this technical problem is presented in this chapter, showing the preparation technique and a proof of concept.

4.1 The Need and Challenge of Reference Electrodes

It is difficult to separate the anode and cathode polarization losses under real fuel cell conditions, especially in DMFC mode. For a hydrogen PEFC the anode can be assumed as non-polarizable for low and medium current densities and therefore all voltage losses can more or less be attributed to the cathode and ohmic losses. In a DMFC, the reaction rate of the methanol oxidation reaction is comparable with the oxygen reduction reaction (ORR) on the cathode side. Hence, the measured overall voltage loss of the fuel cell comprise the anode as well as to the cathode polarization. To make matters worse, a DMFC suffers from reactant crossover through the membrane, causing high mixed potentials. This fact in turn makes half-cell measurements of the respective electrode under investigation senselessly for a direct comparison under real fuel cell conditions. For analyzing the loss mechanisms in a DMFC the influence of methanol on the cathode performance and the coupling of the electrodes, respectively, is essential and can only be made by having a reference electrode (RE) configuration in the cell.

Recently, several papers have been published about reference electrodes in fuel cells. Some of these publications focus on modeling the influence of the position of the reference electrode [8, 9, 10]. It was found that a misalignment of the working and counter electrodes in the range of a few microns (depending on the membrane thickness) results in a highly asymmetric potential distribution near the electrode edges in the membrane, causing an unknown potential shift of the reference electrode towards the overhanging electrode. Additionally, this shift depends on the current applied to the cell, which leads to significant errors in electrochemical impedance spectroscopy (EIS) measurements.

For illustration of this problem, Fig. 4.1(a-c) shows the simulated protonic potential within the membrane of a fuel cell. In all three cases a potential drop of $400 \, mV$ across the membrane is set by the boundary conditions. In Fig. 4.1(a), perfect aligned electrodes and homogeneous conductivity for the protons throughout the membrane thickness L is assumed. These assumptions lead to a symmetric potential distribution in the membrane that gives a stable and well known protonic reference potential at the middle of the membrane (the half overall ohmic potential loss of 200 mV) for the reference electrode measurements. In the case of an electrode misalignment (Fig. 4.1(b)) an asymmetric potential distribution is present, leading to an unknown protonic reference potential that is far away from the half potential loss of $200 \, mV$ (in this arrangement $\Phi^p = 100 \, mV$). In this case the shift of the protonic reference potential depends on the drawn current density. The case of an inhomogeneous conductivity throughout the membrane is investigated in Fig. 4.1(c). Since the conductivity of the membrane is a strong function of the water content [1], which in turn is a function of the operating conditions such as gas humidity (see Fig. 2.3 on page 9), current density, used fuel, etc., this problem has to be discussed although it can not be avoided in most cases. The simulation also shows a strong asymmetric distribution that would effect the reference electrode measurements. Corrective action can be done by measuring the high frequency resistance (HFR) of the electrodes in relation to the reference electrodes $(Z_{c \rightarrow ref}, Z_{a \rightarrow ref})$, that allows to recalculate the potential shift of the protonic reference potential. This procedure is applied in all electrode polarization curves in this thesis.

As just explained, an exact electrode alignment is necessary for the reference electrode to contact a current-independent potential in the center of the membrane. This makes the preparation of a catalyst coated membrane (CCM) including a reference electrode very difficult and hardly feasible because the tolerance is in the range of a few microns. Thus, few publications can be found presenting a reference electrode configuration in a fuel cell [8, 11, 12] to determine polarization data of the cathode and anode. Due to the higher requirements on the reference electrodes for EIS measurements only one paper presents impedance spectra [13].

In this chapter a new concept for a state-of-the-art prepared CCM (or MEA) is presented that will be treated by laser ablation to produce a reference electrode on the same membrane. This technique allows electrical isolation of the electrodes by evaporation of a small part of the catalyst layer with a laser beam, resulting in a small isolation gap. The segmented part can be used as a reference electrode.



Figure 4.1: Simulated potential distribution in a membrane with (a) perfect aligned electrodes and homogeneous conductivity; (b) misaligned electrode configuration and homogeneous conductivity; (c) perfect aligned electrodes and a linear increasing conductivity from bottom to top.

4.2 Laser Ablation Technique

Starting from a customary prepared CCM the catalyst layer is removed at the boundary of the working (WE) and counter electrode (CE), respectively, and the reference electrodes (RE) by laser ablation. Thus, a CCM with electrically isolated catalyst layer regions is obtained (Fig. 4.2).

The CCM laser ablation was carried out with a Nd:YAG-LASER ('Rofin Sinar Laser GmbH') operating at a wavelength in the near infrared of 1064 nm. Due to the high adsorption values of the carbon supported catalyst and the fact that the membrane is transparent to the laser beam, the catalyst layers are very effectively removed on both sides simultaneously without damaging the membrane. The laser beam burns a gap of about $30 \,\mu m$ in the catalyst layers. To ensure sufficient isolation between WE/CE and RE and to avoid edge effects of the potential distribution in the membrane to the reference potential the laser ablation was repeated 10 times with a offset of $30 \,\mu m$. An isolation gap of $300 \,\mu m$ was reached (Fig. 4.2(a)). By means of this technique sharp electrode edges with an exact alignment of the cathode and anode catalyst layers (Fig. 4.2(b)) can be realized which would not be possible with conventional electrode preparation methods. A detailed discussion of MEA laser ablation can be found in Schmitz et al. [14].



(a) Top view: An isolation gap of about $300\,\mu m$ with sharp electrode edges is achieved.



(b) Cross-section view: The electrode edges are exactly on top of each other.



4.3 Test Cell Design

The CCM treated by laser ablation is sandwiched between two gas diffusion layers with micro porous layers. The current collectors are made of titanium. Figure 4.3(a) shows the single channel flow field milled in the current collector with a geometric





Figure 4.3: (a) Disassembled test fuel cell with a geometric catalyst area of $1 cm^2$. (b) The contact to the reference electrode is realized by a wound gold wire at the gas/fuel inlet of the cell.

area of $1 \, cm^2$. The cell temperature is controlled by water channels inside the titanium block connected to a cryostat (Fisherbrand FBC 720). The cell temperature is measured by a thermocouple 1 mm above the flow channel in the titanium plate on the cathode side. The contacts to the laser ablated reference electrodes are realized by gold wires positioned on the gas/fuel inlet of the cell, approximately 2 mm from the working/counter electrodes (Fig. 4.3(b)). The gold wire is wound like a spring to achieve a good and stable contact to the electrodes even when the membrane is swelling or shrinking. Note that the reference electrode on the anode side and cathode side is in the same reactant compartment as the WE and CE, respectively. Therefore, the potential of the reference electrode on the cathode side is not that of a reversible hydrogen electrode (RHE) but the equilibrium potential of the ORR. The potential of the reference electrode on the anode side is the equilibrium potential of the methanol oxidation reaction (MOR) in DMFC mode or the RHE in PEFC mode. The advantage of this configuration is that the reference electrodes are located as close as possible to the WE/CE because no sealing is necessary to separate different reactant compartments. Disadvantageous is that the absolute values of the potentials (referred to the normal hydrogen electrode (NHE)) can not be measured and furthermore poisoning of the reference electrodes can impact the potential measurements. This problem is discussed in the next section.

Figure 4.4 schematically shows an ablated CCM. The five measurable voltages (V1-V5) and impedances (Z1-Z5) are illustrated. The equipotential lines of an ideal symmetric electrode alignment and homogeneous conductivity of the membrane are pictured. Hence, the electronic potentials of the REs (Φ_{ra}^e, Φ_{rc}^e) are connected via the phase boundary to the protonic potential level in the middle of the membrane.

In this work, the voltage loss under load has been separated into cathode overpotential, anode overpotential and ohmic loss as follows:



Figure 4.4: Schematic of an ablated CCM. Five different voltages and impedances are measurable.

• the ohmic loss is calculated by Ohm's law with the measured current density (i_{cell}) and the measured HFR at 10 kHz (Z1)

$$\eta_{\Omega} = i_{cell} \cdot Z1 , \qquad (4.1)$$

where

$$Z1 = Z_{mem} + Z_{contact} \tag{4.2}$$

is the sum of the membrane resistance (Z_{mem}) and the contact resistances $(Z_{contact})$. The electronic losses in the bulk material (current collector, GDL, electrode) are negligible. All further measurable HFRs (Z2 - Z5) are in the same way the sum of the ionomer resistance of the proton pathway and the contact resistances.

the anode overpotential is defined as the potential difference between the anode (current collector) Φ^e_a and the reference potential Φ^e_{ra}, corrected by the ohmic drop between both voltage tabs [15]. This ohmic drop has been taken into account by measuring directly Z5 or by the assumption of a symmetric potential distribution in the membrane and equal contact resistances on the cathode and anode side, which leads approximately to an overpotential correction of the half cell impedance multiplied by the current density

$$\eta_a = \Phi_a^e - \Phi_{ra}^e - i_{cell} \cdot Z5 , \qquad (4.3)$$

$$\approx \Phi_a^e - \Phi_{ra}^e - \frac{1}{2} \cdot i_{cell} \cdot Z1 .$$
(4.4)

• the cathode overpotential is defined as the difference between the cathode (cur-

rent collector) Φ_c^e and the reference potential Φ_{ra}^e with respect to the theoretical open circuit voltage of $1.23 V^1$ in PEFC mode. The data are corrected by the ohmic drop between cathode current collector and the reference electrode, making the same assumptions as for the anode overpotential correction

$$\eta_c = 1.23 - (\Phi_c^e - \Phi_{ra}^e) - i_{cell} \cdot Z2 , \qquad (4.5)$$

$$\approx 1.23 - (\Phi_c^e - \Phi_{ra}^e) - \frac{1}{2} \cdot i_{cell} \cdot Z1$$
 (4.6)

By measuring the voltage between the cathode current collector and the cathode reference electrode Φ_{rc}^{e} it is also possible to monitor the characteristic of the cathode overpotential

$$\eta_c = \Phi_c^e - \Phi_{rc}^e - i_{cell} \cdot Z2 .$$
(4.7)

In doing so the overpotential has a bias to lower values since the potential difference between the reference electrodes are always below the theoretical values. This is extreme in DMFC mode where the electrodes suffers from mixed potential formation.

4.4 Proof of Concept

First, a proof of concept of the laser ablation for isolating reference electrodes from a CCM is given. Figure 4.6(a) shows a voltage-current curve of a DMFC² together with the cathode and anode overpotentials. The operating conditions are listed in the caption. Additionally, the voltage difference between both reference electrodes $(U_{OC,R} = \Phi_{rc}^e - \Phi_{ra}^e)$ is pictured, which shows a stable potential under load of about 610 mV. The cathode overpotential is corrected by the iR-drop whereas the resistance is taken by the HFR_c measured from the cathode (CE) to the cathode reference electrode (see Fig. 4.4). The anode overpotential is also corrected by the iR-drop measured from the anode (WE) to the anode reference electrode (HFR_a). For this operation condition the activation overpotential of the ORR is about twice as large as the overpotential of the MOR. The open circuit voltage is about 605 mV (close to $U_{OC,R}$).

Polarization curves of a CCM³ fed with hydrogen as fuel are depicted in Fig. 4.5(b). The measurements show a higher OCV (875 mV) and a higher limiting current density. The reference potentials are also stable but $U_{OC,R}$ only reaches a value of about

¹In the strict sense this theoretical value is only valid under standard conditions which can not be achieved in operating fuel cells due to several aspects such as mixed potential formation, poisoning effects or temperature gradients.

²A Nafion[®] based CCM (CCM #1) from the Research Center Jülich (IEF-3) was used. Details concerning catalyst loadings are given in Table 5.1 on page 37.

³CCM #2, see Table 5.1 on page 37



(a) Operated with methanol (1M) as fuel, $\dot{V}_{MeOH} = 2 \, ml \, min^{-1}$, $\dot{V}_{O_2} = 12 \, ml \, min^{-1}$, $T_{cell} = 71^{\circ}C$.

(b) Operated with hydrogen as fuel, $\dot{V}_{H_2} = 8 \, ml \, min^{-1}$, $\dot{V}_{O_2} = 12 \, ml \, min^{-1}$, $T_{cell} = 41^{\circ}C$.

Figure 4.5: Measured polarization curve of the cell (U_{cell}) , the OCV between the two reference electrodes $(U_{OC,R})$ and the overpotential of the cathode and anode.

 $820 \, mV$. An explanation for this could be that the reference electrodes have never been under load and therefore the catalyst is not completely activated or is in oxidized state which would cause a lower $U_{OC,R}$. The activation overpotential of the hydrogen oxidation reaction (HOR) is negligible compared to the ORR. The results of the steady state measurements show that oxygen as well as methanol generate a stable reference potential. An isolation gap of $300 \, \mu m$ in case of a Nafion[®] 117 is large enough for the REs not to be influenced by edge effects from the WE/CE.

Figure 4.6(a) shows impedance spectra of CCM #1 at a cell potential of $50 \ mV$ ($T_{cell} = 51^{\circ}C$) using an aqueous methanol solution (1M) as fuel. Both small impedance loops are anode spectra: Z4 is measured versus the cathode reference electrode and Z5 is measured versus the anode reference electrode (see Fig. 4.4). The diameter of the loops are equal, indicating that both reference electrodes are stable for EIS measurements. Z2 and Z3 are the cathode impedance spectra referring to the two different reference electrodes. Their diameters are also the same. The addition of the measured anode and cathode impedance spectra (Z3+Z5) results in the measured total cell impedance. This result is a good proof for time stability of the REs (measuring all 5 spectra one after another needs about 10 minutes).

Figure 4.6(b) shows impedance spectra of CCM #2 at a cell potential of 600 mV ($T_{cell} = 41^{\circ}C$) with hydrogen as fuel. As opposed to the DMFC the anode impedance of a PEFC is small compared to the cathode impedance. The anode impedance shows an inductive behavior in the low frequency range. Explanations for this fact

could be the ad-/desorption process of hydrogen molecules on the active sites or the water dependence of the electrode performance [16, 17].





(a) Impedance spectra at a cell voltage of $50 \, mV$, operated with methanol (1M) as fuel, $\dot{V}_{MeOH} = 2 \, ml \, min^{-1}$, $\dot{V}_{O_2} = 12 \, ml \, min^{-1}$, $T_{cell} = 51^{\circ}C$.

(b) Impedance spectra at a cell voltage of 600 mV, operated with hydrogen as fuel, $\dot{V}_{H_2} = 8 ml min^{-1}$, $\dot{V}_{O_2} = 12 ml min^{-1}$, $T_{cell} = 41^{\circ}C$.

Figure 4.6: Measured impedance spectra of the total cell (Z1), the cathode (Z2, Z3) and the anode (Z4, Z5). The summation of the cathode and anode impedance (Z3+Z5) results in the total cell impedance (Z1) in both cases.

Despite nearly perfect electrode alignment the high frequency resistances of the anode and cathode spectra differ in both DMFC and PEFC measurements. This means that the reference electrodes do not contact the electrolyte potential in the middle of the membrane with a symmetrical potential distribution such as depicted in Fig. 4.1(a). The simulation shows that an inhomogeneous membrane conductivity due to a gradient in the membrane water content results in an asymmetrical potential distribution even with a perfect electrode alignment (Fig. 4.1c). Therefore, HFR_a is smaller than HFR_c in DMFC measurements due to the aqueous methanol solution humidifying the anode side very well. In PEFC measurements it is vice versa due to the higher water content on the cathode side from the product water of the ORR and the electroosmotic drag.

Impedance spectra at different cell potentials indicate a constant ratio of the HFR_{*a*} to HFR_{*c*} in DMFC mode (Fig. 4.7). This means that the asymmetrical potential distribution is not affected by the applied current and therefore does not disturb the EIS measurements.



Figure 4.7: Measured HFRs at different cell voltages. The applied current did not affect the HFRs of the DMFC indicating a stable conductivity distribution within the relatively thick $(178 \ \mu m)$ Nafion[®] membrane.

4.5 Summarized achievements

A new concept for realizing a reference electrode configuration in a polymer electrolyte fuel cell is presented. By means of laser ablation technique a selected part of the electrodes (cathode/anode) of a state-of-the-art CCM was electrically isolated and used as reference electrodes. It was shown that oxygen as well as methanol generate a stable reference potential for both steady-state measurements and dynamic measurements such as electrochemical impedance spectroscopy and current interrupt measurements. The separation of the cathode and anode losses for a PEFC as well as a DMFC is practicable.



Chapter 5

Reaction Kinetics in a Direct Methanol Fuel Cell

5.1 Problem of Methanol Crossover and Mixed Potential

The high energy content of liquid methanol, simple storage and simple refilling make direct methanol fuel cells (DMFC) a promising candidate for portable power applications. However there are several serious technical problems to overcome before they become competitive on the market. The thermodynamic reversible cell potential for the overall cell reaction of a DMFC is 1.21 V at 298 K [18]. However, the open circuit voltage (OCV) is typically only in the range of 600 - 750 mV [19, 20, 21, 22], depending on the operating conditions, membrane type, catalyst and catalyst loading. The question arises »why«?

It is assumed that the relatively high concentration of methanol (compared with gaseous reactants such as oxygen and hydrogen) and the high permeability of the polymer electrolyte membrane combine the possibility of a high flux of methanol to the cathode where it can react with oxygen in an electrochemical reaction. One following consequence is that the electrode on the cathode is always under load even if no external current is drawn from the cell. Thus, the cathode potential is suppressed by the activation overpotential due to the internal parasitic current, quite obvious at OCV. This phenomenon of a deteriorated electrode potential caused by fuel crossover from the anode to the cathode side where methanol is oxidizing on the platinum catalyst, is called mixed potential [23, 24, 25, 26, 22, 19]. Further drawbacks of methanol crossover are the waste of fuel and the poisoning of cathodic electrocatalyst. The blocked Pt-sites by adsorbed intermediates are not available for the desired ORR, therefore the cathodic active surface is reduced leading to higher overpotential under load.

5.2 Methanol Tolerant Catalyst for the ORR in a DMFC

To avoid the oxidation of methanol on the cathode, several methods have been explored. Possibilities are the development of a novel membrane that prevents or at least reduces the permeation of methanol through the membrane [27, 28] or the use of methanol vapor instead of a liquid methanol solution to reduce the amount of dissolved methanol in water at the electrode/membrane interface [29] and therefore the diffusive flux of methanol to the cathode. Another approach to overcome the decrease in cathode performance by methanol crossover is to use a methanol tolerant oxygen reduction electrocatalyst, i.e. an oxygen reduction reaction (ORR) selective catalyst [26, 30, 31, 32, 24]. High methanol tolerance is reported in the literature for nonnoble metal catalysts based on chalcogenides and macrocycles of transition metals or platinum-based binary alloyed catalysts [31]. Investigations of the electrocatalytic activity of such catalysts using rotating disc electrode (RDE) measurements in acidic media show cathode potentials up to 1V [32, 31]. In using such catalysts in a fuel cell, an apparent higher OCV should be measured. Nevertheless, the OCV of technical electrodes with methanol tolerant cathode catalysts in DMFCs does not show such high values. Thus, either the anode potential of the methanol oxidation reaction (MOR) is far above the theoretical value of approx. 20mV as opposed to normal hydrogen electrode [18], or a coupling between the cathode and anode which is not yet completely understood causes this low OCV despite a methanol tolerant catalyst. By means of the new concept of a reference electrode configuration in the test cell presented in Chapter 4, the performance and loss mechanism of a methanol tolerant ruthenium-based catalyst modified with selenium (RuSe_x) was investigated using polarization curves, EIS measurements and current interrupt measurements (CI).

5.2.1 Electrode Preparation and Operating Conditions

Electrode Preparation

The catalyst coated membranes were prepared by scientists from the research center Jülich. For the anode side a PtRu/XC72 catalyst from Johnson Matthey (HiSpec10000) was used. For the cathode side 40w%RuSe_x on 60w%XC72 was used. The catalyst ink was pasted on a decal foil and then hot-pressed on Nafion[®] 117 [33]. The catalyst loadings for the investigated CCMs can be found in Table 5.1. A carbon cloth from E-Tek (thickness $350 \ \mu m$) with a micro porous layer (40%PTFE/60%Vulcan XC72, thickness $80 \ \mu m$) was used as gas diffusion layer for all experiments.

Test Set-up

A SOLARTRON 1286 in combination with a SOLARTRON 1250 frequency response analyzer (FRA) is used for electrochemical measurements. The current and cell po-

	cathode		anode	
No.	catalyst	loading	catalyst	loading
CCM #1	RuSe _x	$0.9 mg cm^{-2}$	Pt/Ru	$2.0 mg cm^{-2}$
CCM #2	RuSe _x	$0.6 mg cm^{-2}$	Pt/Ru	$0.5 mg cm^{-2}$
CCM #3	RuSe _x	$1.26 mg cm^{-2}$	Pt/Ru	$1.9 mg cm^{-2}$
CCM #4	Pt	$1 mg cm^{-2}$	Pt/Ru	$3 mg cm^{-2}$

 Table 5.1: Catalyst loadings of the investigated CCMs.

tential is recorded by the load itself. The cathode overpotential ($\eta_c = \Phi_c^e - \Phi_{rc}^e$), the anode overpotential ($\eta_a = \Phi_a^e - \Phi_{ra}^e$) and the voltage difference of the REs ($U_{OC,R} = \Phi_{rc}^e - \Phi_{ra}^e$) are measured with with a datalogger (HP 34970A). The electrochemical impedance spectra are recorded in the frequency range of $100 \, mHz$ to $10 \, kHz$. The current interrupt measurements are done with a KEPCO load (BOP 20-5M) whereas the potential relaxations are recorded by a digital oscilloscope (TEKTRONIX TDS3014B). The abrupt current interruption is realized by a fast circuit breaker. The gas flow is regulated with gas flow controllers (Bronkhost) and are humidified by passing each gas stream through an externally tempered humidifier. Temperatures of gas lines between humidifier and cell are maintained at 5°C above the humidifier temperature to avoid condensation. A pump (HPLH20/200-PF, Ingenieurbüro CAT) is employed to supply aqueous methanol solution from a reservoir.

5.2.2 Performance of RuSe_x Catalyst

Polarization Curve

Figure 5.1 shows two polarization curves of the CCM #3. First the cell was operated with methanol (1M) before switching to hydrogen as fuel. It is obvious that the hydrogen-driven fuel cell (PEFC) shows much better performance. An increase of the OCV from $610 \, mV$ to $860 \, mV$ and an increase of the peak power density from $16.4 \, mW cm^{-2}$ to $120 \, mW cm^{-2}$ is observed. The huge difference in OCV was actually not expected because the methanol tolerant RuSe_x catalyst should not be sensitive towards methanol permeation. The break-in of OCV is not in agreement with half-cell RDE measurements from the group of Dr. Fiechter from the Hahn-Meitner-Institute [34] who provided the catalyst for the CCMs. A closer look at the polarization curve of the cathode potential for both measurements (Fig. 5.2) shows that the activation overpotentials differ just a little. The cathode overpotential of the methanol-driven cell is slightly higher than that of the PEFC. It is assumed that an additional mass transport limitation in the porous gas diffusion electrode due to the presence of permeated liquid methanol/water solution could cause this difference. The aqueous methanol solution on the anode side results in a high water uptake (up to 22 water molecules



Figure 5.1: Comparison of the performance of the RuSe_x cathode catalyst (CCM #3) between hydrogen ($\dot{V}_{H_2} = 8 \, ml \, min^{-1}$, $T_{cell} = 64^{\circ}C$) and methanol ($\dot{V}_{MeOH} = 2 \, ml \, min^{-1}$, $T_{cell} = 83^{\circ}C$) as fuel. In both cases the oxygen flow rate was $12 \, ml \, min^{-1}$. Changing from hydrogen to methanol shows a drastic decrease of the performance.

per SO_3^- for Nafion[®] [35]). The equilibrium water content on the cathode side with fully humidified air is 14 water molecules per SO_3^- . This results in a capillary pressure driven water flux through the membrane from the anode to the cathode [36, 37]. The ionomer releases water into the porous cathode electrode as long as the capillary pressure of the liquid water in the porous electrode reaches the same value of that in the ionomer. This would lead to a high saturation¹ level of the cathodic porous media (as on the anode side) if there were no water release to the cathodic flow channels. A detailed discussion concerning water management, especially flooding issues in a PEFC is given in Chapter 6.4.

¹The saturation of a porous media is defined as the ratio of the occupied volume by a liquid to the entire pore volume.



Figure 5.2: The steeper increase of the cathode overpotential if methanol is used as fuel could be explained by flooding due to permeated aqueous methanol solution to the cathode causing a limitation for the oxygen diffusion to the active sides.

Electrochemical Impedance Spectroscopy

In Fig. 5.3 the cell impedance spectra of CCM #3 at a current density of $0.033 A cm^{-2}$ in DMFC and PEFC mode is shown. Due to a better membrane humidification the high frequency resistance of the DMFC is slightly lower than that of the PEFC but shows a significantly larger impedance loop. The measured cathode impedance of the DMFC (Fig. 5.4a) differs moderately from that of the PEFC. The loop is slightly enlarged which can be explained by the same effect as discussed for the overpotential curve above: the aqueous methanol solution covers the active sites and finally leads to additional mass transport limitations. A parasitic MOR with strong impact on the cathode can be excluded. A large difference is measured in the anode impedance (Fig. 5.4b). In contrast the impedance of the hydrogen-driven anode is negligible compared to the methanol-driven anode. This comparison shows the slow kinetics of the MOR that has to be improved by developing better catalysts.



Figure 5.3: Measured cell impedance spectra in PEFC ($\dot{V}_{H_2} = 8 \, ml \, min^{-1}$, $T_{cell} = 65^{\circ}C$) and DMFC ($\dot{V}_{MeOH} = 2 \, ml \, min^{-1}$, $T_{cell} = 81^{\circ}C$) mode. In both cases the oxygen flow rate was $12 \, ml \, min^{-1}$.



Figure 5.4: (a) Cathode impedance spectra in PEFC and DMFC mode. With methanol as fuel the loop of the impedance spectrum is a little bit larger than with hydrogen as fuel. (b) The loops of anode impedance spectra are completely different in their size.

Current Interrupt Measurements

Investigations to determine the methanol tolerance of a catalyst are easy to carry out in half cell measurements in liquid electrolyte because the potential of the working electrode is measurable with respect to a reference electrode and the potential of the investigated electrode is not affected by the counter electrode. Under real fuel cell conditions the measurable cell voltage depends on both electrode potentials (WE/CE) influencing each other (e.g. methanol crossover), therefore the potential difference between the cathode and the anode at open circuit is not really a good measure for the methanol tolerance of a catalyst.

One possibility to investigate the methanol tolerance of the cathode catalyst is to measure the cathode exhaust [33]. If there is a large amount of carbon dioxide (CO_2) in the exhaust gas, a high methanol oxidation reaction rate on the cathode can be concluded, since CO_2 is the product of the MOR. A problem of this measurement technique is the diffusion of CO_2 from the anode side through the membrane. Therefore, CO_2 is always present in the cathode gas compartment, which has to be considered in the analysis.

In several publications an overshoot of the cell voltage is measured if there is a sudden load step from a high current to a low current. In most cases the phenomenon is discussed as an interaction between the relaxation of the ORR potential and the methanol crossover building a mixed potential on the cathode side [38, 39, 25]. Thus, in the experiments described here, the current interrupt technique was used to prove the methanol tolerance of the RuSe_x catalyst with the reference electrode configuration. Figure 5.5 shows the cathode potential relaxation of two different CCMs. A current density of $0.1 A cm^{-2}$ was applied before a fast circuit breaker opened the electric circuit and unload the cell. One CCM is prepared with Pt/C (CCM #4) as cathode catalyst, while the other CCM is prepared with RuSe_x/C (CCM #3). Pt/Ru is used as anode catalyst for both CCMs. The curve with the Pt catalyst shows an overshoot behavior of the cathode potential (gray line), while the RuSe_x-based CCM does not show such a behavior (black line). This indicates a high methanol tolerance of the RuSe_x/C catalyst.

By taking a look on the transient cell voltage (Fig.5.6) of the RuSe-based CCM after CI, which would be the only accessible information in case of an absent reference electrode configuration, the conclusion of a methanol-tolerant catalyst could not be drawn by this technique. The cell voltage shows an overshoot behavior in the voltage relaxation. By means of the reference electrode configuration this overshoot of the cell potential can be clearly attributed to an undershoot of the anode potential. This measurement obviously shows the need of a reference electrode configuration.

Presently there are no scientific publications known, which report on monitoring of an anode undershoot relaxation. From the measurements it can be concluded that on the anode side at least two processes with different time constants are taking place and competing with one another. The faster process is responsible for the anode



Figure 5.5: The cathode polarization relaxation curve after current interruption $(0.1 A cm^{-2})$ of a Pt-based electrode shows an overshoot behavior due to methanol crossover that results in a cathodic mixed potential formation. The RuSe_x-based electrode does not show such overshoot behavior, which can be interpreted as a positive evidence of the methanol tolerance of this catalyst. ($\dot{V}_{MeOH,1M} = 2 m l m i n^{-1}$, $\dot{V}_{O_2} = 12 m l m i n^{-1}$, $T_{cell} = 81^{\circ}C$)

potential decrease to low potentials (favorable for fuel cell application), the second process dominates after some seconds (approx. 6s) and forces the anode potential to an adverse high potential.

The undershoot behavior of the anode relaxation curve leads to the conclusion that the anode potential at steady state is at least $100 \ mV$ higher as expected from theory. Unfortunately, this assumption can not be proven with the used reference electrode configuration because the absolute value of the REs are unknown. Here, a hydrogen reference electrode is essential. The increased anode potential consequently results in a low cell voltage even if a methanol tolerant catalyst is used. Figure 5.7 shows the dependence of the anode potential relaxation on the load current and methanol concentration. Starting from a load current of $0.01 \ A \ cm^{-2}$ and $0.04 \ A \ cm^{-2}$ respectively, the anode potential relaxation was measured with two different methanol concentrations ($0.5 \ M$ and $3 \ M$). The curves show clearly that a higher load current results in larger undershoot. The relaxation curves with $0.5 \ M$ methanol solution reach steady state within $30 \ s$. The reason of the undershoot can be poisoning effects of the anode by intermediates such as CH_2OH , CHOH, CHO or CO

described in [29, 25], coupled with a so far not investigated parasitic current on the anode side.

Qualitative investigations of the anodic potential relaxation are made in the next section (5.3) by numerical modeling that gives an explanation for the anode undershoot behavior. To quantify the anode overpotential further fundamental electrochemical investigations and analysis techniques such as e.g. gas chromatography and x-ray adsorption spectroscopy have to be conducted, which was not scope of this work.



Figure 5.6: An undershoot behavior can be measured of the anode potential after current interruption resulting in an overshoot behavior of the cell voltage. (RuSe_x catalyst, $\dot{V}_{MeOH,1M} = 2 \, ml \, min^{-1}$, $\dot{V}_{O_2} = 12 \, ml \, min^{-1}$, $T_{cell} = 81^{\circ}C$).

5.2.3 Remarks to the Experimental Results

The performance of a selenium-modified ruthenium-based (RuSe_x) cathode catalyst was investigated under real fuel cell conditions. Polarization curves and impedance spectra of the RuSe_x catalyst based electrode show comparable cathode losses for both hydrogen and methanol as fuel. In DMFC mode, the missing overshoot behavior of the cathode potential after current interruption indicates the methanol tolerance of the RuSe_x catalyst. Nevertheless, it was found that despite the methanol tolerance of the cathode catalyst there is a large difference in the OCV depending on whether methanol or hydrogen is used as fuel. The relaxation curve of the anode potential shows a strong undershoot behavior (up to $100 \, mV$) which reveals a large capability for the kinetics improvement of the anode. It is assumed that there is a strong



Figure 5.7: Amplitude and relaxation time of the undershoot of the anode potential depends on load current as well as on methanol concentration (RuSe_x catalyst, $\dot{V}_{MeOH,1M} = 2 \, ml \, min^{-1}$, $\dot{V}_{O2} = 12 \, ml \, min^{-1}$, $T_{cell} = 81^{\circ}C$).

influence of *CO* poisoning (or other intermediates) on the anode potential that also causes the lower OCV. A mathematical model presented in the next chapter can give an insight into the dynamic processes of a DMFC and give an explanation of the measured phenomena. Due to the lack of reference electrodes in fuel cells the influence of methanol crossover building a mixed potential (supposedly responsible for the low OCV) is often overestimated in published dynamic DMFC measurements. The explanation for the overshoot behavior of the cell voltage after load change is in most cases completely referred to the methanol crossover which is not true. By means of the reference electrode configuration it can be shown that the high anode potential at steady state has a strong impact on the low cell voltage of a DMFC. Finally, it can be concluded that a reference electrode configuration is necessary in order to distinguish losses of the anode and cathode for examining coupled phenomena, which is not possible in half cell measurements often carried out for DMFC.

5.3 Modeling Catalyst Poisoning and Mixed Potential in a DMFC

5.3.1 Motivation and Literature Overview

The methanol oxidation reaction has been subject of a large number of studies in recent years [40, 41, 42, 43]. Detailed electrochemical analysis revealed a complex reaction mechanism, indicating the MOR as one of the most difficult tasks in the improvement of a direct methanol fuel cell. The slow anode kinetics lead not only to the desired reaction product CO_2 but also form adsorbed CO on the active sites, leading to high activation overpotential for the methanol oxidation on a pure Pt electrode. This indicates that pure platinum is not the best catalyst for fuel cell operation in the range of room temperature to 70°C. CO formed during dissociative adsorption on pure Pt blocks a noticeable fraction of active sites within seconds. At electrode potentials below 0.4 V, Pt is not able to form OH-molecules for the further oxidation of CO to CO_2 , therefore the electrode gets poisoned and the current generation comes to rest. A catalyst for the MOR should be able to dissociate the C - H bond and provide by an catalytic process some O-containing species to form CO_2 .

The presence of water in the anode compartment of a DMFC is not only required for the dilution of the methanol to suppress fuel crossover, it is also needed as oxygen donor for the *CO* oxidation, suggested by Gilman [44]. Unfortunately, below potentials of 0.4 - 0.45 V pure Pt is not able to dissociate water in a sufficient rate to provide *OH*, which leads to high anode overpotential for the formation of *CO*₂. General consensus is found that the oxidation/adsorption of methanol or the removal of *CO* is the rate-determining step depending on the applied potential. Gasteiger et al. [45] suggest that the *CO* oxidation is the rate-determining step in the potential region between 0.4 - 0.7 V. IR spectroscopy indicates that *CO* indeed accumulates on the surface at low potentials, since the water dissociation rate by Pt catalyst is too low.

Despite the problem of strong poisoning by adsorption products, Pt is the best catalyst known for breaking C - H and O - H bonds in alcohol molecules. Therefore, the research of binary and ternary catalysts based on platinum for a further oxidation of the adsorbed CO has been paid a lot of attention. After meeting the first requirement of a high activity towards water dissociation at low potentials, the co-catalyst must also fulfill long-term stability in fuel cell conditions. At present, the most promising anode catalyst is PtRu.

The reason for the enhanced methanol oxidation rate on PtRu can be explained by the so called bi-functional mechanism [46]. The Pt catalyst oxidizes methanol to CO and Ru dissociates water, forming adsorbed OH. Finally, following the Langmuir-Hinshelwood mechanism the adsorbed CO reacts with adsorbed OH to CO_2 , whereby surface diffusion of CO is assumed [47]. Besides the promoter effect of Ru through the supply of OH_{ads} , there is experimental indication of additional effects of Ru on

the overall reaction such as negative potential shift in the dissociative adsorption of methanol and a lowering of the *CO* adsorption energy for the alloy [48, 49].

The problem of methanol crossover can hardly be solved as long as perfluorosulfonic acid membranes such as Nafion[®] are used as separator between anode and cathode compartment. The fact that hydration of protons is required for a proper ionic conductivity and that water is needed for the methanol oxidation to CO_2 , necessitates that water has always to be present in the anode compartment. Water and methanol are interchangeable in the hydration and osmotic process because the free energy of association with protons is approximately the same for both solvents. This in turn leads to high methanol flux through the membrane causing mixed potential on the cathode side.

In the literature, different DMFC models highlighting various physical and electrochemical aspects are published. Shivhare et al. [50] developed a simplified steadystate anode model. The model is focused on the anode kinetics and therefore accounts for the CO catalyst poisoning as well as for the water activation by the bifunctional mechanism. The simulation results show that CO coverage does not play an important role in the loss mechanism of the anode. Ge and Liu [51] developed a 3D model subjected to mass transport processes in the channel, GDL and CL. The reaction kinetics is modeled as a lumped Tafel approach without considering multi-steps reaction and the influence of residues. A cathodic mixed potential is calculated by the assumption of a leak current due to methanol crossover, implemented in the Tafel equation by adding to the external load current. A similar model in 2D is presented by Yang et al. [52]. The steady-state model from Liu and Wang [53] focused on mixed potential and the influence of surface coverages of CO and OH only for the cathode. Mass transport limitations are considered in the two-phase formulation. The anode side is not regarded. The effect of pulsed-current load of a DMFC on the performance is investigated by Vilar et al. [54]. Their dynamic model is reduced to the anode side, subjected to a detailed bi-functional methanol oxidation kinetics. The model predicts an undershoot relaxation that is attributed to a small electrical short-circuit though the membrane. For simplification, the electrodes are not spatially resolved.

The fact of the low OCV of a DMFC measured with a methanol tolerant catalyst and the transient response of the anode potential after current interruption, both presented in the latter chapter, induce a closer look on the anode kinetics and its parasitic processes. In the literature the presented cell-voltage overshoot is mostly attributed to mixed potential on the cathode side. Therefore, the main research activities are focused on preventing methanol crossover and parasitic MOR on the cathode. Less concentration is given on the dynamics of the anode kinetics. It is believed that the bi-functional mechanism of a Pt-Ru alloy catalyst is sufficient for the oxidation of methanol to CO and further to CO_2 by a hydroxyl ion OH but the influence of oxy-

gen crossover to an anode mixed potential has not been investigated so far. In spite of a much lower oxygen flux through the membrane compared to the methanol flux, the resulting parasitic ORR at the anode side can have a strong impact due to the slow anode kinetics, intensified by partially blocked Pt-sites by *CO*.

In the following this phenomena is investigated by a new developed DMFC model.

5.3.2 Model Description

The present model is developed to investigate the coupled reaction mechanism of a DMFC and therein associated voltage losses in the catalyst layers. The model accounts for the crossover of (i) methanol from anode to cathode and (ii) oxygen from cathode to anode. The reactant crossover results in parasitic internal currents which finally are responsible for high overpotentials in both electrodes, so-called mixed potentials, most evident at no-load condition in the open circuit voltage. A simplified and general reaction mechanism for the MOR derived from a more complex mechanism was selected [55, 56], that accounts for the coverage of active sites by intermediate species occurring during the MOR. Additionally, the effect of oxygen crossover to the anode side is implemented, which is a novel approach in DMFC modeling and not yet reported in the appropriate literature.

The model describes a complete five-layer membrane electrode assembly (MEA), with cathode gas diffusion layer (CGDL), cathode catalyst layer (CCL), membrane, anode catalyst layer (ACL) and anode gas diffusion layer (AGDL), as depicted in Fig. 5.8.

In this model performance losses are mainly addressed to electrochemical processes. For simplification, the gas diffusion electrode is modeled as a homogeneous catalyst layer, where details on the electrode morphology, i.e. agglomerate approach [57, 58, 59, 60, 6], are neglected. Although under these assumptions mass transport losses are not correctly represented, the model does not loose its significance because the electrochemical phenomena such as mixed potential and catalyst poisoning are the determining loss mechanism in DMFCs [61].

Since the limiting current density of DMFCs is significantly lower compared to H_2 -PEFCs on a two-phase flow description concerning liquid water in the cathodic porous media and on CO_2 -bubble formation on the anode were passed.

Reaction Mechanism

The model description starts with the assumptions of the basic reaction processes occurring in the electrodes.

Oxygen Reduction Reaction: The desired reaction in the CCL is the oxygen reduction reaction. The simplest description for its kinetics in acidic environment is a



Figure 5.8: Schematic of a five-layer membrane electrode assembly. The solving variables are denoted and their computational domains are marked by white arrows.

four-electron step mechanism after adsorption on an active site

$$O_2 + (\mathsf{Pt}) \xrightarrow[k_{O2,ads}]{k_{O2,ads}} (\mathsf{Pt} - O_2) , \qquad (5.1)$$

$$(\mathsf{Pt} - O_2) + 4 H^+ + 4 e^- \iff 2 H_2 O + (\mathsf{Pt}),$$
 (5.2)

where the reaction is catalyzed by platinum catalyst.

It is assumed that the ORR is not restricted to the CCL. A Nafion[®]-based membrane shows a low but not negligible gas permeability. This leads to the situation that a small amount of dissolved oxygen diffuses through the membrane to the anode side, where it also can be reduced on free Pt-sites following reaction 5.1 - 5.2.

Methanol Oxidation Reaction: It is widely accepted that during methanol oxidation reaction, first methanol adsorbs on a Pt catalyst site and then oxidizes. Unfortunately, methanol does not oxidize to CO_2 in a single step. One intermediate of the reaction is carbon monoxide CO that remains as residue on the catalyst site. The latter is inactive for further reactions as long as the CO-adsorbate blocks the catalyst. This phenomenon is called CO-poisoning. An appreciable blocking by other intermediates such as CH_2OH , CHOH, CHO, acting as catalyst poison, is not reported in the

literature. Thus, the reaction of methanol to CO is assumed as rate-determining step

$$CH_3OH + (\mathsf{Pt}) \xrightarrow[k_{M,ads}]{k_{M,ads}} (\mathsf{Pt} - CH_3OH) ,$$
 (5.3)

$$(\mathsf{Pt} - CH_3OH) \xrightarrow{k_{\mathsf{MOR}}} (\mathsf{Pt} - CO) + 4H^+ + 4e^-.$$
(5.4)

Ruthenium is mostly added to Pt as co-catalyst on the anode side to promote the bi-functional mechanism, proposed by Watanabe and Motoo [62]. Fig. 5.9 gives an illustration of the bi-functional MOR mechanism, described in subsection 5.3.1. It is assumed that the catalytic activity of Pt for the MOR is at least two orders of magnitude higher then Ru. Therefore, the electro-oxidation of methanol on Ru is neglected. A bi-functional catalyst, like Pt-Ru alloy catalyst, enhance the CO oxidation reaction (COOR) [62]. The Ru catalyst activates water molecules to hydroxyl radicals (reaction 5.5), which react with CO adsorbates to carbon dioxide CO_2 (reaction 5.6). Here, it is assumed that water preferentially adsorbs onto Ru-sites

$$H_2O + (\mathsf{Ru}) \xrightarrow[k_{OH,red}]{k_{OH,red}} (\mathsf{Ru} - OH) + H^+ + e^-, \qquad (5.5)$$

and that the adsorbed OH species are mobile enough to reach the Pt-sites where CO become oxidized

$$(\mathsf{Pt} - CO) + (\mathsf{Ru} - OH) \xrightarrow{k_{CO,ox}} CO_2 + H^+ + e^- + (\mathsf{Pt}) + (\mathsf{Ru}) .$$
 (5.6)

Due to the missing Ru catalyst in the cathode CL, reaction 5.5 is not present on the cathode side.

A second possible reaction pathway is the heterogeneous oxidation of CO to CO_2 in case of accessible oxygen. This reaction pathway is often utilized in hydrogen PEFC fed with reformat gas, where CO is present in the range of several *ppm*. In giving a small amount of oxygen into the hydrogen reformat feed stream, the CO-poisoning of the anode catalyst gets significantly reduced (known as oxygen bleeding) by a heterogeneous oxidation reaction [63]. This reaction is also addressed in the model for the CO adsorbate at the Pt-sites

$$2\left(\mathsf{Pt} - CO\right) + O_2 \xrightarrow{k_{\mathsf{bleed}}} 2CO_2 + (2\,\mathsf{Pt}) \ . \tag{5.7}$$

Without assuming this heterogeneous reaction, there is no possibility to clean the Pt catalyst from *CO* on the cathode side, since no Ru catalyst is available to form

OH-species for further oxidation. Consequently, the methanol oxidation on the cathode would poison the active sites by-and-by until no current can be drawn from the cell. Obviously this scenario does not occur in real DMFCs, confirming the assumed reaction pathway 5.7.



Figure 5.9: Bi-functional mechanism of the methanol oxidation reaction on PtRu catalyst: (a) electro-oxidation of methanol to carbon monoxide, (b) water activation forming hydroxyl (*OH*) radicals, (c) electro-oxidation of *CO* by an *OH*-radical.

Governing Equations

The model based on a system of coupled partial differential equations, whereby continuity equations for eight variables have to be solved. The solving variables are oxygen concentration c_{O_2} , methanol concentration c_M , electronic potential Φ^e , protonic potential Φ^p and surface coverages of oxygen Θ_{O_2} , methanol Θ_M , carbon monoxide Θ_{CO} and hydroxyl ions Θ_{OH} .

The concentrations are defined in all five layers, the electronic potential is defined in the electronic conductive regions (CLs and GDLs), the surface coverages are defined in the CLs and the protonic potential is defined in the layers where ionomer is present, namely the CLs and the membrane (denoted by white arrows in Fig. 5.8).

Reaction Rates: The volumetric reaction rates describe the conversion of the reactants and intermediates dependent on their kinetic parameters, coverages and applied overpotentials.

The oxygen reduction reaction can be described by Butler-Volmer kinetics, where only adsorbed oxygen on the Pt-sites, expressed as Θ_{O_2} , takes part in the reaction

$$q_{\text{ORR}} = \gamma_{c,a} \, k_{\text{ORR}} \, e^{\frac{73.2 \cdot 10^3}{R} (\frac{1}{353} - \frac{1}{T})} \, \Theta_{O_2} \left(e^{\frac{\Phi^e - \Phi^p - \Delta \Phi_{\text{ORR}}^0}{b^*_{\text{ORR}}}} - e^{-\frac{\Phi^e - \Phi^p - \Delta \Phi_{\text{ORR}}^0}{b_{\text{ORR}}}} \right) \,. \tag{5.8}$$

The temperature dependent Tafel slope for the ORR is defined as

$$b_{\text{ORR}}^* = \frac{(1 - \alpha_{\text{ORR}}) n_{\text{ORR}} F}{R T} \text{ and } b_{\text{ORR}} = \frac{\alpha_{\text{ORR}} n_{\text{ORR}} F}{R T},$$
 (5.9)

where α_{ORR} is the symmetry factor, n_{ORR} the number of transferred electrons, F the Faraday constant, R the gas constant and T the temperature. Thus the assumed oxygen reduction reaction depends on the reaction constant k_{ORR} , the Tafel slope of the ORR, the reversible potential $\Delta \Phi_{\text{ORR}}^0$ of the ORR, the catalyst loading $\gamma_{c,a}$ and the applied overpotential, determined by Φ^e and Φ^p , which are the potentials in the electronic and ionic conductive phase, respectively.

The reaction constant k_{ORR} as well as all following reaction constants k_i are functions of the catalyst type (CT), catalyst support (CS) and the active surface area (A), which in turn depends on the loading and dispersion of the catalyst and the three-phase boundary formation

$$k_i = k_i(\text{CT,CS,A}) . \tag{5.10}$$

Therefore the published values differ strongly, depending on the electrode system and preparation. In this model a simple constant is used merging all mentioned characteristics. A semi-empirical adsorption isotherm, known as Frumkin isotherm, is assumed for the description of the oxygen adsorption process in the catalyst layer. The Frumkin isotherm takes the interaction between the adsorbed species into account

$$q_{O_2,ads} = \gamma_{c,a} \, k_{O_2,ads} \left(1 - \Theta_{O_2} - \Theta_{CO} - \Theta_M \right) c_{O_2} \, e^{-g_1 \, \Theta_{O_2}} \,, \tag{5.11}$$

where the dimensionless constant g_1 is a measure of the mean interaction energy (attraction constant). Adsorption only takes place at free catalyst sites, expressed as $(1-\sum_{i}\Theta_i)$.

It is assumed that methanol oxidizes in a four-electron step mechanism to CO, preferentially on Pt-sites. This leads to a Butler-Volmer expression

$$q_{\text{MOR}} = \gamma_{c,a} \, k_{\text{MOR}}^* \, \Theta_M \, e^{\frac{\Phi^e - \Phi^p - \Delta \Phi_{\text{MOR}}^0}{b_{\text{MOR}}^*}} - \gamma_{c,a} \, k_{\text{MOR}}' \, \Theta_{CO} \, e^{-\frac{\Phi^e - \Phi^p - \Delta \Phi_{\text{MOR}}^0}{b_{\text{MOR}}}} \,, \tag{5.12}$$

where

$$k_{\text{MOR}}^* = k_{\text{MOR}} \ e^{-\frac{98.3 \cdot 10^3}{R \ T}} , \tag{5.13}$$

 Θ_M and Θ_{CO} is the methanol and carbon monoxide surface coverage, respectively, $b_{MOR}^* = \frac{(1-\alpha_{MOR}) n_{MOR} F}{RT}$ and $b_{MOR} = \frac{\alpha_{MOR} n_{MOR} F}{RT}$ are the Tafel slopes of the MOR. The values of the reversible potential of the MOR $\Delta \Phi_{MOR}^0$, the symmetry factor α_{MOR} and the reaction rates (k_{MOR}, k'_{MOR}) are listed in Table 5.2. Again, the methanol adsorption is expressed as Frumkin isotherm

$$q_{M,\text{ads}} = \gamma_{c,a} \, k_{M,\text{ads}} \left(1 - \Theta_{O_2} - \Theta_{CO} - \Theta_M \right) c_M \, e^{-g_2 \, \Theta_M} - \gamma_{c,a} \, k_{M,\text{des}} \, \Theta_M \, e^{g_2 \, \Theta_M} \,, \quad \text{(5.14)}$$

where $k_{M,ads}$ and $k_{M,des}$ are the rate constants for the adsorption and desorption process.

The hydroxyl ion formation onto Ru catalysts, also called water activation, is coupled with an electron transfer, which can also be expressed by the Butler-Volmer expression

$$q_{\text{act}} = k_{H_2O,\text{ox}}^* \left(1 - \Theta_{OH}\right) e^{\frac{\Phi^e - \Phi^p - \Delta \Phi_{OH}^0}{b_{\text{act}}^*}} - k_{OH,\text{red}}^* \Theta_{OH} e^{-\frac{\Phi^e - \Phi^p - \Delta \Phi_{OH}^0}{b_{\text{act}}}},$$
(5.15)

where

$$k_{H_2O,\mathsf{ox}}^* = k_{H_2O,\mathsf{ox}} \ e^{-\frac{73.6\cdot10^3}{R T}}$$
(5.16)

$$k_{OH,\text{red}}^* = k_{OH,\text{red}} \ e^{-\frac{25.4 \cdot 10^3}{R T}}$$
(5.17)

are the temperature dependent rate constants for the forward and reverse reaction, respectively, $\Delta \Phi_{OH}^0$ is the equilibrium potential, $b_{\text{act}}^* = \frac{(1-\alpha_{\text{act}})n_{\text{act}}F}{RT}$ and $b_{\text{act}} = \frac{\alpha_{\text{act}}n_{\text{act}}F}{RT}$ are the Tafel slopes of the water activation reaction. The adsorption process of water prior to the activation is not explicitly modeled, valid for fast adsorption rates.

A Langmuir-Hinshelwood mechanism is assumed for the *CO* oxidation by hydroxyl ions, which strongly depends on the potential modeled with a simple Tafel expression

$$q_{\text{COOR}} = k_{CO,\text{ox}}^* \Theta_{CO} \Theta_{OH} e^{\frac{\Delta \Phi_{\text{COOR}}^0 - (\Phi^e - \Phi^p)}{b_{\text{COOR}}}}, \qquad (5.18)$$

where

$$k_{CO,ox}^* = k_{CO,ox} \ e^{-\frac{12.6 \cdot 10^3}{R \ T}}$$
(5.19)

is the reaction rate constant, $b_{\text{COOR}} = \frac{(1-\alpha_{\text{COOR}}) n_{\text{COOR}} F}{R T}$ the corresponding Tafel slope and $\Delta \Phi_{\text{COOR}}^0$ the equilibrium potential.

The heterogeneous oxidation of CO with O_2 is modeled according to a Langmuir-Hinshelwood mechanism

$$q_{\text{bleed}} = k_{\text{bleed}} \Theta_{O_2} \, (\Theta_{CO})^2 \, e^{(-\frac{90 \cdot 10^3}{RT})} \,, \tag{5.20}$$

where an Arrhenius expression with a reaction rate constant k_{bleed} is chosen to count for the temperature dependance.

Oxygen Concentration: Oxygen enters the five-layer MEA at the cathode GDL, diffuses to the cathode catalyst layer, where it dissolves into the ionomer to reach the active sites for the ORR. If not all oxygen is consumed in the cathode CL, that means there is an oxygen concentration unequal to zero at the interface $CL \leftrightarrow$ membrane, the dissolved oxygen can diffuse through the membrane forced by a concentration gradient between cathode and anode CL.

The oxygen flux in gaseous $j_{O_2}^g$ and dissolved phase $j_{O_2}^d$ is modeled by simple Fick's diffusion

$$j_{O_2}^{g,d} = -\frac{D_{O_2}^{\text{eff},\Omega}}{L^{\Omega}} \frac{\partial c_{O_2}^{g,d}}{\partial y} , \qquad (5.21)$$

where $D_{O_2}^{\mathrm{eff},\Omega}$ is the effective diffusion coefficient in domain Ω

$$D_{O_2}^{\mathsf{eff},\Omega} = \begin{cases} D_{O_2}^g ((1-s)\epsilon_{O_2}^{\Omega})^{1.5} (\frac{T}{353})^{1.5} & \text{if} \quad \Omega = \mathsf{CGDL} \land \mathsf{CCL} ,\\ D_{O_2}^d & \text{if} \quad \Omega = \mathsf{Mem} \land \mathsf{ACL} . \end{cases}$$
(5.22)

 L^{Ω} denotes the thickness of the layer Ω since the model domains are normalized to one. In the porous media a Bruggeman expression accounts for the reduced diffusion pathway by the solid matrix and water saturation. Since the diffusion process of dissolved oxygen in the ionomer is of several magnitudes slower than for gaseous oxygen in the open gas pores, the oxygen diffusion in the CL is modeled only in gaseous phase. The local distributed gaseous oxygen $c_{O_2}^g$ in the CL is converted to the dissolved oxygen concentration $c_{O_2}^d$ by Henry's law

$$c_{O_2}^d = H \, c_{O_2}^g \,, \tag{5.23}$$

where H is the Henry constant.

Taking the oxygen adsorption process and the heterogeneous *CO*-oxidation into account, mass balance equation yields

$$\frac{\partial j_{O_2}^{g,d}}{\partial y} = L^{\Omega} \left(q_{O_2}^{\Omega} - \epsilon_{O_2}^{\Omega} \frac{\partial c_{O_2}^{g,d}}{\partial t} \right)$$
(5.24)

whereas the sink terms are defined only in the catalyst layers

$$q_{O_2}^{\Omega} = \begin{cases} -q_{O_2, \text{ads}} - q_{\text{bleed}} & \text{if} \quad \Omega = CCL \wedge ACL ,\\ 0 & \text{if} \quad \text{else} , \end{cases}$$
(5.25)

and $\epsilon_{O_2}^{\Omega}$ is the fraction of space accessible for the oxygen in layer Ω . The accumulation term in the CCL accounts only for the gaseous oxygen concentration, i.e. $\epsilon_{O_2}^{\Omega} = \epsilon_p^{\Omega}$. In the membrane and ACL $\epsilon_{O_2}^{\Omega}$ is the ionomer fraction and pore space, since oxygen is dissolved in the water and ionomer in these domains.
Methanol Concentration: The anode is fed with methanol via the anode GDL, from where methanol has to diffuse towards the anode catalyst layer, reaching active sites. Due to the use of an aqueous methanol solution, a concentration discontinuity between methanol in the secondary pores and in the primary pores is neglected. Methanol crossover is assumed in the case of a finite methanol concentration at the interface ACL \leftrightarrow membrane. The methanol flux j_M is modeled by Fick's diffusion and forced by the electro-osmotic drag

$$j_M = -\frac{D_M^{\text{eff},\Omega}}{L^{\Omega}} \frac{\partial c_M}{\partial y} - \frac{j_p \,\alpha_{\text{drag}}}{F} , \qquad (5.26)$$

with the electro-osmotic drag coefficient

$$\alpha_{\rm drag} = \frac{2.5\,\lambda}{22}\,\zeta \;, \tag{5.27}$$

where

$$\zeta = \frac{c_M}{\frac{(1-c_M)v_M}{v_{H_2O}} + c_M}$$
(5.28)

accounts for the fraction of methanol in the aqueous solution dragged by the protons instead of water molecules. In the transport equation, $D_M^{\text{eff},\Omega}$ is the effective diffusion coefficient of methanol, j_p the local current density, α_{drag} the electro-osmotic drag coefficient, $\lambda = 22$ the water content (water molecules per sulphonic acid sites) of a fully hydrated ionomer and v_i the molar volume of species *i*. Again a Bruggeman correction term is used for the effective diffusion coefficient

$$D_{M}^{\text{eff},\Omega} = \begin{cases} \epsilon_{i}^{1.5} D_{M} & \text{if} \quad \Omega = \text{CCL} \land \text{Mem} ,\\ (\epsilon_{i} + \epsilon_{p})^{1.5} D_{M} & \text{if} \quad \Omega = \text{ACL} ,\\ \epsilon_{p}^{1.5} D_{M} & \text{if} \quad \Omega = \text{AGDL} , \end{cases}$$
(5.29)

Methanol mass conservation equation can be expressed by

$$\frac{\partial j_M}{\partial y} = L^{\Omega} \left(q_M^{\Omega} - \epsilon_M^{\Omega} \frac{\partial c_M}{\partial t} \right) , \qquad (5.30)$$

where the sink terms are only defined in the catalyst layers

$$q_M^{\Omega} = \begin{cases} q_{M,\text{ads}} & \text{if} \quad \Omega = \text{CCL} \land \text{ACL} ,\\ 0 & \text{if} \quad \text{else} , \end{cases}$$
(5.31)

and ϵ^Ω_M is the volume fraction in layer Ω where methanol is present.

Surface Coverage: The transient surface coverage of O_2 , MeOH, CO onto Pt and OH onto Ru are described by ordinary differential Eqs. 5.32 to 5.35:

$$\Gamma_{Pt} \frac{\partial \Theta_{O_2}}{\partial t} = +q_{O_2, ads} - q_{ORR} , \qquad (5.32)$$

$$\Gamma_{Pt} \frac{\partial \Theta_{MeOH}}{\partial t} = +q_{M,ads} + q_{MOR} , \qquad (5.33)$$

$$\Gamma_{Pt} \frac{\partial \Theta_{CO}}{\partial t} = -q_{\text{COOR}} - 2 \, q_{\text{bleed}} - q_{\text{MOR}} \,, \tag{5.34}$$

$$\Gamma_{Ru} \frac{\partial \Theta_{OH}}{\partial t} = + q_{\text{act}} - q_{\text{COOR}} , \qquad (5.35)$$

where Γ_i is the active site density of catalyst *i*.

Electronic and Protonic Potential: Ohm's law is used for the description of the charge flux

$$j_{p/e} = \mp \frac{\sigma_{p/e}^{\text{eff},\Omega}}{L^{\Omega}} \frac{\partial \Phi^{p/e}}{\partial y} , \qquad (5.36)$$

where the subscript p/e stands for protons and electrons. The ionic conductivity of the ionomer σ_p is a strong function of the water content for which Springer et al. [1] has found an analytical expression (Eq. 5.37). Since the water content is not calculated in the model a constant value of 22 is assumed, that corresponds to an equilibrium value of a saturated membrane in liquid environment which is fulfilled in the anode compartment fed with aqueous methanol solution

$$\sigma_p^{eff,\Omega} = (\epsilon_i^{\Omega})^{1.5} (0.514 \,\lambda - 0.326) \, e^{1268 \,(\frac{1}{303} - \frac{1}{T})} \quad \text{with} \quad \lambda = 22 \;. \tag{5.37}$$

A Bruggeman correction accounts for the ionomer fraction ϵ_i^{Ω} in layer Ω . The charge balance equation reads

$$\frac{\partial j_{p/e}}{\partial y} = L^{\Omega} \left(q_{p/e}^{\Omega} + C_{DL} \frac{\partial (\Phi^e - \Phi^p)}{\partial t} \right) , \qquad (5.38)$$

where $q_{p/e}^{\Omega}$ are the volumetric charge transfer rates defined as

$$q_{p/e}^{\Omega} = \begin{cases} F\left(4 q_{ORR} + 4 q_{MOR} + q_{COOR} + q_{act}\right) & \text{if} \quad \Omega = \text{CCL} \land \text{ACL} \\ 0 & \text{if} \quad \text{else} \end{cases},$$
(5.39)

and C_{DL} is the double layer capacity that accounts for dis-/charge current when the Galvani potential changed.

Boundary conditions

The following boundary conditions are chosen for the boundary value problem:

Oxygen concentration $c_{O_2}^g$: A fix oxygen concentration at the outer surface of the cathode GDL is assumed, calculated by the ideal gas law at atmospheric pressure $(p = 1.01325 \cdot 10^5 Pa)$

$$c_{O_2}^g[-1] = \frac{p}{RT}$$
 (5.40)

Oxygen dissolves into the hydrated ionomer within the cathode CL, described by Henry's law, where it can react on active sites or diffuse towards the anode. If not all oxygen is reduced at the cathode and anode CL, respectively, a Cauchy-type bound-ary condition is chosen for the outflow

$$j_{O_2}^d[3] = \Omega_{O_2} c_{O_2}^d[3] . (5.41)$$

Methanol concentration c_M : Similar boundary conditions are chosen for the methanol concentration as for the oxygen concentration. Depending on the molarity of aqueous methanol solution, a defined concentration is assumed at the anode inlet

$$c_M[4] = c_M^{molarity} . ag{5.42}$$

Not oxidized methanol can leave the cathode CL

$$j_M[0] = \Omega_M \, c_M[0] \,. \tag{5.43}$$

Electronic potential Φ^e : Like in the experiments the simulated DMFC is operated in potentiostatic mode. Thus, the cathode potential is set to the cell voltage U_{cell} on the outer surface of the CGDL

$$\Phi^e[-1] = U_{cell} , \qquad (5.44)$$

and the anode potential is set to zero

$$\Phi^e[4] = 0 . (5.45)$$

Protonic potential Φ^p : Since the protons are not allowed to penetrate into the GDLs on the cathode and anode side, their fluxes are taken to zero at the interfaces CL \leftrightarrow GDL

$$\frac{\partial \Phi^p[0]}{\partial y} = \frac{\partial \Phi^p[3]}{\partial y} = 0 .$$
(5.46)

Numerical Details

The governing equations are solved using COMSOL Multiphysics[™], a commercial software package based on finite element methods. A direct Linear System Solver (UMFPACK) and quadratic Lagrange polynomials as test functions are used. The solver is allowed to take free time steps. The five model domains are discretized with non-uniform grid of 611 elements whereas the interface regions between the domains are meshed with smaller elements.

5.3.3 Simulation Results

The aim of this DMFC model is to give an explanation of the experimental results presented in the previous subsection 5.2.2. The simulation results reproduce qualitatively the effects of mixed potentials which in turn can explain the observed behavior of the dynamic anode potential relaxation at various operating conditions. The model prediction of this dynamic behavior indicates that the impacts of multi-step reactions, bi-functional mechanism and mixed potential formation are essential in DMFC modeling.

Polarization Curves

Before the dynamic simulations with a methanol tolerant RuSe_x catalyst get discussed, a short excursion to steady-state simulations of polarization curves is given, whereby a non-methanol tolerant catalyst such as platinum is assumed as cathode catalyst. This means, that the same activity of the anode and cathode catalyst towards MOR is assumed, likewise for the activity towards the ORR but certainly with a higher value than for the MOR. If nothing else is stated all shown results in this chapter are simulated at a temperature of 81° C.

Simulated polarization curves of both electrodes and the cell voltage are plotted in Fig. 5.10. Even though the theoretical values of 1.23V and 21mV are used as equilibrium potential of the ORR and MOR in the model, the voltage-current curve starts with an OCV of about 640 mV, highlighting the drastic influence of mixed potentials. The cell voltage shows an exponential decline in the activation controlled region, that can be completely attributed to the characteristics of the anode overpotential. The anode overpotential shows an offset of 130 mV at no-load condition, which is about 110 mV above the theoretical value, affected by a parasitic ORR due to oxygen crossover. A strong mass transport controlled region is visible at about $0.23 A cm^{-2}$.

The cathode overpotential shows a nontypical linear function of current density with a slight slope and an offset of $420 \, mV$ at OCV. This result shows that the cathode suffers strongly by a parasitic internal current due to methanol crossover. An explanation for this nontypical cathode behavior can be given by the schematic depicted in



Figure 5.10: Simulated polarization curves of the anode and cathode predict mixed potential formation on both electrodes resulting in a low OCV of the voltage-current curve. An exponential increase of the cathode overpotential with current density is not observable.

Fig. 5.11(a). The three dashed curves show the typical exponential characteristics of the cathode overpotential with current generation for different fixed parasitic currents. The fact of a parasitic MOR on the cathode needs an ORR to counterbalance the involved charge generation, hence the cathode is under load even no external current is drawn. The largest overpotential is observed for the blue curve due to the high parasitic current. Since the parasitic current is a function of the methanol crossover which decreases with increasing methanol consumption on the anode, the apparent cathode overpotential (red curve) has to be between the blue curve (low current \rightarrow high fuel crossover) and the black curve (high current \rightarrow no crossover) depending on the external drawn cell current. Thus the typical exponential shape of the cathode overpotential is lost for such conditions. Measurements published by Eccarius et al. [64] approve such cathode characteristics (Fig. 5.11(b)).

The reduced OCV and the low performance of the DMFC with the platinum cathode catalyst can be analyzed by the potential and methanol distribution within the fuel cell, plotted in Fig. 5.12 and 5.13. It is shown that at open circuit condition the potential difference between the anodic electronic potential Φ_a^e and protonic potential Φ^p is much higher than the theoretical value of $21 \, mV$. The discrepancy between the expected



(a) Schematic of the cathode overpotential under load for different constant parasitic currents. The apparent cathode overpotential accounts for the change off parasitic currents under different load conditions.



(b) Measured cathode losses for different molarities (2 M, 0.5 M, 0.25 M) published by S. Eccarius (taken from [64]) approve the linear characteristics of the cathode overpotential.

Figure 5.11: The cathode overpotential shows a nontypical linear function of current density due to high parasitic MOR on the cathode depending on the load conditions.

theoretical value and the simulation results is caused by a small oxygen crossover to the anode where a parasitic reduction reaction takes place. In case of a hydrogen PEFC this small amount of oxygen would not lead to a noteworthy anode overpotential since the hydrogen electrode is hardly polarizable. But for the slow methanol oxidation reaction this small parasitic reduction current deteriorates the electrode potential to almost $120 \, mV$. Because the electronic potential Φ_a^e is set to zero at the surface of the anode GDL by the boundary condition (like it is done in the experiment by the potentiostat) the protonic potential falls to negative values relative to Φ_a^e . The higher activation losses can be assigned to the cathode. Due to the high electrical conductivity of the GDL and carbon support in the CL the potential gradient ($\nabla \Phi^e$) across these layers can not be seen in this figure. At the highest current density of $0.2 \, A \, cm^{-2}$ a small ohmic drop is observable across the membrane.



Figure 5.12: Simulated potential distribution across the membrane electrode assembly. Both the parasitic methanol oxidation on the cathode and the parasitic oxygen reduction on the anode lead to a reduced cell voltage.

The methanol concentration across the cell as a function of the current density is visualized in Fig. 5.13(a). It shows that methanol is completely oxidized in the cathode CL. Due to the high mass transport limitation of methanol in the anode GDL the methanol crossover to the cathode side decreases with increasing current density. According to this Fig. 5.13(b) depicts the decreasing parasitic MOR on the cathode side with increasing load. The plot highlights that the MOR takes place within the first 10% of the CCL at the interface to the membrane due to the high overpotential for the





(a) Methanol concentration profile within the fuel cell as a function of the current density.



(b) Methanol completely oxidizes within the first 10% of the CCL due to the extremely high consumption rate at high overpotential.

Figure 5.13: The methanol crossover and hence the parasitic MOR on the cathode side decreases with increasing current density due to mass transport limitation of methanol in the anode GDL.

In Fig. 5.14 the polarization curves of a DMFC based on a high methanol-tolerant cathode catalyst such as $RuSe_x$ are plotted. It is assumed that the activity of the $RuSe_x$ catalyst towards MOR is several magnitudes smaller than the activity of a Pt catalyst ($k_{MOR}^{RuSe} = 10^{-9} k_{MOR}^{Pt}$), but unequal to zero. Additionally, it is well known and thus considered in the simulation, that the RuSe_x catalyst shows a relative low activity for the ORR compared to Pt. The model parameter used for the simulations in this section are listed in Table 5.2.

The exponential shape of the cathode overpotential shows that there is little parasitic MOR at this electrode, contrary to the case with the Pt catalyst (see Fig.5.10). Nevertheless, the assumed low activity of the RuSe_x catalyst for the ORR leads to a steep increase in the cathode overpotential when an external cell current is drawn, which in turn leads to comparable performance of a non methanol-tolerant catalyst with high activity for the ORR such as platinum. The assumed small parasitic methanol oxidation on the cathode catalyst together with the fact of a lowered activity towards ORR (compared to Pt) results in a significant cathode mixed potential formation. Both mixed potentials on anode and cathode leads to the low OCV of $620 \, mV$ at 60° C. Measured OCVs at different temperatures show an increase with temperature, depicted in Fig. 5.15. The same characteristic is also given by the model. The simulated OCVs predict a slight offset of about 20 mV, towards higher cell voltages compared to the experimental data. Although the kinetic model parameters are not well adjusted (fitted) to experimental data, the temperature dependancy shows a good agreement since the temperature is a sensitive parameter involved in all Arrhenius approaches. The OCV is nearly independent on methanol concentration.



Figure 5.14: Simulated polarization curves with RuSe_x as cathode catalyst. Due to the methanol tolerance of RuSe_x the cathode overpotential shows an exponential increase with current, contrary to the overpotential with Pt catalyst shown in Fig. 5.10.



Figure 5.15: Comparison of the simulated and measured OCV at different temperatures. The simulation predicts the measured increase of OCV with increasing temperature, but with a small shift 20 mV towards higher voltages.

Dynamic Simulations

A further benchmark for the developed model is to reproduce the measured transient response of the anode and cathode potential in a gualitative manner. The overshoot of the cathode potential observed with a Pt-based cathode catalyst should vanish for a methanol-tolerant catalyst like it was measured for RuSe_x (see Fig. 5.5), whereby the anode undershoot is present for both CCMs. The simulated characteristics of the anode undershoot behavior on switching to no-load should depend on the load current and the inlet methanol concentration like it was measured in the experiment. This is in summary:

- The magnitude of the anode potential undershoot increases with increasing load current density from 0.01 to $0.03 A cm^{-2}$ in the measurement. No difference is visible between 0.03 and $0.04 \, Acm^{-2}$, indicating that a kind of asymptotic behavior is reached at higher currents (Fig. 5.16(a)).
- The undershoot increases with increasing methanol concentration (Fig. 5.16(b)), combined with longer relaxation times.

0.16

0.12

0.08

0.04



. ^e - ∲_{ref,a} , 0.00 ڇ -0.04 -0.08 0 5 10 15 20 25 30 35 time / s

molarity 0.5 M

1.0 M

1.5 M

3.0 M

(a) A higher load before current interruption leads to a larger anode potential undershoot, whereby a saturation is reached at $0.04 A cm^{-2}$.

(b) A higher methanol concentration also leads to an enlarged undershoot behavior with larger relaxation times.

Figure 5.16: Measured relaxation curves of the anode polarization for different load current and molarity are shown. Since the change in molarity effects also the reference potential, the steady-state anode potentials are normalized to zero for comparison of their transients.

In Fig. 5.17 the simulated relaxation curves of the anode and cathode potential together with the cell voltage is shown for both cathode catalysts, Pt and RuSe_x. The anode undershoot is identical for both cases, indicating that the cathode catalyst does not impact the anode side. The cathode overpotential shows a small undershoot in case of Pt catalyst due to methanol crossover which in turn results in parasitic currents. The overpotential with the oxygen-selective $RuSe_x$ catalyst shows a slow transient without an undershoot. Steady-state is not reached with 35 s. The simulated characteristics are in qualitative agreement with the experimental data.



Figure 5.17: Potential relaxation curve of the cathode and anode from a load current of $0.2 A cm^{-2}$. The cathode overpotential with platinum as cathode catalyst differs significantly from the overpotential with RuSe_x catalyst.

In Fig. 5.18(a) simulated anode potential relaxation curves for different load currents are shown. In agreement with the measurements the magnitude of the anode undershoot first increases with the load current and finally ends up in an asymptotic behavior for higher currents. The time to reach equilibrium also increases with the load current.

In Fig. 5.18(b) the anode polarization relaxation after CI at $0.1 A cm^{-2}$ is shown for different molarities. The anode overpotentials under load vary slightly for different molarities. After CI the undershoot to the lowest anode potential is observed for the highest molarity that ends with the longest relaxation time at the lowest steady-state level. The magnitude of the undershoots are among each other comparable which is not in agreement with the experimental data.

An explanation of the presented anode potential relaxation can be given by mixed potential formation combined with CO catalyst poisoning depicted in Fig. 5.19. Under load the OH promotion on the Ru-sites is sufficient for the further oxidation of CO



(a) The minima of anode relaxation curves for different load currents predict an asymptotic saturation for higher currents.



(b) Dependancy of the anode potential relaxation curve on the inlet methanol concentration. The higher molarity improves the steady-state potential.

Figure 5.18: The impact of the load current and methanol molarities on the transient response after CI is analyzed.

to CO_2 because the electrode potential is high enough to dissociate water. Thus the OH surface coverage is about 27% and the CO surface coverage is about 48%. After current interruption the anode electrode potential first remains stable for some milliseconds due to double layer discharging, than decrease to low values. With a small time delay the OH surface coverage decreases too. At this point the bi-functional mechanism comes to rest and thus the CO coverage increases, leading to a strong catalyst poisoning that makes the electrode potential very sensitive to a parasitic oxygen reduction reaction. Thus, after approx. 3s the potential increases again.



Figure 5.19: The anode undershoot behavior is caused by the dynamic change of the *CO* adsorbate in the anode catalyst layer. The high poisoning at no-load condition leads to mixed potential formation due to a low parasitic ORR on the anode side.

Local Analysis

The advantage of using such a detailed kinetic model is to provide the opportunity to determine the local conditions within the fuel cell such as surface coverage of adsorbed intermediates, concentrations and potentials. In the following a local analysis of the transients of certain solving variables after a current interruption from a current density of $0.1 A cm^{-2}$ for a Pt-cathode catalyst is made.

Fig. 5.20 shows the transients of the distributed methanol Θ_M and hydroxyl ion Θ_{OH} surface coverage in the anode catalyst layer. Under load $(t = -10 s \dots 0 s)$ the methanol coverage is nearly homogeneous within the ACL at a value of 0.5, with a small increase in the region of the membrane interface (Fig. 5.20(a)). This increase at the interface can be attributed to the oxygen crossover, discussed in the next section. A relative smooth transient to a lower value of 0.1 is observed after current interruption (t>0), except at the membrane interface. Steady-state is reached after about 25 s. At no-load condition the coverage at the interface. This increase indicates an insufficient adsorption rate of methanol under load. The coverage of OH on the Ru-sites shows a very homogeneous distribution within the ACL (Fig. 5.20(b)), with a value of about 0.19 under load. The coverage decreases rapidly within 3 s to almost zero when turning to no-load because the water dissociation rate at low anode overpotential is insufficient to maintain a high coverage.



(a) After current interruption the methanol coverage decreases from about 0.5 to 0.1 within 25 s due to CO poisoning.

(b) A low and homogeneous coverage of OH-species of about 0.19 is observed before CI, decreasing rapidly at no-load condition.

Figure 5.20: Transients of the surface coverage of methanol and OH-species on the anode after current interruption show an insufficient bi-functional mechanism of the MOR, observable in a vanishing OH-coverage at OCV.

The phenomena of the steep gradient of methanol coverage near the membrane in-

terface can be explained by the coverage of carbon monoxide. Figure 5.21 shows the lapse of the carbon monoxide at the cathode and anode. A low coverage is observed on the cathode side near the membrane interface. The coverage on the cathode is almost stable in time after CI, indicating a relative constant parasitic MOR independent on the load conditions as long as no methanol mass transport limitation is present on the anode side. Since on the cathode the heterogeneous reaction with oxygen is the only process for a further oxidation of the adsorbed CO to CO_2 , the assumed rate constant of this reaction has a strong influence on the degree of CO-poisoning of the CCL. Here, a sufficient rate constant is assumed to prevent a high catalyst blocking. This assumption could be too conservative, because the impact of catalyst poisoning might even be underestimated and could lead to a deteriorated electrode potential. Thus, measuring surface coverages by special in-situ characterization techniques is essential to adjust the rate constant. On the anode side the same heterogeneous reaction is allowed for oxygen permeating through the membrane. Therefore, a steep decrease of Θ_{CO} is observed near the membrane interface which in turn leads to free Pt-sites for the adsorption of methanol, establishing the increasing Θ_M . The coverage of CO slowly increases after CI within the electrode, since as already mentioned not sufficient OH-ions are provided from the Ru-sites at low overpotentials. The anode catalyst gets poisoned.



Figure 5.21: Transients of the *CO*-coverage after CI. The *CO*-coverage on the anode raises from 0.5 to 0.9. The small *CO*-coverage on the cathode side at the interface to the membrane is hardly influenced by the CI.

The consumption of methanol due to the MOR is depicted in Fig. 5.22(a). A ho-

mogeneous MOR with a small increase near the membrane interface is shown in agreement with the distribution of Θ_M (see Fig. 5.20(a)), indicating a constant overpotential within the CL. After CI, the reaction stopped abruptly in the ACL, except for a small region near the membrane interface where the MOR has to counterbalance the still present parasitic ORR.

The parasitic MOR on the cathode side is depicted in Fig. 5.22(b). It shows that methanol is oxidized within the first 10% of the catalyst layer with a high rate, increasing after CI due to increasing methanol crossover, depicted in Fig. 5.23(a)). The distribution of the methanol concentration within the fuel cell shows clearly that a high methanol permeability of the membrane in combination with a low methanol diffusivity in the GDL results in a relative low methanol concentration in the ACL, even at no load condition. Hence, it can be concluded that a DMFC anode always suffers from mass transport limitations.



(a) The simulation predicts a nearly homogeneous methanol consumption within the anode catalyst layer except near the membrane interface where an increase is observed due to oxygen crossover.

(b) A very high parasitic current within the first 10% of the cathode CL is observed. After CI the parasitic current droped followed by an asymptotic increase.

0

-10

3500

3000

1500

1000

500

0

Figure 5.22: The time evolution of the methanol consumption in the anode and cathode catalyst layer due to the MOR after current interruption at time t = 0 s is shown.

The transient oxygen consumption by the ORR after CI within the CCL is depicted in Fig. 5.23(b). Under load a minimum of q_{ORR} is observed at the interface to the membrane due to the reduced number of active sites which are not blocked by *CO* (see Fig. 5.21). The minimum of q_{ORR} is also present near the membrane interface at no-load condition. Directly after current interruption, the ORR shows a sharp decline, followed by a smooth increase. This increase is caused by counterbalancing the increasing parasitic MOR due to increasing methanol crossover as already shown before in Fig.5.23(a). A comparison of the oxygen consumption before (around $750 \ mol \ m^{-3}s^{-1}$) and after CI (around $430 \ mol \ m^{-3}s^{-1}$) at steady-state shows the high parasitic current at OCV.



(a) Methanol concentration distribution within the cell after CI. Only a slight increase of methanol crossover is predicted, since the methanol distribution is governed by the parasitic MOR on the cathode throughout the experiment.



(b) An increase of the ORR is observed after CI to counterbalance the parasitic MOR on the cathode side. The ORR is nearly homogeneous distributed in the CL with a small decline near the membrane interface due to *CO*blocking.

Figure 5.23: Switching to no-load conditions leads to an increase of the methanol crossover and hence to an increase of the parasitic MOR that has to be counterbalanced in the CCL by the ORR.

By using a methanol tolerant cathode catalyst such as $RuSe_x$ the electrochemical conditions on the anode side are not affected, as shown in Fig. 5.17 for the anode overpotential. But taking a look on the cathode a completely different situation is predicted by the model with regard to the methanol distribution and the resultant methanol and oxygen surface coverages.

In Fig. 5.24 the methanol concentration distribution within the cell is depicted, showing a considerable amount of methanol in the cathode CL since the ORR selective catalyst oxidizes hardly methanol. Thus the methanol concentration in the CCL is determined by the boundary condition of methanol towards the gas diffusion layer. An arbitrary mass transport coefficient is used in the formulation of a Cauchy boundary condition that could be identify for the model validation by measuring the methanol concentration in the cathode exhaust by mass spectroscopy or gas chromatography (not done in this work).

Since the adsorption process of methanol on the $RuSe_x$ catalyst is still allowed with only a marginal charge transfer reaction, a large fraction of the catalyst sites can be blocked by adsorbed methanol molecules in case of fast adsorption rates and binding energies. For the oxygen this would imply a lowered amount of accessible active



Figure 5.24: Transient of the methanol concentration within the fuel cell after CI. The ORR selective RuSe_x catalyst leads to a non-vanishing concentration in the CCL, whose value is determined by the outflow boundary condition.

sites. Thus the choice of the involved constants for the ad-/desorption process is critical for modeling the cathode performance. Thus, it has to be emphasized again that in-situ characterization techniques regarding the investigation of adsorbates are essential for parameter extraction by inverse modeling.

In the presented simulations the involved constants for the ad-/desorption processes are chosen under the assumption that the catalyst sites are mainly occupied by oxygen at no-load condition. As already mentioned, this strong assumption has to be proven by experimental measurements of surface coverages. The simulated transient of the oxygen coverage on the cathode after current interruption is plotted in Fig. 5.25(a). At $100 \ mA \ cm^{-2}$ the oxygen coverage has a value of 0.6, homogeneously distributed in the CL and after CI Θ_{O_2} increases to nearly 1. This shows that under load the consumption of oxygen by the ORR is too fast for the adsorption process to maintain the coverage in the range of 1. Under load methanol adsorbs on the free RuSe_x sites, shown in Fig.5.25(b).

5.3.4 Remarks to the DMFC model

The aim of the presented model was to find an interpretation of the so far unexplained anode undershoot, shown in the experimental subsection 5.2.2. For this purpose a time-dependent complex fuel cell model based on a system of coupled PDEs describing the physical and electrochemical processes was developed. Essential for this model is the description of the anode kinetic by using a bi-functional mechanism,



(a) The oxygen coverage increases after CI to almost 1.0.

(b) The adsorbed methanol gets suppressed by oxygen after CI.



which can lead to CO-poisoning in case of a too slow OH-supply. This assumption alone is not sufficient for the prediction of an anode potential undershoot since the anode has to be under load even if no external current is drawn. Accounting for a low oxygen crossover through the membrane seems to be obvious but is so far not described in the literature. The simulations show that a small amount of oxygen on the anode is actually enough for deteriorate the anode potential.

The description of the kinetics by means of exponential functions (Butler-Volmer approach) leads to a highly non-linear PDE system, that is numerically not easy to be solved. Since the simulations show that certain solving variables are nearly constant in y-position within the model domain and therefore do not have to be spatially resolved, the complexity of the model can be reduced.

Some kinetic parameters as used for the new approaches presented here are not described in the scientific literature. Therefore some parameters of the model had to be assumed.

At current status the model does not enforce the claims of an exact prediction of the operating state of a DMFC since there is a lack of information in experimental data for the model validation. Nevertheless the model identifies the determining loss mechanism of a DMFC:

- mixed potential formation on both electrodes and the resulting low OCV,
- poisoning effects of the catalyst layers and their dynamic effects on the electrode potentials.

The model predicts qualitative the characteristics of the polarization curves, the temperature dependent OCV and the potential relaxation curve after CI. Further experimental results are necessary for model validation, in particular information about surface coverages of the intermediates is required, since they have a strong influence on the electrode polarization. The measured interrelationship of the steady-state current and overpotential is not sufficient for the validation of such a complex model, as the following two examples explain::

- In the present simulation the poor performance of the methanol-tolerant RuSe_xcatalyst is explained by the lower catalytic activity towards the ORR compared
 to platinum. On the basis of this simulation results the poor performance of
 the RuSe_x catalyst could also be explained by strong poisoning effects. In
 case of high adsorption rates of methanol or high binding energies of adsorbed
 methanol molecules on the methanol-tolerant catalyst, the cathode catalyst can
 get blocked by methanol leading to less accessible active sites for the ORR.
 Thus, in-situ measurement techniques such as spectroscopy techniques like
 x-ray adsorption spectroscopy (XAS), fourier-transformations-IR-spectroscopy
 (FTIR) or Differential Electrochemical Mass Spectroscopy (DEMS) have to be
 applied to get more detailed information about reaction mechanism, reaction
 rates and surface coverages.
- 2. A second negative effect of the preferable reduced parasitic MOR on a methanol tolerant catalyst is the changed water management. Due to the reduced cathode losses the electrode temperature would be several Kelvin lower than for the Pt catalyst. Therefore a higher water saturation in the electrode may be expected, leading to higher mass transport limitation. This process is not implemented in the model but might be of higher importance in real experiments.

For a better parameter extraction the next step should be the application of the model towards the simulation of electrochemical impedance spectroscopy.

5.3.5 Nomenclature and Parameter List

Symbol	Description	Value / Eq.	Unit	Ref.
Solving varia	ables			
			1 -3	
c_M	methanol concentration		mol m	-
$c_{O_2}^{a,g}$	oxygen concentration (dissolved, gaseous)		$mol m^{-3}$	-
Θ_{CO}	surface coverage of carbon monox- ide		-	-
Θ_M	surface coverage of methanol		-	-
Θ_{O_2}	surface coverage of oxygen		-	-
Θ_{OH}	surface coverage of hydroxyl ions		-	-
Φ^e	electronic potential		V	-
Φ^p	protonic potential		V	-
Physical cor	nstants			
-		0.0.107	$\alpha = 1$	
F'	Faraday constant	96485	$Cmol^{-1}$	-
R	gas constant	8.314	$J K^{-1} mol^{-1}$	-
Ctaurotrada				
Structural va	alues			
TCL	CL thickness	$20 \ 10^{-6}$	200	mossured
L_{IGDL}	GDL thickness	$20 \cdot 10$ $430 10^{-6}$	111 m	mossured
L_{IMem}	mombrano thicknoss	$430 \cdot 10$ 180 10 ⁻⁶	111 m	mossured
	volume fraction of open pores in CL	0.25	-	[65 58]
$_{,GDL}^{\epsilon_{O_2}}$	volume fraction of open pores in CE	0.23	-	[05, 50]
ϵ_{O_2}	GDL	0.74	-	[00]
ϵ_i^{CL}	volume fraction of ionomer in CL	0.45	-	assumed
ϵ_i^{Mem}	volume fraction of ionomer in mem-	1	-	-
ı	brane			
Physical properties, kinetic parameters and local variables				
$b_{ORR}(b^*_{ORR})$	Tafel slope of the ORR	Eq. 5.9	V	-
C_{DL}	double layer capacity	$2 \cdot 10^7$	$F m^{-3}$	[6]
D_M^{CL}	methanol diffusion coefficient in CL	$2.8 \cdot 10^{-9}$	$m^2 s^{-1}$	[51]
$D_M^{\overline{G}DL}$	methanol diffusion coefficient in	$2.8\cdot 10^{-9}$	$m^2 s^{-1}$	[51]
	GDL			
D_M^{Mem}	methanol diffusion coefficient in membrane $@$ 330 K	$9.46 \cdot 10^{-10}$	$m^2 s^{-1}$	[67]

Symbol	Description		Lipit	Def
Symbol	Description	value / Eq.	Unit	Rei.
$D_{O_2}^d$	oxygen diffusion coefficient in ionomer	$2.0 \cdot 10^{-8}$	$m^2 s^{-1}$	[68]
$D_{O_2}^g$	oxygen diffusion coefficient in gas phase	$3.2\cdot 10^{-5}$	$m^2 s^{-1}$	[69]
g_1 g_2 H k_{bleed} $k_{CO,ox}$ $k_{H2O,red}$ $k_{H2O,ox}$ $k_{M,ads}$ $k_{M,des}$ $k_{M,des}$ k_{MOR} k_{MOR} k_{Pt}^{V} MOR k_{Pt}^{V} k_{ORR} k_{RuSe}^{Pt} k_{ORR} k_{RuSe}^{Pt} k_{ORR} $k_{O2,ads}^{Pt}$	phase lateral interaction parameter lateral interaction parameter Henry constant rate constant for oxygen bleeding rate constant for CO oxidation rate constant for OH reduction rate constant for H ₂ O oxidation methanol adsorption constant methanol desorption constant rate constant for the MOR _{forward} rate constant for the ORR rate constant for the ORR oxygen adsorption constant	$\begin{array}{c} 5\\ 4\\ 0.0254\\ 3.03\cdot 10^{18}\\ 1.25\cdot 10^5\\ 3.966\cdot 10^{11}\\ 7.6896\cdot 10^{19}\\ 2.3606\cdot 10^5\\ 3.3696\cdot 10^3\\ 8.3\cdot 10^{13}\\ 3.3\cdot 10^2\\ 1\cdot 10^{-12}\\ 1.5\cdot 10^{-9}\\ 1.5\cdot 10^{-13}\\ 7.4\cdot 10^6\end{array}$	$ \frac{1}{s} = 1$	assumed [70] assumed assumed assumed assumed assumed assumed assumed assumed assumed assumed assumed
n_{act} n_{ORR} n_{MOR} n_{COOR} q_{ORR} $q_{O_2,ads}$	number of transferred electrons number of transferred electrons number of transferred electrons number of transferred electrons Source/sink due to ORR Source/sink due to oxygen adsorp- tion	1 4 1 Eq. 5.8 Eq. 5.11	- $mol m^{-3} s^{-1} mol m^{-3} s^{-1}$	[50] - [50] - -
$q_{ extsf{MOR}}$ $q_{M, extsf{ads}}$	Source/sink due to MOR Source/sink due to methanol ad- sorption	Eq. 5.12 Eq. 5.14	$mol m^{-3} s^{-1}$ $mol m^{-3} s^{-1}$	-
q_{act} q_{COOR} q_{bleed} s_{GDL} s_{CL} $lpha_{drag}$ $lpha_{act}$	Source/sink due to water activation Source/sink due to COOR Source/sink due to oxygen bleeding saturation saturation electro-osmotic drag coefficient symmetry factor of the water activa- tion	Eq. 5.15 Eq. 5.18 Eq. 5.20 0.55 0.18 Eq. 5.27 0.1	$mol m^{-3} s^{-1}$ $mol m^{-3} s^{-1}$ $mol m^{-3} s^{-1}$ - -	- - estimated estimated - assumed
$lpha_{ ext{COOR}}$ $lpha_{ ext{MOR}}$ $lpha_{ ext{ORR}}$ $\gamma_{c,a}$	symmetry factor of the COOR symmetry factor of the MOR symmetry factor of the ORR cathode/anode catalyst loading	0.5 0.818 0.478 1.26/1.9	-	assumed assumed assumed measured

5 Reaction Kinetics in a Direct Methanol Fuel Cell

Symbol	Description	Value / Eq.	Unit	Ref.
$\Delta \Phi^0_{OH}$	reversible potential of the water ac-	0.4	V	assumed
011	tivation			
$\Delta \Phi^0_{MOB}$	reversible potential of the MOR	0.043	V	[3]
$\Delta \Phi_{OBR}^0$	reversible potential of the ORR	1.23	V	[3]
$\Delta \Phi_{COOB}^{0}$	reversible potential of the COOR	0.346	V	assumed
Γ_{Pt}	active site density	78.15	$mol m^{-3}$	assumed
Γ_{Ru}	active site density	78.15	$mol m^{-3}$	assumed
λ	water content of ionomer	22	-	
σ_e	electrical conductivity	500	$S m^{-1}$	[71]
Ω_{O_2}	oxygen transfer coefficient	$1 \cdot 10^{-3}$	$m s^{-1}$	assumed
Ω_M	methanol transfer coefficient	$1 \cdot 10^{-5}$	$m s^{-1}$	assumed
Operating conditions				
T	operating temperature	354.15	K	measured

5.3 Modeling Catalyst Poisoning and Mixed Potential in a DMFC

 Table 5.2: Nomenclature and parameter values used for the simulation.



Chapter 6

Water Management in Polymer Electrolyte Membrane Fuel Cell

6.1 Motivation and Literature Overview

In the low-temperature PEFC the greatest challenge that needs to be overcome before the full potential of this technology can be realized, is to optimize the water management. This however, is a very complex task since two-phase phenomena are still poorly understood. To develop a better knowledge, several diagnostic tools have been applied in the last two decades. Categorizing these tools, they can be subdivided into imaging techniques and measurements of physical/electrochemical properties. Some advanced measurements combine both, which allow for a better analysis of the complex couplings between two-phase phenomena and the other processes occurring in a fuel cell.

Although of lot of progress has been made concerning water management, the flooding phenomenon is captured inadequately. While flooding events in the gas channel can be measured by a drop in the fuel cell performance or by an increase of the pressure drop along the flow channel caused by a reduced flow path cross-section due to liquid water evolution [72, 73, 74, 75, 76, 77], it is hardly feasible to detect the local position of the accumulated water without sophisticated measurement techniques such as neutron and synchrotron radiography. Since an excess of liquid water in the flow channel, GDL as well as CL leads to mass transport losses and degradation phenomena, the identification of the flooded structure and its local position is of major interest.

The easiest way to analyze the liquid water transport in the flow channel of a single cell is to use a transparent plate as flow-field structure. By means of digital cameras, high-speed cameras and thermography cameras the liquid water movement,

droplet growth out of the GDL into the channel, the droplet detachment by convective driving forces and the temperature distribution can be recorded. Pioneer work was achieved by Tüber et al. [78] who studied small fuel cells for portable applications with a transparent cell for the first time. Similar transparent test cell setups for liquid water analysis followed by e.g. Weng et al. [79], Liu et al. [80, 53] and Su et al. [81]. The visualization technique is restricted by the penetration depth of the optical light. Thus, to gather information about the behavior of water within the GDL or even the CL, the media has to be modified, i.e. cutting some GDL fibers to arrange a visual duct to the CL. This approach can be problematic since this invasive technique can dramatically disturb the two-phase transport properties of the cell (see Chapter 6.5).

Neutron radiography is a very strong minimal-invasive diagnostic tool that provides an insight into an operating fuel cell. This technique is based on the strong interaction of neutrons to hydrogen-containing compounds such as water. Depending on the quality of the neutron beam and detector system a spatial resolution down to several $100\,\mu m$ and time resolution of a few seconds was presented in the latest publications. In 1999, Bellows et al. [82] presented the neutron imaging technique applied to fuel cell research for the first time, measuring the water gradient profiles within the Nafion[®] membrane of an operating PEM fuel cell. At that time, they reached a low spatial resolution of $500 \,\mu m/pixel$ and low image acquisition rates of $5 \,s$ per image, which is far away from an adequate analysis of the dynamic two-phase flow. Up to now, several groups with access to a neutron source improved the spatial and time resolution. For example, Satija et al. [83] reached a resolution of $160 \,\mu m$ at $2 \, s$ per image. They presented a movie, that visualizes qualitatively the water evolution and movement during 2000 s of operation. A very high temporal resolution of 30 images/sis presented in [84, 85] with a spatial resolution of $129 \,\mu m$. Nevertheless, the significance concerning the two-phase flow is more or less restricted to the flow channel. This is because the interesting scale of two-phase flow in the GDL is determined by the GDL thickness and the pore structure that requires a resolution of at least several microns.

A large step in visualizing the liquid water is done by Hartnig et al. [86], who presented high-resolution synchrotron X-ray radiography data with a resolution down to $3 \mu m$. By means of this technique, an adequate diagnostic tool is found that provides detailed information with a sufficient spatial and temporal resolution. Even the through-plane water distribution in the GDL could be resolved which is essential for model validation. Water in a PEM fuel cell can also be detected by magnetic resonance imaging (MRI), demonstrated by Tsushima et al. [87, 88]. The drawback that made this diagnostic tool less useful is the requirement of non-magnetic materials, making investigations of common carbon-based GDL difficult.

The in-situ measurement of physical/electrochemical properties like current mapping, EIS, pressure drop measurements or ex-situ component analysis such as contact an-

gle or bubble point measurements can also provide useful information of two-phase phenomena.

Hakenjos et al. [89] developed a segmented transparent test cell to investigate the water management by the combined spatially resolved measurement of current, temperature and water distribution. A special feature was the additional measurement of the local electrochemical impedance spectra [90]. Several research groups use current mapping in segmented test cells for analyzing the flow field design and operating conditions with respect to the water management, e.g. Mench and Wang [91] or Noponen et al. [92]. At this point the work of Hartnig et al. [93] and Schneider et al. [94] has to be mentioned. They combined neutron imaging with the spatially resolved current measurement and impedance, respectively. The local detection of liquid water blocking parts of the flow channel can be correlated with the current distribution and impedance.

Besides the synchrotron X-ray radiography [86] no imaging diagnostic tool is able to resolve the two-phase flow in the pore structure of the GDL or even the CL. The measurement of the physical/electrochemical properties mentioned above are mainly related to water distribution in the in-plane direction. For developing a two-phase model of a porous medium, knowledge of liquid-phase transport on the pore scale is essential. Thus, applying dynamic electrochemical measurement techniques on a very small fuel cell, where lateral effect can be neglected, combined with inverse modeling is a practicable way to gain more information about two-phase phenomena in PEM fuel cells. In this and further chapters a variety of technological advances is presented to explore water management in PEFC.

6.2 Analysis of Wettability of GDLs by ESEM imaging

Capillary force is the most important transport mechanism for liquid water in the porous structure of a GDL and CL. The pressure difference across the interface between the liquid phase and the gas phase, described by the Young-Laplace equation

$$\Delta p = \frac{2\,\sigma_w \cos[\Theta]}{r_c} \tag{6.1}$$

is called the capillary pressure and acts as the main driving force for the liquid water in the capillary network. In Eq. 6.1 σ_w is the surface tension, Θ is the contact angle¹ and r_c the pore radius. In case of hydrophobic wettability ($\Theta > 90^{\circ}$ C) of the porous media, the Young-Laplace equation describes that the needed pressure difference for filling the pores decreases with increasing pore size. Since the hydrophobic GDL is not a network of capillaries with uniform pore radius but reveals a characteristic pore size distribution, only pores up to a certain size get flooded at a specific water pressure.

¹The contact angle is the angle between the liquid/vapor interface and the solid surface.



Figure 6.1: Contact angles of $131^{\circ}C-140^{\circ}C$ were measured on the surface of a new untreated Toray TGP-H-090.

The small pores that need a high water pressure for filling remain still free of water and are available for the gaseous reactant transport. Besides the pore radius, the contact angle is the second quantity that strongly influences the capillary pressure and therefore is of major interest for understanding the water transport in GDLs. A standard experimental approach to determine the wettability is measuring the contact angle by the Sessile drop technique. As depicted in Fig. 6.1 a defined droplet is placed on the GDL surface and the angle between the solid and the liquid surface is measured.

The wetting properties of two different GDL materials, a Toray TGP-H-090 and a Freudenberg H2315 I3, were investigated. Measurements of a new Toray TGP-H-090 result in an average contact angle of 136.5°, presented in Alink et al. [7]. The contact angle of the Freudenberg GDL with a value of 134° C is quite similar, indicating at least high hydrophobic properties on the macroscopic GDL surface of both materials. Concerning two-phase transport in the GDL, the question arises whether this measurement technique is more related to the surface structure, roughness, etc. or to the fibers themselves. By taking a look on the distribution of condensed water by means of ESEM imaging (Fig. 6.2), a relationship between the contact angle on the macro scale (GDL surface) and the micro scale (fibers) can not be drawn for the Toray paper. The hydrophobic character on the macro scale is changed to mixed wettability properties on the micro scale. Consequently, a definite qualitative value of the contact angle can not be extracted like it can be done on the macroscopic scale (Fig.6.1).

Figure 6.3 shows a typical sequence of ESEM images during a condensation experiment with the Toray paper. The condensation of the first droplets starts on visually unpredictable positions. On several fibers liquid film formation is observable, which causes merging of water droplets extended over many pores. The surface curvature of the liquid phase is low and only weakly constrained by the pore morphology. Only a few parts of the GDL show hydrophobic properties.

A completely different scenario of the water droplet growth is shown in Fig. 6.4, where



Figure 6.2: The contact angle of the Toray paper on the micro scale shows a completely different characteristic than the contact angle on the macro scale in Fig. 6.1.

a GDL from Freudenberg (H2315I3) is investigated. The whole structure shows a highly hydrophobic behavior. The droplets all show spherical shapes with large contact angles. Water film formation around fibers is not observable and therefore the tendency of large water accumulation is suppressed.

The comparison of the ESEM images with the Sessile drop technique of both materials shows that the contact angle on the macro scale (the droplet covers several fibers) is primarily governed by the surface morphology of the GDL structure, not by the fibers themselves. The same conclusion can be drawn with respect to bubble point measurements², that are also used for characterizing water transport properties of porous media. Similar bubble points were measured for both GDLs (Toray 4.7 kPaand Freudenberg 4.9 kPa) showing that this measurement technique does not reflect the different wetting properties on the micro scale of these GDLs too.

For a constructive design improvement of a flow-field concerning flooding issues, the knowledge of local temperature distribution seems to be important due to the dependency of vapor saturation pressure on the temperature, which in term determines condensation phenomena. Figure 6.5 highlights that the condensation is dependent on the composition of the material as well. Figure 6.5(a) shows the surface of a used Toray paper that faced the CL before disassembling the fuel cell. Some impurities visible on the fibers could be pieces of the electrode quarried out during decomposition. As can be seen in Fig. 6.5(b) these impurities act as condensation nuclei and have a strong influence on when and where were condensation process begins.

²the hydrostatic pressure of a water column test at which a continuous liquid water path through the media is developed



Figure 6.3: A typical sequence of a condensation experiment with a Toray paper. By increasing the vapor pressure in the sample chamber from high vacuum to around 750 Pa condensation starts on the sample that has a temperature of $1^{\circ}C$. Some hydrophilic region, where water film formation is observed, leads to accumulation of large amounts of water.



Figure 6.4: The Freudenberg GDL shows higher hydrophobic behavior than the Toray paper. The growing water droplets did not cover the fibers, thus the large-area filling of cavities is suppressed.



Figure 6.5: Impurities on the GDL fibers can act as condensation nuclei.

6.3 Voltammetry experiments

Since the two GDLs show a completely different characteristic of the wetting properties on the micro scale, both were investigated in-situ by dynamic voltammetry measurements. The experiments were carried out with the small test fuel cell (geometric area of $1 \text{ } cm^2$) and test bench that are both described in Chapter 4. Due to the reference electrode configuration used, a separation of the anode overpotential from the remaining cell losses is possible. This is important for the validation of the fuel cell model (presented in section 6.4) where the anode losses are neglected.

A GORETM PRIMEA[®] Series 5510 MEA with a membrane thickness of $35 \,\mu m$ was used in both cases. For analyzing water transport, flooding effects and membrane dehydration, dynamic measurements were performed to gain insight into the occurring processes. The current response of the cell was investigated for three different inlet gases humidification conditions, denoted as case (1): $air_{dry}/H_{2_{dry}}$, case (2): $air_{dry}/H_{2_{hum}}$ and case (3): $air_{hum}/H_{2_{hum}}$. Detailed operating conditions such as the dew point temperature of the inlet gases and flow rates are summarized in Table 6.1.

Toray TPG-H-090		case	cathode	anode
gas flow rate:	$\dot{V}_{\Omega}/ml min^{-1}$	(1)-(3)	100 (air)	50 (<i>H</i> ₂)
dew point temperature		(1)	dry	dry
of inlet gases:	T_{DP}^{Ω} / K	(2)	dry	309
		(3)	309	309
coolant temperature:	$T_{coolant} / K$	(1)-(3)	313	313
Freudenberg H2315 I3		case	cathode	anode
gas flow rate:	$\dot{V}_{\Omega}/ml min^{-1}$	(4)/(5)	100/40 (air)	50/20 (<i>H</i> ₂)
dew point temperature		(4)	dry	dry
of inlet gases:	T_{DP}^{Ω} / K	(5)	dry	dry
coolant temperature:	$T_{coolant} / K$	(4)-(5)	313	313

 Table 6.1: Operating conditions in the voltammetry experiments.

Voltammetry experiments were conducted in the cell voltage range between $900 \, mV$ and $60 \, mV$ with a scan rate of $10 \, mV \, s^{-1}$. Several sweeps were applied sequentially to reach and ensure reproducibility of the dynamic characteristic of the voltage-current curve. The cell impedance was recorded at $10 \, kHz$ during all experiments. The temperature was measured with a thermocouple in the anode plate $1 \, mm$ above the flow field.



(a) The Toray paper shows hysteresis behavior both in the low and high current range.

(b) The Freudenberg GDL does not exhibit the hysteresis knee at high current densities.

Figure 6.6: Comparison between the characteristic of dynamic voltammetry measurements with attached GDLs from Toray and Freudenberg.

Figure 6.6 shows a comparison between the characteristic of the dynamic voltammetry measurements with the attached Toray paper (Fig. 6.6(a)) and the Freudenberg GDL (Fig. 6.6(b)) at the same operating conditions (case (3)/(4)). The results show distinct characteristics, that can be correlated to the ESEM images (Fig. 6.3 and 6.4). The polarization curve of the Toray paper shows a stable and reproducible behavior over the whole current density range. A hysteresis behavior is observed both in the low current range and in the high current range, which can be explained by dehydration and flooding effects, as described in detail in section 6.4. The presence of water within the GDL and CL is indicated by the large difference of the performance in forward and backward mode. The response of the saturation to the load current is in the order of seconds.

The polarization curve performed with the Freudenberg GDL does not exhibit the hysteresis knee at high current densities, indicating a lower saturation or much faster transient behavior between drainage and imbibition of the pore structure. Figures. 6.6 (a) and (b) (bottom) also show the recorded cell impedance during the voltammetry sweep. Here, the impedance equipped with the Freudenberg GDL shows a lower dynamic behavior which also indicates a lower saturation change within one potential cycle.



Figure 6.7: Decreasing the air flow rate to $40 \, ml \, min^{-1}$ did not lead to a hysteresis knee at high current densities for the Freudenberg GDL as measured for a Toray paper. The flooding events are rather observed in stochastic breakdowns of the current.

Trying to provoke the hysteresis behavior at high currents by reducing the gas flow (Fig. 6.7) resulted in an unstable operation at high current densities. Since the stochastic breakdowns of the current are not predictable by a temporal decline of the current, which could be correlated with a temporal increase of the saturation of the GDL, it is assumed that suddenly merged droplets within the gas channel block the feed stream for a short time, leading to oxygen starvation until the increasing gas pressure expels the liquid water from the gas channel. Independent on inlet gas humidification or cell temperature, the measured voltage-current curves never showed the hysteresis knee like for the Toray paper. Comparable limiting current density values are observed for both GDLs that seems to be inconsistent to the assumption of a lower saturation value for the Freudenberg GDL. An explanation for this inconsistency could be given by a computational study from Sinha et al [95]. They predict a change of the saturation curvature from a concave shape to a convex one by decreasing the fraction of hydrophilic pores. Thus, the Freudenberg media could have a lower average saturation across the layer whereas having a higher saturation level at the interface to the CL (see Fig.6.8). In case that mass transport in the CL is the limiting process at low cell voltage, no higher limiting current density would be expected, because the saturation level in CL could be as high as for the Toray paper or, even higher.



Figure 6.8: Schematic of convex and concave saturation profiles across the GDL. Sinha et al. [95] predict a change of the shape depending on the fraction of hydrophobic pores.

6.4 Modeling Liquid Water and its Transient Effects in a PEMFC

6.4.1 Introduction

It is known that the cathode of a PEM fuel cell is the limiting component for high performance. The slow kinetics of the oxygen reduction reaction (ORR) lead to a strong decrease of the cell voltage in the low current density region. Additionally, mass transport limitations and instability of the cell voltage occur in the high current density region, where typically liquid water blocks the pathway to the active sites. Therefore, accumulation and transport of liquid water is a major factor in the operation of a lowtemperature PEM fuel cell.

Water is typically introduced through both anode and cathode gas streams, additionally produced by the ORR at the cathode catalyst layer (CCL) and forced to the CCL by electro-osmotic drag from the anode side. An excess of liquid water in the porous media, whereby both the catalyst layer and the gas diffusion layer (GDL) could be concerned, reduces the diffusion path available for the transport of gaseous oxygen or forces oxygen to dissolve and diffuse through water to reach the active sites. This phenomenon is called flooding and it is most problematic in the cathode.

Dissolved water in the ionomer is essential for optimal proton conductivity in the CL and membrane. The conductivity of the ionomer, which consists of a fluorocarbon polymer backbone with chemically bonded sulfonic acid groups as side chains, is a
very strong function of its water content [1]. Dehydration of the ionomer strongly increases the resistance to the proton transport, causing ohmic losses. Additionally, the active area in the CL depends on the amount of dissolved water in the ionomer due to the need of a large three-phase boundary (reactant, electronic and protonic phase) for the redox reaction. This means that the catalyst/carbon support needs to be in contact to the protonic phase, which occurs only if the ionomer is well hydrated. Therefore, increasing the power density of a PEM fuel cell is basically a water management problem. At present, many transport phenomena during fuel cell operation cannot be directly observed or measured. Thus, inverse modeling is a powerful tool to gain qualitative insights into the dynamics of liquid water transport and its effect on fuel cell performance.

Much model development and simulation work has been done in recent years concerning water distribution in a PEM fuel cell to analyze the corresponding loss mechanisms [96, 97, 98, 99, 100, 101, 102, 103, 104, 71, 105]. The models differ strongly in the complexity of the applied physics, the examined components and dimensions of the modeling domains.

One-dimensional models are widely used for testing new modeling approaches because the governing equations can be implemented quickly and the computing time required for parameter studies or time-dependent problems is short [106, 107, 108, 109, 110, 111]. One part of the water management investigations focus on water transport in the membrane forced by diffusion, convection and electro-osmotic drag. Investigations have been made concerning the dependance of the water content distribution on the cell current or its transient behavior while undergoing a load change [112].

Wu et al. [111] developed a 1D, transient PEM fuel cell model to analyze dynamic characteristics corresponding to various changes in working conditions, such as relative humidity or cell voltage. The phenomena of hydration/dehydration is investigated using different membrane types. Overshoots and undershoots are observed, whereas the model does not account for liquid water. Transient analysis of the water content in the membrane was also investigated by Yan et al. [113] with an isothermal, one-phase model. Chen et al. [114] include the effect of membrane swelling in the transient analysis of the water transport in the membrane (vapor and dissolved) and its influence on performance. The influence of liquid water in the CL and GDL on the performance and the interaction of liquid water in the porous media with the dissolved water in the membrane were not considered in these models.

With regard to liquid water, Eikerling [115] developed a detailed cathode model focused only on the catalyst layer (GDL and membrane are not considered). He analyzed the impact of the electrode structure and its physical properties, like wettability, on the liquid water distribution. In doing so, he made the assumption that the electrode consists of a network of agglomerates, similar to [58, 116, 57, 6], highlighting the role of a bimodal pore size distribution for the water distribution. The relative proportion of primary and secondary pores and their wetting properties determine the interplay between reaction and transport processes. With strong simplifications, analytical solutions are shown for three distinct states: a dry state, an optimal wetting state and a fully flooded state. Transient analysis was not done.

Madhusudana et al. [117] present a dynamic agglomerate model, but neglect the effect of liquid water. Overshoot and undershoot behavior of the current density to voltage step changes are attributed to species transportation in the agglomerate structure.

The influence of the cell geometry concerning e.g. channel or shoulder width/length on the saturation distribution in the porous media was analyzed in two-dimensional or three-dimensional CFD models, among others, by [118, 119, 97, 120, 112]. Siegel et al. [120] used an agglomerate approach for the catalyst layer structure in a 2D, twophase model. They investigated the saturation profile in the porous media along the channel and its effect on the cell performance. Therefore, the blockage of the active area by liquid water (saturation *s*) is modeled by the factor (1 - s) in the expression for the reaction kinetics.

Wang and Wang [112] investigate the fuel cell performance under load changes with a 3D, along-the-channel model. The water content distribution is analyzed in terms of the voltage response. The model accounts also for the catalyst layer, but neglects liquid water transport in the porous media.

A three-dimensional analysis of the distribution of reactants and products under the channel and particularly under the rib is done by Berning and Djilali [97]. For simplification, the catalyst layer is assumed to be a spatially non-resolved interface between the membrane and GDL. Maximum saturation values in the cathode GDL of about 10% at a current density of $1.2 A cm^{-2}$, located under the rib towards the CL, are predicted by the model.

The capillary pressure-saturation relationship $p_c[s]$ is modeled by the Leverett J-function, which is the most common approach in two-phase fuel cell models. This approach leads to a strong driving force for the capillary transport of liquid water, resulting in a low saturation level in the case of a fixed saturation of zero at the boundary towards the gas channel. An alternative expression for the capillary pressure-saturation relationship was suggested by Natarajan and Nguyen [118, 119], extracted by fitting an empirical function to the measured $p_c[s]$ -curve of a GDL. The corresponding liquid water diffusion obtained with this expression is four orders of magnitude smaller, which means that extremely high saturation gradients would be necessary in order to induce a flux of liquid water [97]. Thus, the simulation results with a 3D cathode model show high saturation levels close to 1.

A capillary pressure-saturation relationship was also measured by Acosta et al. [121] and fitted to an empirical function. They distinguish between the imbibition and drainage curve, leading to a saturation level of about 0.11 and 0.5 respectively for a conventional gas distributor modeled in 2D.

Kumbur et al. [122] investigated the effectiveness of the Leverett approach. They discuss the existence of immobile saturation and compare different approaches for the

relative permeability (Wyllie, Corey, Brooks-Corey and Van Genuchten model). They also suggest the existence of a saturation discontinuity between two porous media with different porosities and wettabilities (GDL/MPL), discuss the characteristics of a material with mixed wettability and analyze the influence of contact angles on the saturation distribution. A polynomial fit of the $p_c[s]$ -function was made based on experimental pressure curves.

Nam and Kaviany [123] also suggested immobile saturation several years ago. They investigated the tortuosity effect for the case of liquid water present in a GDL and analyzed the enhancement of the saturation level with different material layers of different wettabilities.

A comprehensive 1D transient fuel cell model which accounts for liquid saturation in the GDL and CL, on both the anode and cathode sides, was developed by Ziegler et al. [124]. The model was expanded from the steady-state model of Weber and Newman [36, 37] for time-dependent analysis. Both models account for the Schroeder paradox. Ziegler et al. compared their model against potential sweep experiments. Similar sweep experiments, presented in [125], are used to validate a 1D transient model developed by Shah et al. [126]. The model takes into account the agglomerate structure of the catalyst layers, water in the forms of vapor, liquid and dissolved in the ionomer. A feature of this model is the boundary condition for saturation at the interface GDL \leftrightarrow channel. The assumption of vanishing saturation was abandoned, instead a water flux as a function of the saturation was set. This allows a high saturation level in the case of a low water outflow. To describe the saturation at the interior boundary GDL \leftrightarrow CL, a continuous saturation was assumed contrary to the suggestion of a continuous capillary pressure [123, 122]. This results in a saturation distribution with a maximum value in the catalyst layer.

In the next section a transient PEM fuel cell model, based on the assumptions of [127], where the GDL, CL and membrane are spatially resolved in 1D with an agglomerate approach for the structure of the CL, is presented. Unlike the model of Shah et al. [126], a discontinuity of the saturation due to the continuous capillary pressure is assumed and an immobile saturation due to the mixed wettability of the GDL structure is introduced. The model is validated with experimental data for current response, impedance and temperature evolution during voltammetry measurements.

6.4.2 Model Description

The present model is developed to investigate the dynamic transients of a PEMFC in detail. For this purpose, all components which are responsible for a characteristic response with a certain time constant are considered in the model. These are the cathode gas diffusion layer (GDL) that suffers flooding in the case of insufficient water removal, the cathode catalyst layer (CCL) where the three-phase boundary, the activation overpotential and flooding have a strong influence on the oxygen reduction

reaction (ORR) and the membrane with a conductivity that is highly sensitive to its water content and is thus responsible for ohmic losses. Due to the fast kinetics of the hydrogen oxidation and the high hydrogen diffusivity, the polarization losses on the anode side are neglected in the model. The anode is treated as a spatially reduced interface for the boundary conditions. To obtain a realistic temperature distribution within the membrane electrode assembly (MEA), the latter is sandwiched between two model domains that serve for the bipolar plates (BPs).

Altogether, the model consists of 5 model domains (Ω) which are schematically depicted in Fig. 6.9. All layers are normalized to a thickness of one for both the numerical applications and for better visualization. The real thickness is denoted by L^{Ω} .



Figure 6.9: Schematic diagram of the model domains. The white arrows depict the domains where the solving variables are defined. The catalyst layer (CL) consists of a network of agglomerates where the oxygen reduction reaction takes place. When water is present in the CL, it is assumed that the water covers the agglomerates in the form of a thin water film which causes an additional mass transport resistance for the reactant.

Considering one agglomerate

Experimental data of Ihonen et al. [65] suggest an agglomerated structure in the catalyst layer with a bimodal pore size distribution. Carbon particles supporting the catalyst (10 - 20 nm radius) agglomerate to form clusters (agglomerates), which are filled with ionomer acting as a binder. The resulting ionomer-flooded pores with a

radius of about 3 - 10 nm (called primary pores) enable proton conductivity and diffusion of dissolved reactants in the agglomerates. The larger pores between neighboring agglomerates are called secondary pores (10 - 50 nm). The ORR take place inside the agglomerates where the carbon-supported catalyst forms a three-phase boundary together with the ionomer and the dissolved oxygen. It is assumed that the agglomerates are spherically shaped with a mean radius R_a and homogeneously distributed in the CL. The contact between the agglomerates is sufficient to ensure the free flow of protons and electrons. The tortuosity of the flow path is included in the calculation by a Bruggeman correction. Before the oxygen reaches the catalyst in the applomerates, it has to dissolve in the ionomer and diffuse to the active sites. In the presence of liquid water in the secondary pores of the CL, water covers the hydrophilic part of the agglomerates which is the ionomer phase. For mathematical simplification, it is assumed that the water covers the entire agglomerate and forms a thin water film surrounding the agglomerates with a layer thickness d. This implies an additional transport barrier for the oxygen. The oxygen first has to dissolve in water, then diffuse through the water film to reach the ionomer of the agglomerate where the reaction can take place by diffusing to the active sites.

The diffusion of dissolved oxygen is described by Fick's law

$$j_{O_2}^{\nu}[r] = -D_{O_2}^{\nu} c_{O_2,s}^d \frac{\partial \tilde{c}_{O_2}^d[r]}{\partial r} , \qquad (6.2)$$

where $j_{O_2}^{\nu}$ is the oxygen flux in the medium ν ($\nu = \underline{w}$ ater/ \underline{a} gglomerate), $D_{O_2}^{\nu}$ is the effective oxygen diffusion coefficient in the medium ν and $\tilde{c}_{O_2}^d$ the normalized dissolved oxygen concentration referred to the dissolved oxygen concentration on the water-film surface $c_{O_2,s}^d$ (interface void - water film)

$$\tilde{c}_{O_2}^d[r] = \frac{c_{O_2}^d[r]}{c_{O_2,s}^d} \,. \tag{6.3}$$

The distance from the center of the agglomerate is denoted by the spherical coordinate r in brackets. The dissolved oxygen concentration on the water-film surface is calculated from the gaseous oxygen concentration $c_{O_2,s}^g$ above the water film in the secondary pores of the CL using Henry's law

$$c_{O_2,s}^d = H c_{O_2,s}^g , (6.4)$$

where *H* is known as the Henry constant [70]. The effective oxygen diffusion coefficient $D_{O_2}^a$ in the agglomerate is calculated by the Bruggeman correlation

$$D_{O_2}^a = \epsilon_a^{1.5} \ D_{O_2}^i. \tag{6.5}$$

where ϵ_a is the fraction of primary pores filled with ionomer and $D_{O_2}^i$ is the diffusion coefficient of dissolved oxygen in the ionomer. The diffusion coefficient of dissolved oxygen in the water film is used from bulk water diffusion at 60°C (in m^2s^{-1}) according to Bird, Stewart and Lightfoot [128]

$$D_{O_2}^w = 4.82 \cdot 10^{-9} . \tag{6.6}$$

The oxygen mass balance is given by Eq. 6.7. Oxygen is not consumed in the water film, whereas the oxygen is reduced in the agglomerate by the ORR described by Tafel kinetics

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 j_{O_2}^{\nu}[r] \right) = \begin{cases} 0 & \text{if} \quad R_a < r \le R_a + d \\ -k_0 \lambda \ c_{O_2,s}^d \ \tilde{c}_{O_2}^d[r] \ e^{\frac{\alpha n F \eta}{RT}} & \text{if} \quad 0 \le r \le R_a \ , \end{cases}$$
(6.7)

where k_0 is the reaction rate, α the symmetry factor, *n* the number of transferred electrons, *R* the gas constant and *T* the local temperature. Following Andreaus et al. [129] and Vielstich et al. [130], who both suggest a dependance of the transfer resistance and reaction rate on the ionomer water content and water activity, respectively, a linear dependancy of the ORR rate on the ionomer water content λ (definition see section 6.4.2) is introduced.

The following boundary conditions are used to calculate the current production per agglomerate.

• The concentration of dissolved oxygen on the surface of the water film is related to the local gaseous oxygen concentration in the secondary pores by Henry's law and here assumed as known. The normalized concentration is set to one

$$\tilde{c}_{O_2}^d[R_a+d] = 1$$
 . (6.8)

• A continuous oxygen concentration at the interface water film $[R_a^+] \leftrightarrow$ agglomerate $[R_a^-]$

$$\tilde{c}_{O_2}^d[R_a^+] = \tilde{c}_{O_2}^d[R_a^-] .$$
(6.9)

• A continuous oxygen flux at the interface water film $[R_a^+] \leftrightarrow$ agglomerate $[R_a^-]$

$$j_{O_2}^w[R_a^+] = j_{O_2}^a[R_a^-] . ag{6.10}$$

• A vanishing oxygen flux in the center of the agglomerate

$$\frac{\partial \tilde{c}_{O_2}^d[0]}{\partial r} = 0 . \tag{6.11}$$

An analytical solution for the oxygen flux $j_{O_2}[R_a, y]$ at the agglomerate surface ($r = R_a$) as a function of the local overpotential $\eta[y]$, water film thickness d[y] and dissolved

oxygen concentration on the surface $c_{O_2,s}^d[y]$ can be found. Using Faraday's law, the current generation of one agglomerate can be calculated by integrating the oxygen flux over the agglomerate surface ∂S

$$j_{gen}^{a}[y] = \oint_{\partial S} 4 \ F \ \vec{j}_{O_{2}}[R_{a}, y] \cdot d\vec{A} = \frac{4 \pi R_{a} 4 F c_{O_{2},s}^{d}[y] D_{O_{2}}^{w} D_{O_{2}}^{a} (1 + d[y]) (-1 + \Sigma \operatorname{coth}[\Sigma])}{d[y] D_{O_{2}}^{a} \Sigma \operatorname{coth}[\Sigma] + d[y] (D_{O_{2}}^{w} - D_{O_{2}}^{a}) + D_{O_{2}}^{w}}$$
(6.12)

where

$$\Sigma = R_a \sqrt{\frac{k_0 \lambda e^{\frac{\alpha n F \eta[y]}{RT}}}{D_{O_2}^a}}$$
(6.13)

is known as the Thiele modulus [131].

The relationship between the local water-film thickness d[y] and the saturation s[y] of the secondary pores in the CL can be determined by the following calculation.

Considering a unit cell with the volume of one spherical agglomerate $(V_a = \frac{4}{3}\pi R_a^3)$ and the surrounding void space (secondary pores) per agglomerate V_p^{dry} , the porosity of the CL can be determined by

$$\epsilon_p^{CL} = \frac{V_p^{dry}}{V_p^{dry} + V_a} \,. \tag{6.14}$$

From this it follows

$$V_p^{dry} = \frac{V_a \ \epsilon_p^{CL}}{\epsilon_p^{CL} - 1} \ . \tag{6.15}$$

The saturation of the secondary pores in the CL is expressed by the ratio of the volume of the thin water film V_{wf} to the secondary pore volume in the dry state

$$s = \frac{V_{wf}}{V_p^{dry}} , \qquad (6.16)$$

where

$$V_{wf} = \frac{4\pi}{3} ((R_a + d)^3 - R_a^3) .$$
(6.17)

Inserting Eq. 6.15 and 6.17 into Eq. 6.16, a relationship between the water film thickness (surrounding the agglomerates) and the saturation of the CL at the local y-position is obtained

$$d[y] = R_a \left(-1 + \frac{\left((\epsilon_p^{CL} - 1)^2 \left(1 + (s[y] - 1) \ \epsilon_p^{CL} \right) \right)^{\frac{1}{3}}}{1 - \epsilon_p^{CL}} \right) .$$
(6.18)

Combining Eq. 6.18 and 6.12 results in the current generation of an agglomerate $j_{gen}^{a}[y]$ as a function of the local overpotential, gaseous oxygen concentration and saturation. The analytical expression for $j_{gen}^{a}[y]$ is used in the following as source/sink terms for the continuity equations of the oxygen concentration and the overpotential in the homogeneous model of the cathode CL that are described in the next sections.

Activation and ohmic overpotential

The activation overpotential η is the driving force for the ORR and is defined as the deviation of the difference of the electronic potential Φ^e and protonic potential Φ^p from the theoretical open circuit potential $\Delta \Phi^0 = 1.23 V$

$$\eta = \Delta \Phi^0 - (\Phi^e - \Phi^p) . \tag{6.19}$$

The total overpotential of a fuel cell is the sum of the activation overpotential in the catalyst layers and the ohmic overpotentials due to finite conductivity of the fuel cell components and contact resistances at the interfaces of the different layers.

The model takes into account the activation overpotential in the cathode CL, proton migration in the cathode CL and in the membrane. The local change in electronic potential in the CL is negligible compared to the change of the protonic potential due to a much higher electrical conductivity of the carbon matrix than the proton conductivity of the ionomer and is thus assumed to be constant through the CL. The anode activation overpotential is also neglected due to the fast kinetics of the hydrogen oxidation reaction. The above described ohmic overvoltages of the electrons in the GDLs and BPs as well as the contact resistances are summarized into one model domain, more precisely into the anode bipolar plate (ABP), and modeled with a constant conductivity ity $\sigma_{contact}$.

Ohm's law is used for the description of the charge flux

$$j_{p,e} = -\frac{\sigma^{\Omega}}{L^{\Omega}} \frac{\partial \eta}{\partial y} , \qquad (6.20)$$

where the superscript Ω stands for the model domain (CL, membrane and ABP). The proton conductivity of the ionomer phase depends on the water content λ and is defined according to Springer et al. [1]

$$\sigma^{\Omega} = \begin{cases} \epsilon_i^{1.5} \left(0.514 \,\lambda - 0.326 \right) e^{1268(\frac{1}{303} - \frac{1}{T})} & \text{if} \quad \Omega = \{ L^{CL}, L^{mem} \} \\ \sigma_{contact} & \text{if} \quad \Omega = L^{ABP} \end{cases}$$
(6.21)

For the ionomer volume fraction in the membrane, a value of $\epsilon_i = 1$ is used and in the catalyst layer $\epsilon_i = \epsilon_i^{CL}$, whereas a Bruggeman correction accounts for the reduction of the pathway for the protons in the CL.

The charge balance equation reads

$$\frac{\partial j_{p,e}}{\partial y} = \begin{cases} L^{CL} \left(-q_{ORR} - C_{DL} \frac{\partial \eta}{\partial t} \right) & \text{if} \quad \Omega = L^{CL} \\ 0 & \text{if} \quad \Omega = \{L^{mem}, L^{BP2}\} \end{cases},$$
(6.22)

where C_{DL} is the double layer capacity and q_{ORR} is the current generation per agglomerate j_{agglo} multiplied by the agglomerate density Λ in the CL

$$q_{ORR} = j_{aen}^a * \Lambda . \tag{6.23}$$

The agglomerate density is determined by the agglomerate volume and the void space

$$\Lambda = \frac{1}{V_a + V_p^{dry}} = \frac{3\left(1 - \epsilon_p^{CL}\right)}{4\pi R_a^3} \,. \tag{6.24}$$

Water content

The water content of the ionomer is defined as the ratio of the number of water molecules to the number of charge sites (SO_3^-) in the cathode catalyst layer and in the membrane. The flux of dissolved water in the ionomer j_{λ} is determined by diffusion and electro-osmotic drag

$$j_{\lambda} = \underbrace{-\frac{\epsilon_{i}^{1.5} \rho_{i} D_{\lambda}^{i}}{EW L^{\Omega}} \frac{\partial \lambda}{\partial y}}_{\text{diffusion}} + \underbrace{\frac{\alpha_{drag}}{F} j_{p}}_{\text{electro-osmotic drag}}, \qquad (6.25)$$

where EW and ρ_i denote the equivalent weight and the density of the ionomer, respectively. The diffusion is forced by the gradient of the dissolved water concentration in terms of the water content. It is assumed that the diffusion coefficient is a function of the water content according to [132]

$$D_{\lambda}^{i} = 2.1 \cdot 10^{-7} \,\lambda \, e^{-\frac{2436}{T}} \,. \tag{6.26}$$

The electro-osmotic drag coefficient in the second term on the right-hand side is defined as

$$\alpha_{drag} = \frac{2.5\lambda}{22} . \tag{6.27}$$

The mass conservation equation describes the change in the dissolved water flux

$$\frac{\partial j_{\lambda}}{\partial y} = L^{\Omega} \left(q_{ad} - q_{ur} + \frac{q_{ORR}}{2F} - \frac{\epsilon_i \rho_i}{EW} \frac{\partial \lambda}{\partial t} \right) , \qquad (6.28)$$

coupled with phase transition and water generation. The adsorption of water vapor into the ionomer at a water content below the equilibrium water content λ_{eq} (Eq. 6.30) and the desorption in the inverse case follows

$$q_{ad} = \begin{cases} k_{ads} c_v^* c_v \left(\lambda_{eq} - \lambda\right) \left(1 - s\right) & \text{if} \quad \lambda \le \lambda_{eq} \\ k_{des} \frac{\rho_i}{EW} \left(1 - s\right) \left(\lambda_{eq} - \lambda\right) \left(1 - RH\right) & \text{if} \quad \lambda > \lambda_{eq} \ \land \ RH \le 1 \ , \end{cases}$$
(6.29)

where k_{ads} and k_{des} are the adsorption and desorption constants, respectively. The equilibrium water content is a function of the water activity (a_w) given by Springer et al. [1], where the water activity is equal to the relative humidity RH.

$$\lambda_{eq}[a_w] = 0.043 + 17.81a_w - 39.85a_w^2 + 36.0a_w^3 \,. \tag{6.30}$$

Water vapor concentrations c_v^* and c_v are defined in section 6.4.2.

According to the cluster-network model of Weber and Newmann [36, 37], a maximum water uptake of the ionomer up to $\lambda_v^{max} = 14$ (given by Eq. 6.30 at RH = 100 %) is assumed if the membrane is in contact with water vapor. In the case of liquid water on the membrane surface, ionomer restructuring due to expanding hydrophobic channel occurs, resulting in a maximum water content of $\lambda_l^{max} = 22$. The fraction of expanded channels and thus the water content is a strong function of the existing capillary pressure p_c^i in the ionomer. A relationship is suggested by Weber and Newmann [37]

$$\lambda[p_c] = \lambda_v^{max} + \frac{1}{2} \left(\lambda_l^{max} - \lambda_v^{max} \right) \left(1 - \operatorname{erf} \left[\frac{\ln[-1.6 \, \sigma_w \, \cos[\Theta_m]] - \ln[10^5 \, p_c^i]}{0.3 \, \sqrt{2}} \right] \right) \,, \quad \text{(6.31)}$$

where erf is the error function. The uptake of liquid water by the ionomer if the capillary pressure p_c^{CL} in the secondary pores of the CL (defined in section 6.4.2) is higher than in the pore network of the ionomer p_c^i and the liquid water release from the ionomer in the inverse case is given by

$$q_{ur} = \begin{cases} k_u \left(p_c^i - p_c^{CL} \right) & \text{if} \quad p_c^i \le p_c^{CL} \\ k_r \left(p_c^i - p_c^{CL} \right) & \text{if} \quad p_c^i > p_c^{CL} \end{cases}$$
(6.32)

The phase transition of water in the CL together with the physically relevant conditions are illustrated in Fig. 6.10.

It is assumed that the ORR produces water in dissolved form $q_{ORR}/2F$. A water accumulation term accounts for the time dependance. The source/sink terms are confined in the CL and vanish in the membrane.

Saturation

The saturation *s* is defined in the GDL and CL as the volume of liquid water divided by the volume of secondary pores in the dry state. A high saturation reduces the



Figure 6.10: Schematic of the phase transition between water vapor, liquid water and dissolved water. The driving forces are the vapor pressure vs. saturation pressure, capillary pressure in the secondary pores vs. the capillary pressure in the ionomer and the water activity vs. the equilibrium water content.

flow pathway for the oxygen in the porous media that finally results in an increased mass transport resistance. The transport of the liquid water in a porous media is not completely understood but it is well known that the flow in (both hydrophilic and hydrophobic) porous media occurs always from the higher saturation region towards the lower saturation region. The gradient of the capillary pressure is mostly stated as the dominant force for the water transport. I use Darcy's law for modeling the liquid water transport in porous media

$$j_s = -\frac{K_{abs}^{\Omega} K_{rel}}{L^{\Omega} \mu} \frac{\partial p_c}{\partial y} , \qquad (6.33)$$

where K_{abs}^{Ω} is the absolute permeability and μ is the water viscosity. The relative permeability K_{rel} and the capillary pressure p_c are sensitive functions of the saturation. There is no consensus in the description of the functional variation of the capillary pressure with saturation $p_c[s]$. The most common approaches are the Leverett Jfunction, the Van Genuchten model [133] and the Brooks-Corey model [134, 135] which all have their origin in hydrology (ground water simulation, water/oil flow in unconsolidated rock, etc.). Natarajan et al. [118] suggest a simple exponential approach, agreeing with observed polarization curves.

Environmental scanning electron microscope (ESEM) images of a Toray TGP-H-090 clearly show a mixed wettability of the fiber structure with hydrophobic regions and hydrophilic regions (Fig. 6.11). This leads to the assumption of immobile saturation

 (s_{im}) in the model description. Starting from a completely dry GDL, generated liquid water from the CL first fills all the hydrophilic parts of the adjacent GDL pores. If these hydrophilic pores are filled, the local saturation exceeds s_{im} and the water moves by capillary force towards the lower saturation region, where again the hydrophilic pores get filled first. If all hydrophilic regions of the GDL are filled with liquid water then a mobile phase continuity from CL to the gas channel is reached. Below the threshold of s_{im} , water occupying the hydrophilic pores has to evaporate for saturation to decrease further. For the expression of $p_c[s]$ we followed the most widely employed



Figure 6.11: ESEM image of a Toray TGP-H-090 GDL shows partly hydrophilic regions, leading to the model assumption of immobile saturation.

form, the Leverett J-function, but considering the immobile saturation, in the modified form suggested in [123]

$$p_c^{\Omega} = \sigma_w \, \cos[\Theta^{\Omega}] \, \sqrt{\frac{\epsilon_p^{\Omega}}{K_{abs}^{\Omega}}} \, J^{\Omega}[s] \;, \tag{6.34}$$

whereby the saturation of the empirical J-function, originally proposed by Udell [136], is replaced by $\frac{s-s_{im}}{1-s_{im}}$:

$$J^{\Omega}[s] = 1.417 \left(\frac{s - s_{im}^{\Omega}}{1 - s_{im}^{\Omega}}\right) - 2.12 \left(\frac{s - s_{im}^{\Omega}}{1 - s_{im}^{\Omega}}\right)^2 + 1.263 \left(\frac{s - s_{im}^{\Omega}}{1 - s_{im}^{\Omega}}\right)^3$$
(6.35)

The difference to the original approach can be seen in Fig. 6.12.

I assume a continuous capillary pressure p_c at the interface between CL \leftrightarrow GDL. Due to the different pore size distribution, porosity and wetting properties (contact angle) of the two media (CL/GDL), a continuous capillary pressure results in a discontinuous

saturation distribution across the interface [123, 122]. Using the chain rule for the derivation of the capillary pressure $\frac{\partial p_c}{\partial y} = \frac{\partial p_c}{\partial s} \frac{\partial s}{\partial y}$, Darcy's law (Eq. 6.33) can be written as a simple diffusion equation for the saturation

$$j_s = -\frac{D_s^{\Omega}}{L^{\Omega}} \frac{\partial s}{\partial y}$$
(6.36)

where the diffusion coefficient itself is a function of the saturation

$$D_s^{\Omega} = \frac{K_{abs}^{\Omega} K_{rel}}{\mu} \frac{\partial p_c^{\Omega}}{\partial s} , \qquad (6.37)$$

with a relative permeability following the cube of saturation

$$K_{rel} = (s - s_{im})^3 . ag{6.38}$$



Figure 6.12: A scaled Leverett function is applied for the capillary pressure-saturation relationship.

The continuity equation yields

$$\frac{\epsilon_p^{\Omega}}{\nu_w} \frac{\partial j_s}{\partial y} = L^{\Omega} \left(q_{ec}^{\Omega} + q_{ur} - \frac{\epsilon_p^{\Omega}}{\nu_w} \frac{\partial s}{\partial t} \right) , \qquad (6.39)$$

where the interfacial mass-transfer rate between water vapor and liquid water q_{ec}^{Ω} is assumed to be proportional to the saturation in the porous media Ω and proportional to the difference between the existing relative humidity and fully humidified gas

$$q_{ec} = \begin{cases} k_{eva} \frac{RT}{\nu_w} s \,\epsilon_p^\Omega \, c_v^* \, (RH-1) & \text{if} \quad RH \le 1\\ k_{con} \, (1-s) \,\epsilon_p^\Omega \, c_v^* \, c_v \, (RH-1) & \text{if} \quad RH > 1 \;. \end{cases}$$
(6.40)

For relative humidity (*RH*) below 100%, liquid water evaporates (upper term) while for supersaturated gas, water vapor condenses (lower term). The evaporation rate k_{eva} and the condensation rate k_{con} are assumed to be constant [137]. Relative humidity is calculated by the vapor concentration ($c_v \cdot c_v^*$) (defined in section 6.4.2) and the saturation pressure $p^{sat}[T]$ for a given temperature

$$RH = \frac{(c_v \cdot c_v^*) RT}{p^{sat}[T]} , \qquad (6.41)$$

with a saturation pressure (in Pa) according to [1]

$$\log_{10} \left[\frac{p^{sat}[T]}{101325} \right] = -2.1794 + 0.02953 \left(T - 273.15 \right) - 9.1837 \cdot 10^{-5} \left(T - 273.15 \right)^{2} + 1.4454 \cdot 10^{-7} \left(T - 273.15 \right)^{3}.$$
(6.42)

Oxygen concentration

The oxygen concentration is defined in the CL and GDL. Simple Fick diffusion is used for the oxygen flux

$$j_{O_2}^g = -\frac{D_{O_2}^{eff,\Omega} c_{O_2}^{g*}}{L^{\Omega}} \frac{\partial c_{O_2}^g}{\partial y}$$
(6.43)

where $c_{O_2}^g$ is the normalized gaseous oxygen concentration referred to the oxygen concentration at the boundary to the gas channel $c_{O_2}^{g*}$, calculated by the ideal gas law with the known oxygen partial pressure p_{O_2} at the cell inlet and the channel temperature T_{ch}

$$c_{O_2}^{g*} = \frac{p_{O_2}}{R \, T_{ch}} \,. \tag{6.44}$$

The values of the GDL porosity published in fuel cell models are prevalently below 0.5 [114, 6, 107, 138, 113]. According to the manufacturer, common GDLs have a porosity higher than 0.7 in the uncompressed state [139]. The discrepancy between these two values can not only be explained by the high compression level in the assembled cell. The answer can be found in the model assumptions. A single-phase model (1,2 or 3D) does not account for liquid water occupying a part of the void space which results in a lowered effective porosity [140, 6]. A two-phase 1D model needs a low porosity as a model parameter to account for in-plane inhomogeneities

not only over the entire MEA but also on the scale of a few millimeters as a result of shadowing in the rib \leftrightarrow channel geometry. A simple diffusion simulation in 2D shows that the shadowing by the rib results in minimized apparent porosity for a reduced 1D model.

The effective oxygen diffusivity accounts therefore not only for the porosity (with a realistic value) and the local saturation but also for the spatial reduction to a 1D model with the geometry factor Ξ

$$D_{O_2}^{eff,\Omega} = \left(\Xi \,\epsilon_p^{\Omega} \,(1-s)\right)^{1.5} D_{O_2}^g \,. \tag{6.45}$$

The temperature and pressure dependance of the free oxygen diffusivity follows the Chapman-Enskog formula [128]

$$D_{O_2}^g = 3.2 \cdot 10^{-5} \left(\frac{T}{353}\right)^{1.5} \frac{1}{P} .$$
 (6.46)

Taking the reaction into account, the mass balance yields

$$\frac{\partial j_{O_2}^g}{\partial y} = L^\Omega \left(-\frac{q_{ORR}}{4F} - \epsilon_p^\Omega \left(1 - s \right) c_{O_2}^{g*} \frac{\partial c_{O_2}^g}{\partial t} \right) \,. \tag{6.47}$$

Water vapor concentration

The governing equation for the vapor flux j_v in the porous media is given by

$$j_v = -\frac{D_v^{eff,\Omega} c_v^*}{L^\Omega} \frac{\partial c_v}{\partial y} , \qquad (6.48)$$

where c_v is the normalized vapor concentration referred to the inlet vapor concentration c_v^* . The latter is calculated by the saturation pressure p^{sat} (Eq. 6.42) for a given humidification temperature T_{DP}^c of the cathode humidifier applying the ideal gas law

$$c_v^* = \frac{p^{sat}[T_{DP}^c]}{RT} . ag{6.49}$$

The effective diffusion coefficient $D_v^{eff,\Omega}$ accounts for the porosity of the porous media by the Bruggeman correlation and the clogging of liquid water, which hinders vapor diffusion. The factor Ξ accounts for the shadowing effects of the rib in a real fuel cell (see section 6.4.2)

$$D_v^{eff,\Omega} = \left(\Xi \epsilon_p^{\Omega} \left(1 - s\right)\right)^{1.5} D_v^g , \qquad (6.50)$$

where D_v^g is the temperature-dependent diffusivity in a non-porous condition according to Um and Wang [69]

$$D_v^g = 7.35 \cdot 10^{-5} \left(\frac{T}{353}\right)^{1.5} \frac{1}{P}$$
 (6.51)

The mass conservation equation can be expressed as

$$\frac{\partial j_v}{\partial y} = L^{\Omega} \left(-q_{ad} - q_{ec}^{\Omega} - \epsilon_p^{\Omega} (1-s) c_v^* \frac{\partial c_v}{\partial t} \right)$$
(6.52)

where adsorption/desorption q_{ad} , evaporation/condensation q_{ec} and a water vapor accumulation term are included.

Temperature

The heat flux is described by conduction in the solid media and by convection in the form of liquid water, defined in all five layers. Heat convection by the gas flux is neglected. The resulting equation for the heat flux is

$$j_{T} = \underbrace{-\frac{\kappa^{\Omega}}{L^{\Omega}}\frac{\partial T}{\partial y}}_{conduction} + \underbrace{\epsilon_{p}^{\Omega} s C_{w} T j_{s}}_{convection by liq. water}, \qquad (6.53)$$

where κ^{Ω} is the thermal conductivity of the medium Ω and $C_i = \rho_i c_i$ is the product of the density of the species *i* and the specific heat capacity. The energy equation reads

$$\frac{\partial j_T}{\partial y} = L^{\Omega} \left(q_h^{\Omega} - C^{\Omega} \frac{\partial T}{\partial t} \right) , \qquad (6.54)$$

where the source term q_h^{Ω} stands for Joule heating, latent heat or reaction and activation loss, depending on the model domain Ω .

In the cathode bipolar plate, Joule heating by the cell current i_{cell} due to the finite electrical conductivity $\sigma_{contact}$ is assumed

$$q_h^{CBP} = L^{CBP} \frac{i_{cell}^2}{4\,\sigma_{contact}}\,,\tag{6.55}$$

where the total electrical and contact resistance (see section 6.4.2) is split into components for the cathode BP (25%), the cathode GDL (25%) and the anode BP (50%, including the anode GDL).

Joule heating and latent heat caused by the phase transition in the GDL yields

$$q_h^{GDL} = L^{GDL} \left(\frac{i_{cell}^2}{4\,\sigma_{contact}} + h_{gl}\,q_{ec} \right) \,. \tag{6.56}$$

In the CL, the reaction heat of the ORR is the dominant factor, but also latent and ohmic heat is included

$$q_{h}^{CL} = L^{CL} \left(\underbrace{\left(\frac{\Delta S T}{4} + F \eta\right) \frac{q_{ORR}}{F}}_{reaction \ heat} + \underbrace{h_{gl} q_{ec}}_{latent \ heat} \right) - \underbrace{j_{p} \frac{\partial \eta}{\partial y}}_{ohmic \ heat}$$
(6.57)

Proton migration in the membrane produces heat due to the finite protonic conductivity

$$q_h^{Mem} = -j_p \frac{\partial \eta}{\partial y} . \tag{6.58}$$

The heat production in the anode bipolar plate corresponds to that of the cathode BP

$$q_h^{ABP} = L^{ABP} \frac{i_{cell}^2}{2\,\sigma_{contact}} \,. \tag{6.59}$$

The heat capacity C^{Ω} of certain domains Ω are listed below, where the newly introduced subindices (*tit* and *c*) stand for titanium and carbon.

$$\begin{array}{ll} \mathsf{CBP:} & C^{CBP} = C_{tit} \\ \mathsf{GDL:} & C^{GDL} = \epsilon_p^{GDL} \, s \, C_w + \epsilon_p^{GDL} (1-s) C_{air} + (1-\epsilon_p^{GDL}) C_c \\ \mathsf{CL:} & C^{CL} = \epsilon_p^{CL} \, s \, C_w + \epsilon_p^{CL} (1-s) C_{air} + (1-\epsilon_p^{CL}) C_c \\ \mathsf{Mem:} & C^{mem} = C_{mem} \\ \mathsf{ABP:} & C^{ABP} = C_{tit} \end{array}$$

$$\begin{array}{l} \mathsf{(6.60)} \end{array}$$

Boundary conditions

For the discussion of the boundary conditions, refer to Fig. 6.9 where the solving variables and their area of validity are indicated. If nothing else is stated, continuity in the solving variable and continuous flux at the interior boundaries is assumed. **Overpotential** η : Since the protons are not allowed to penetrate into the GDL, their flux at this interface (y = 0) is taken to be zero

$$\frac{\partial \eta[0]}{\partial y} = 0 . \tag{6.61}$$

At the boundary of the anode bipolar plate (y = 3), the overpotential is set to a value dependent on the simulated cell voltage U

$$\eta[3] = 1.23 \ V - U - \eta_a \tag{6.62}$$

where η_a is the anode overpotential which is not calculated in the model but can be extracted from the experimental data for reference electrodes [15].

Oxygen concentration $c_{O_2}^g$: The average oxygen concentration at the interface GDL \leftrightarrow flow channel depends strongly on the stoichiometry and flow rate due to oxygen consumption along the channel. To take the air flow rate \dot{V}_c into account, a Cauchy-type boundary condition is chosen

$$j_{O_2}^g[-1] = \dot{V}_c \,\Omega_{O_2}^c \, c_{O_2}^{g*} \, (1 - c_{O_2}^g) \,. \tag{6.63}$$

It gives a relationship between the air flow rate, the deviation of the normalized oxygen concentration from 100% and a specific oxygen transfer coefficient $\Omega_{O_2}^c$, chosen large enough that $c_{O_2}^g$ never falls below 90%, even for a high load (which is realistic for small test fuel cells).

It is assumed that the membrane is an impermeable barrier for gaseous oxygen which implies zero flux at y = 1

$$\frac{\partial c_{O_2}^g[1]}{\partial y} = 0 . \tag{6.64}$$

Water vapor concentration c_v : The flux boundary condition for the water vapor concentration is defined similarly to the oxygen concentration described above

$$j_v[-1] = \dot{V}_c \,\Omega_v^c \, c_v^* \, (1 - c_v) \,, \tag{6.65}$$

where Ω_v^c is the specific water vapor transfer coefficient at the interface GDL \leftrightarrow channel. As for oxygen, the membrane is also impermeable for the water vapor

$$\frac{\partial c_v[1]}{\partial y} = 0 . \tag{6.66}$$

Water content λ : Since dissolved water, in terms of λ , has no transport mechanism in the gas diffusion layer, its flux is taken to be zero at the interface between CL and GDL

$$\frac{\partial \lambda[0]}{\partial y} = 0 . \tag{6.67}$$

The boundary condition for the water content on the anode side is extremely complex and needs a detailed explanation. In consideration of the fact that on the anode



Figure 6.13: The schematic diagram of a spatially resolved anode illustrates the vapor distribution in the cases of desorption (dashed) and adsorption (solid). The reduced anode interface accounts for ad-/desorption and water vapor diffusion, implemented as a lumped boundary condition.

side, neither the catalyst layer nor the gas diffusion layer is spatially resolved, the relevant transport mechanism and phase transitions therein have to be reduced to an interface with a sophisticated boundary condition. For better understanding of the layer reduction to a simplified interface, an illustration of the local variables is given in Fig. 6.13. In order to allow dehydration of the ionomer on the anode side, the water content λ is not fixed to a certain value but a Cauchy-type boundary condition is used as follows.

The equilibrium water vapor partial pressure at the membrane surface $p_v^{a,mem}$ for a given water content at the anode interface ($\lambda[2]$) is calculated by means of the inverse function $\lambda_{eq}^{-1}[a_w]$ of Eq. 6.30 and the saturation pressure $p^{sat}[T]$

$$p_v^{a,mem} = p^{sat}[T] \,\lambda_{eq}^{-1}[a_w] \,. \tag{6.68}$$

The vapor pressure can be converted by means of the ideal gas law to a vapor concentration

$$c_v^{a,mem} = \frac{p_v^{a,mem}}{RT} . \tag{6.69}$$

Neglecting vapor diffusion in the catalyst layer, the CL thickness is used for a simple adsorption/desorption region, where a linear dependance of the adsorption/desorption process on the difference between the equilibrium vapor concentration $c_v^{a,mem}$ at the membrane surface and the existing vapor concentration $c_v^{a,GDL}$ between CL and GDL is assumed. The vapor flux at the boundary CL \leftrightarrow GDL can be written as

$$j_{ad}^{a} = L^{CL} k_{ad}^{a} (c_{v}^{a,GDL} - c_{v}^{a,mem}) , \qquad (6.70)$$

where L^{CL} is the anode CL thickness and k^a_{ad} the adsorption/desorption rate, expressed as

$$k_{ad}^{a} = \begin{cases} 5 \cdot 10^{-5} k_{des} & \text{if } c_{v}^{a,mem} > c_{v}^{a,GDL} \\ 5 \cdot 10^{-5} k_{ads} & \text{if } c_{v}^{a,mem} \le c_{v}^{a,GDL} \end{cases}$$
(6.71)

The vapor diffusion in the GDL, forced by the vapor concentration gradient, is written as

$$j_{diff}^{a} = -D_{v}^{eff,\Omega} \, \frac{(c_{v}^{a,cha} - c_{v}^{a,mem})}{L_{GDL}} \,, \tag{6.72}$$

where $D_v^{eff,\Omega}$ is the effective vapor diffusion coefficient and $c_v^{a,cha}$ is the vapor concentration in the anode channel.

The condition of continuity of both fluxes, provided that there is no phase change in the GDL, results in

$$j_{ad}^{a} = j_{diff}^{a} = \frac{-D_{v}^{g} \left(c_{v}^{a,mem} - c_{v}^{a,cha}\right) L^{CL} k_{ad}^{a}}{D_{v}^{g} + L^{CL} k_{ad}^{a} L^{GDL}} .$$
(6.73)

As a boundary condition for the water content on the anode side, the dissolved water flux is coupled with the derived vapor flux

$$j_{\lambda} = \frac{-D_v^g \left(c_v^{a,mem} - c_v^{a,cha}\right) L^{CL} k_{ad}^a}{D_v^g + L^{CL} k_{ad}^a L^{GDL}} - \frac{\dot{V}_a}{\nu_g} \Omega_w^a \left(\lambda - 14\right) \theta[\lambda - 14] , \qquad (6.74)$$

where the last term on the right-hand side accounts for the case of high water content $(\lambda > 14)$ when the ionomer releases liquid water, carried out by the hydrogen gas stream. A high value of $\Omega_w^a = 600 \, m^{-2}$ is chosen for fast water release and $\theta[x]$ is the Heavyside function (equal to 1 for x > 0 and 0 elsewhere).

This boundary condition for the water content on the anode side is motivated by experimental data presented in Fig. 6.14(a). The graph shows two comparable cyclic sweep experiments, whereby for one measurement the anode impedance $Z_{a \rightarrow ref}$ and the current density is measured simultaneously (black line) and the second measurement where the cathode impedance $Z_{c \rightarrow ref}$ together with the current density were recorded (red line). The current density response show similar results for both measurements, indicating that both measurements could be compared among each other. Taking a look to impedance show considerable differences. The anode impedance is about





(a) Measured anode impedance $Z_{a \rightarrow ref}$ show a strong coupling between anode dehydration and drawn current density. An increasing anode impedance at high current density is still visible after giving same water droplets into the anodic inlet gas stream.

(b) Schematic shows the effect of a high electro-osmotic drag leading to a decrease of the water content on the anode side in case of an insufficient water uptake of the membrane from the anode gas compartment.

Figure 6.14: The derived boundary condition for the anode water content is motivated by some experimental data that exclude a simple Dirichlet boundary condition.

two time higher than the cathode impedance. Both show a periodic behavior with a doubled frequency as the current density. The impedances increase with increasing current and also increase with decreasing current. The first could be explained by the schematic in Fig. 6.14(b). Assuming a homogeneous water content distribution at a certain level at no-load condition (green line), a strong gradient in the water content towards the cathode could appear in case of a high electro-osmotic drag and water generation at high current that could not get balanced by the water back diffusion (red line). If additionally the vapor adsorption on the anode is insufficient to provide the anode with dissolved water molecules, the anode side would dehydrate (blue line). By making the simplified estimation that the measured anode/cathode impedance refers to the half membrane thickness, one can see that at high currents the water content distribution leads to an increase of the anode impedance (black line in Fig. 6.14(a)). The cathode impedance is not so much affected by the current change because the water content is partly above the homogeneous distribution and party below, leading integrally to a lower current dependance (red line). The scenario of a homogeneous distribution is not stable in time in the experiment. Since less water is generated at low current the membrane dryies out and the impedance increase. After several 100 s some water droplets are admixed into the anodic inlet gas stream that cause a drop in the resistance in both measurements leading to higher peak current density values. One can clearly see that the dehydration peak in the impedance at low current density has almost disappeared (the liquid water acts as buffer), but the dehydration effect at high current density due to the high electro-osmotic drag could not be avoided. By means of the above derived anode boundary condition for the water content, the model is able to capture this measured feature.

Saturation *s*: The accumulation and removal of liquid water on top of the GDL (towards the channel) is a complicated process. Water forms droplets which are blown out by the convective force of the gas stream. The greater the flow velocity in the channel, the more efficient the removal of liquid water. Such a sophisticated dynamic approach can hardly be reproduced in a 1D model. As a strongly simplified approach, an outflow condition for the saturation as a quadratic function of the difference between the saturation itself and the immobile saturation s_{im} is implemented

$$j_{s}[-1] = \begin{cases} -\frac{\dot{V}_{c}}{\nu_{g}} \Omega_{s}^{c} (s - s_{im})^{2} & \text{if} \quad s \ge s_{im} \\ 0 & \text{if} \quad s < s_{im} \end{cases}$$
(6.75)

where the flow rate has a linear influence on the liquid water flux. The interior boundary of the saturation differs from the other solving variables by having a discontinuity in its distribution. Continuous capillary pressure is assumed at the interface GDL \leftrightarrow CL

$$p_c^{GDL}[0] = p_c^{CL}[0], (6.76)$$

which is the physically realistic boundary condition. This results in a saturation discontinuity at the interface (in the case of different structural properties and wettabilities such as porosities and contact angles) but with a continuous liquid water flux

$$j_s^{GDL}[0] = j_s^{CL}[0] . ag{6.77}$$

A zero-flux boundary for liquid water is assumed at the interface $CL \leftrightarrow$ membrane

$$\frac{\partial s[1]}{\partial y} = 0 . \tag{6.78}$$

Temperature T: With regard to the water-cooled fuel cell (which provided the measured data used for the model validation), Cauchy boundary conditions are used that consider a linear dependance of the heat removal on the difference between the temperature at the outer side of the BPs and the cooling-water temperature

$$j_T[-2] = j_T[3] = \Omega_T \left(T - T_{coolant} \right),$$
 (6.79)

where Ω_T is the heat transfer coefficient dependent on the coolant flow rate.

Numerical details

The governing equations are solved using *COMSOL Multiphysics*[™], a commercial software package based on finite element methods. A Direct Linear System Solver (UMFPACK) and quadratic Lagrange polynomials as test functions are used. The solver is allowed to take free time steps. The five model domains are discretized with a non-uniform grid of 265 elements whereas the CL and the regions near the interfaces between the domains are refined with smaller elements.

6.4.3 Experimental

The experiments were made with a small test fuel cell (geometric area of $1 cm^2$) in a test bench that are both described in detail in Gerteisen [15]. Note that, due to the reference electrode configuration used, the anode overpotential is separated from the remaining cell losses, which is important for the validation of a fuel cell model where the anode losses are neglected. An untreated gas diffusion layer of type Toray TGP-H-090 was utilized. A GORETM PRIMEA[®] Series 5510 MEA with a membrane thickness of $35 \,\mu m$ was used. For analyzing water transport, flooding effects and membrane dehydration, dynamic measurements were performed that give a good insight into the processes that occur. Voltammetry and chronoamperometry experiments were used . To prove the validity of the model, the current response of the cell is investigated for three different humidification conditions of the inlet gases, denoted as case (1): $air_{dry}/H_{2_{dry}}$, case (2): $air_{dry}/H_{2_{hum}}$ and case (3): $air_{hum}/H_{2_{hum}}$. Detailed operating conditions such as the dew point temperature of the inlet gases and flow rates are summarized in Table 6.2.

		case	cathode	anode
dew point temperature	T_{DP}^{Ω} / K	(1)	dry	dry
of inlet gases:		(2)	dry	309
		(3)	309	309
coolant temperature:	$T_{coolant} / K$	(1)-(3)	313	313
gas flow rate:	$\dot{V}_{\Omega}/mlmin^{-1}$	(1)-(3)	100 (air)	50 (<i>H</i> ₂)

Table 6.2: Operating conditions in the voltammetry experiments.

Voltammetry experiments were conducted in the voltage range between $900 \, mV$ and $60 \, mV$ with a scan rate of $10 \, mV \, s^{-1}$. Several sweeps were applied sequentially to reach and ensure reproducibility of the dynamic characteristic of the voltage-current curve. The cell impedance at $10 \, kHz$ was recorded during all experiments. The temperature was measured with a thermocouple in the anode plate $1 \, mm$ above the flow field .

Chronoamperometry is a measurement technique in which the cell voltage is switched between two values, and the resulting cell current response is monitored as a function of time. The characteristic of the current response and cell impedance, triggered by a voltage change from

- step (1): 600 mV to 300 mV
- step (2): 700 mV to 400 mV
- step (3): 800 mV to 500 mV

and vice versa, was investigated.

6.4.4 Results and Discussion

Voltammetry experiments

Voltammetry experiments were used to validate the developed model with measured data. Therefore, the experimental results are briefly discussed to establish an understanding of the measured dynamic effects. Figure 6.15(a) shows the polarization curves of voltammetry experiments for three different humidification conditions (cases (1)-(3)). The corresponding cell impedance is depicted in Fig. 6.15(b). The forward (900 to $60 \, mV$) and the backward sweeps ($60 \text{ to } 900 \, mV$) are labeled by arrows. For comparison with the simulation results, the cell voltage is corrected by the anode losses and denoted by the superscript "*" on the axis label in the graphs. The polarization characteristic is strongly influenced by the humidification conditions in such a way that under completely dry conditions (case (1)), the highest limiting current density is reached at the expense of ionomer dehydration at low current density. Figure 6.15(b) shows for case (1) that the impedance increases throughout a backward sweep and further increases in the forward sweep up to a maximum value of approx. $230 \, m\Omega \, cm^2$; thereafter the water production is sufficient to humidify the ionomer itself. The increasing impedance in the low current density range is responsible for the hysteresis effect in the polarization curve in that region. The observed lower limiting current density in the case of higher humidification (cases (2) and (3)), leads to a decline from $1.6 A cm^{-2}$ to $1.3 A cm^{-2}$ and $0.9 A cm^{-2}$, respectively, indicating higher oxygen transport limitations due to increased flooding phenomenon. The saturation level during the voltammetry experiment is strongly time-dependent and causes hysteresis loops in the high current density region in all three cases. The dehydration of the ionomer is considerably reduced in case (2), compared to the completely dry conditions in case (1), and almost prevented for case (3).



(a) Voltammetry experiments conducted under different humidification conditions show strong hysteresis effects.



(b) Measured cell impedances show a large dynamic range in dehydration and humidification of the ionomer.

Figure 6.15: Voltammetry experiments with a scan rate of $10 \, mVs^{-1}$ were conducted to validate the developed model.

Model validation

The simulation results for the three different sets of operating conditions are shown in Fig. 6.16. The values of the model parameters used for the simulation are listed in the parameter list in section 6.4.6 and are also used in simulations that are discussed in the next sections.



(a) The simulated current-voltage characteristic show strong hysteresis effects with about the same limiting current density as the measurement.

(b) The increase of the impedance lies in the same range as the experiment.

Figure 6.16: The simulated polarization curves and impedance characteristics show a similar influence on the humidification conditions as the measurement.

Under all three different operating conditions, the model predicts the same currentvoltage characteristics as the measurements, as shown in Fig. 6.16(a). In all three cases the simulations show hysteresis effects in the high current density region with about the same limiting current density. In case (1), the pronounced hysteresis loop in the low current density region is also observed. The time-dependent behavior of the simulated impedance (Fig. 6.16(b)) is in good agreement with the measurement. In case (1) with completely dry conditions, the simulated impedance also shows a strong variation with the same maximum value as the experiment. In case (2), the dehydration of the ionomer is less pronounced and the impedance in case (3) is nearly constant, as found in the measured data.

A comparison of the temperature change throughout a sweep experiment is made in Fig. 6.17. On the left-hand side, the measured temperature is shown for the three different sets of humidification conditions. It is evident that the cell cooling is not sufficient to keep the temperature constant during a potential sweep. The high current density in case (1) is responsible for a temperature rise of 3.5 K from 313.5 K to



(a) The temperature of the cell increases up to $2-3.5\,K$ depending on the load.





Figure 6.17: A qualitative agreement between the measured temperature in the anode plate and the simulated temperature is achieved.

317 K. For comparison, the simulated temperature at the interior boundary between the anode plate and the anode interface T[2] is analyzed, depicted in Fig. 6.17(b).

The simulated temperature shows the same qualitative characteristic as the measurement. The temperature variation falls in the same range of 3.5 K for case (1), 3 K for case (2) and 2 K for case (3).

Analysis of the solving variables

In this subsection, the origin of the hysteresis effects is discussed in detail on the basis of the profiles of certain solving variables. The following plots show snapshots of some profiles either at 0.7 V or 0.4 V during a simulated voltammetry experiment. For



(a) A comparison of the water content profile shows a strong dehydration of the ionomer in cases (1) and (2).

(b) The steep ohmic drop in the membrane in case (1) leads to a minimized activation overpotential in the CL, resulting in low current generation.

Figure 6.18: A snapshot of the profiles of the water content and the overpotential between forward and backward sweeps at 0.7V is given.

the analysis of the hysteresis loop in the low current density region, which is most pronounced in case (1), to the water content λ at 0.7 V is referred. In Fig. 6.18(a), a large difference in the water content between forward and backward sweeps is present in cases (1) and (2). The low water content in the forward mode results in a high ohmic drop in the membrane which finally results in a minimized activation overpotential in the cathode CL for the ORR (Fig. 6.18(b)). In addition, the lower water content reduces the area of the three-phase boundary zone and therefore decelerates the reaction kinetics (see Eq. 6.7). The fact that oxygen transport limitation is not responsible for the lowered current generation, which might be possible in the case of different saturation levels, is shown in Fig. 6.19. In the forward mode, more oxygen is available for the ORR than in the backward mode. Figure 6.20(b) shows that the rela-



Figure 6.19: A comparison of the profiles of the normalized oxygen concentration (0.7 V) during a forward and a backward sweep. Higher transport limitations are observed in the backward sweep.

tive humidity in the CL remains at nearly 100% except for forward sweeps of cases (1) and (2) where dry cathode inlet gases are used. The difference of saturation between forward and backward sweeps at 0.4 V is depicted in Fig. 6.20(a). The saturation level in a backward sweep is always above its level in the forward mode. The largest difference is observed in case (1), where the saturation differs up to 20% in the GDL. The simulated saturation level of the GDL is uncommonly high compared to previous publications [138, 97, 123, 102, 104, 71]. The reason for it is based firstly on the assumption of an existing immobile saturation of $s_{im} = 0.2$, and secondly in the choice of Cauchy boundary conditions at the interface GDL \leftrightarrow channel. The most common assumption for the boundary condition is vanishing saturation at the interface towards the channel. The high capillary force in the presence of a large saturation gradient, predicted by the Leverett J-function, results in a fast liquid water outflow. This implies a small curvature of the saturation profile and finally a low saturation level in the GDL in the case of a Dirichlet boundary condition: s = 0 at the interface GDL \leftrightarrow channel. Wang et al. [141] predicts a maximum saturation level of only about 6.3% at a current density of about $1.4 A cm^{-2}$ in the case of the commonly made assumptions. Such a low saturation level would not lead to mass transport limitations at a current density of about $1.0 A cm^{-2}$ (using realistic values of the GDL porosity), that are clearly observed in the experiments.

From the presently known scientific publications, Shah et al. [127] are among the few using a Cauchy boundary condition, leading to a saturation of up to 0.6 - 0.8. Unlike in this model, they assume continuity of the saturation at the interface CL \leftrightarrow GDL and therefore reached the maximum saturation level in the CL.



(a) Continuity in the capillary pressure at the interface results in a discontinuity in the saturation. A higher saturation is found in the backward mode.

(b) The relative humidity (RH) for case (3) remains at nearly $100\,\%$ during the entire sweep.

Figure 6.20: Comparison of the profiles of the saturation (0.4 V) and the relative humidity (0.7 V) during a forward and a backward sweep.

Figure 6.21(a) shows the time-dependent system response in terms of current density and saturation at the interface GDL \leftrightarrow channel for case (1). Both the maximum of current density ($\Delta \varphi_1$) and saturation ($\Delta \varphi_2$) display a phase shift relative to the minimum of the applied cell voltage. The cumulative saturation during the forward mode causes increasing mass transport limitation, which becomes the dominant loss mechanism in the high current density region. This in turn leads to a current density maximum which is considerably earlier than the voltage minimum (about 25 s). The saturation increases beyond this voltage minimum up to a phase shift of about $\Delta \varphi_2 = 90^{\circ}$ (45 s). The evolution of the ionomer water content at the interface GDL \leftrightarrow CL is analyzed in Fig. 6.21(b). The maximum of the water content shows only a small phase-shift relative to the voltage ($\Delta \varphi_3$), whereas the minimum of the water content shows a strong delay with respect to the voltage maximum ($\Delta \varphi_4$).

The evolution of the water content profile for case (2) is visualized in Fig. 6.22. In the region of maximum current density, labeled as (1), a water content of nearly 17 is reached in the CL. A strong gradient of the water content is observed in the y-direction due to the strong electro-osmotic drag at high current densities. The decreasing electro-osmotic drag during the backward sweep and the back diffusion leads to a balancing of the water content in the membrane (region (2)). In region (3), the introduced water from the humidified hydrogen stream at the anode and the water generation from the ORR in the cathode CL is insufficient to prevent dehydration of the



(a) The maximum current density is reached about 20 s before the lowest cell voltage is reached $(\Delta \varphi_1)$. The maximum saturation (interface channel \leftrightarrow GDL) has a delay $(\Delta \varphi_2)$ of about 42 s relative to the minimum cell voltage.



(b) The characteristic of the water content (interface GDL \leftrightarrow CL) follows that of the current density in principle. However, the decrease of the water content is a little delayed ($\Delta \varphi_4$) with respect to the cell current due to the liquid water reservoir in the catalyst layer.

Figure 6.21: The time-dependent characteristic of the applied cell voltage together with the system response in terms of cell current, saturation (s[-1]) and water content $(\lambda[0])$ is shown for case (1).



Figure 6.22: The 3D diagram visualizes the evolution of the water content profile during two cycles of the sweep experiment for case (2). The water content is dominated by electro-osmotic drag and water generation (region 1), back diffusion (region 2) and dehydration (region 3).

ionomer. The water content falls to a value of 7.1.

The water flux through the cell in all three existing phases is visualized by a bar plot in Fig.6.23(a). Depending on the water phase its flux is analyzed at different y-positions. For a better comparison of the bars the flux directions are defined as shown in the inset on the right-hand side. The water flux belong to the snapshots at 0.7 V or 0.4 V during the simulated voltammetry experiment of case (1) discussed before.

As aforementioned, the cell is nearly dried out at a cell voltage of 0.7V in forward operation mode. Thus, there is a low water flux which is not further astonishing. But it is very interesting to see, that the liquid water flux has a negative value, indicating that there is a flux from the GDL into the CL. This result shows that the GDL acts as a liquid water buffer to hold up the ionomer hydration level for a while. A high water flux is observed at high currents in forward and backward mode. The back diffusion and electro-osmotic drag are the dominant water transport mechanism, whereby the net flux of both mechanisms are in the range of the liquid or vapor flux. This result shows that the membrane is a very good intermediator of the water household between anode and cathode. The simulation show that at low current density the vapor flux is responsible for the water discharge out of the cell, at high current density the liquid water transport together with the vapor diffusion. The water release on the anode is less than 20% in all cases.





(a) A comparison of the different water transport modes show that the dissolved water in the membrane plays a crucial role. The membrane is a good intermediator to counterbalance the humidification level in both electrode compartments.

(b) The reaction heat is the dominant source term in the energy balance equation. In case of low current density and a high amount of liquid water the latent heat of evaporation is not negligible.

Figure 6.23: Analysis of the water flux and heat source at different cell voltages during a forward and backward sweep.

The heat production is plotted in Fig. 6.23(b), subdivided in reaction heat of the ORR, ohmic heat caused by finite proton conductivity, ohmic heat due to electrical contact resistances and latent heat caused by phase change. The ORR has the largest influence in the heating of the cell at all four operating conditions. The cooling effect by water evaporation is not negligible at low current density values such as $0.27 Acm^{-2}$, but plays no significant role at high currents. The membrane impedance contribute twice as much as the contact resistance to the heat source.

Chronoamperometry

A comparison between measured and simulated chronoamperometry experiments is made in Fig. 6.24 and 6.25. The fuel cell was operated with dry air and humidified hydrogen ($T_{DP}^a = 311 K$) with the same flow rate as in the voltammetry experiments (see Table 6.2).

Overshoots in the measured current density are recorded on switching from high to low cell voltages (Fig. 6.24(a)). The characteristic of the overshoots depends on the voltage level before and after the step change. A change from 0.6 to 0.3 V (step (1)) causes a peak current density of $1.3 A cm^{-2}$ that drops off to a value of $0.9 A cm^{-2}$ within the first 20 s. The peak current density of step (2) reaches the same value but shows a less rapid decay than step (1). The peak in case (3) is not very pronounced,





(a) An overshoot is observed in all three cases on switching to the low cell voltage. The response differs on returning to the higher voltage, depending on the voltage level.

(b) A qualitatively good agreement with the experiments was achieved in the simulations, but with a longer time constant.

Figure 6.24: Comparison between measured and simulated current response for chronoamperometry experiments.

but shows an apparent delay relating to the step change, that is not observed for step (1) and (2) to this degree.

Switching from the low to the high cell voltage, the characteristic of the current response differs for all three steps. Step (1) shows an increase in the current density immediately after the voltage change and reaches equilibrium within 100 s. Step (2) shows a short increase or plateau before the current density starts to decrease. The current density in step (3) decreases continuously to a steady-state value.

The simulation shows a qualitatively similar characteristic (Fig. 6.24(b)). However, the time constants of the response differ from the measured ones. The simulation of steps (1) and (2) predicts a distinct overshoot in the current density with the same peak value of $1.5 A cm^{-2}$. A sharp peak is observed for step (1), but step (2) shows a much slower decay than the measured data. Step (3) shows a linear decrease of the current without a clear peak. A delay of the maximum current relative to the step change is predicted by the model, in agreement with the measurement. The simulated current response to the potential step from low to high cell voltage is in agreement with the measurement. An increase of the current density for step (1), an increase in the current density followed by decrease for step (2) as well as the fast decay to a steady-state value for step (3) are predicted.

The corresponding cell impedance was recorded during the chronoamperometry measurements and is depicted in Fig. 6.25(a). Almost no change in the impedance was measured for step (1). The ionomer starts to dehydrate when the fuel cell is driven





(a) An increase in the impedance at cell voltages of $700\,mV$ and above shows that the self-humidification by product water is insufficient.

(b) The simulation predicts dehydration in the voltage range of $700 \, mV$ and above, but the simulated impedance is not as high as the measured impedance.

Figure 6.25: Comparison between measured and simulated impedance responses during chronamperometry experiments.

at a cell voltage of $700 \, mV$ (step (2)). Stepping back to $400 \, mV$, the impedance drops very rapidly to a low impedance level, similar to the value of step (1). At a cell voltage of $800 \, mV$, the impedance rises very fast to a value of $0.35 \, \Omega \, cm^2$ and drops again very fast on switching to higher current density and overpotential.

The simulation of the impedance response describes the measured impedance qualitatively. While switching between $600 - 300 \, mV$, dehydration of the ionomer can not be observed. In the range between $700 - 400 \, mV$, the ionomer starts to dehydrate at a cell voltage of $700 \, mV$. Strong dehydration of the ionomer at a cell voltage of $800 \, mV$ for step (3) is predicted by the model, but is obviously not as pronounced as in the measured data. A reason for this could be the shrinking of the ionomer in the case of high dehydration, resulting in an increase of the contact resistance that is not implemented in the model.

6.4.5 Conclusion

In PEM fuel cells, water is present as vapor, in liquid form and dissolved in the ionomer. The effects of water in all three phases, basically pore flooding and ionomer dehydration, are investigated with a newly developed 1D transient model. The model accounts for the loss mechanisms in the cathode GDL, cathode CL and membrane. The electrode structure is modeled as a network of spherical agglomerates. An excess of liquid water in the catalyst layer leads to coverage of these agglomerates,

forming a water film which limits oxygen transport. Liquid water is modeled as saturation in the void space. Its transport properties depend strongly on the capillary pressure-saturation relationship in porous media, which in turn is a function of the wettability and pore structure. Based on ESEM images, immobile saturation is introduced due to the observed partly hydrophilic regions in the GDL. A continuous capillary pressure at the interface $CL \leftrightarrow GDL$ is assumed, resulting in a discontinuous saturation distribution. Finite phase transition rates between the ionomer and pore space, namely adsorption/desorption and liquid water uptake/release, enable membrane dehydration in the case of dry operating conditions, resulting in an increased ohmic resistance.

The simulation results for dynamic current-voltage characteristics are in excellent agreement with measured data. The measured hysteresis loop in the limiting current density region is reproduced by the model and explained by pore flooding. The measured cell impedance during a voltage sweep, which is a measure for the timedependent water content, is in agreement with the simulation over a wide range of operating conditions and current densities. Simulations of chronoamperometry experiments are performed with the validated parameter set. The model captures qualitatively the current and impedance responses of measured chronoamperometry data. The model forms a suitable basis for identifying the dominant loss mechanisms at different operating points. Based on the simulation results, suggestions for a better choice of fuel cell components can be made, guidance for their physical properties like pore structure, wettability or thickness can be obtained or simply optimal operating conditions can be found. The latter leads us to the topic of fuel cell control. A good understanding of the response on dynamic load changes is required to control a fuel cell within a stable operating point. This can be realized by implementing the model in a simplified form in a model-based control algorithm.

Parameter studies and a sensitivity analysis would be the next steps in ongoing work. An upgrade to a multi-dimensional model is intended for the future.
6.4.6 Nomenclature and Parameter List

Symbol	Description	Value / Eq.	Unit	Reference
Solving	ariables			
Solving v	anables			
$c_{O_2}^g$	normalized gaseous oxygen		_	
02	concentration			
c_v	normalized vapor concentra-		_	
e	tion saturation		_	
T	local temperature		K	
η	overpotential		V	
λ	water content		_	
Physical	constants		_	
F	Faraday constant	96484	$C mol^{-1}$	
R	gas constant	8.314	$J K^{-1} mol^{-1}$	
Structura	l values			
- CBP				
L^{CDI}	thickness of cathode bipolar plate	$3 \cdot 10^{-3}$	m	
L_{GDL}^{GDL}	GDL thickness	$280 \cdot 10^{-6}$	m	
L^{CL}	CL thickness	$10 \cdot 10^{-6}$	m	
L^{mem}	membrane thickness	$35 \cdot 10^{-6}$	m	
L^{ADP}	thickness of anode bipolar plate	$3 \cdot 10^{-3}$	m	
R_a	mean agglomerate radius	$0.2 \cdot 10^{-6}$	m	[142]
ϵ_a	volume fraction of primary	0.4	_	[117]
ϵ^{CL}	volume fraction of secondary	0.25	_	[65 58]
c_p	pores in CL	0.20		[00, 00]
ϵ_i^{CL}	volume fraction of ionomer in	0.3	_	
ϵ_{m}^{GDL}	volume fraction of open pores	0.7	_	[143]
p	in GDL			L - J
Λ	agglomerate density	Eq. 6.24	m^{-3}	
[1]	geometry factor	0.55	—	calculated
Physical properties, local variables and boundary conditions				

 a_w water activity Eq. 6.41 -

Symbol	Description	Value / Eq.	Unit	Reference
1		_		
$c^d_{O_2,s}$	dissolved oxygen concentra-	Eq. 6.4	$mol m^{-3}$	
\tilde{c}^d	tion at aggiomerate surface	Fa 63	_	
$^{\circ}O_2$	concentration in anotomerate	ц. 0.0	_	
$c_{O_2}^{g\ast}$	gaseous oxygen concentra- tion at inlet	Eq. 6.44	$mol m^{-3}$	
c_v^*	vapor concentration at inlet	Eq. 6.49	$mol m^{-3}$	
\ddot{C}_{DL}	double layer capacity	0	$F m^{-3}$	
$C_{tit} =$	heat capacity of titanium	$9.4\cdot 10^6$	$J m^{-3} K^{-1}$	[144]
$\rho_{tit} c_{tit}$			- 9 - 1	
$C_{GDL} =$	heat capacity of GDL	$1.61 \cdot 10^{\circ}$	$J m^{-3} K^{-1}$	[126]
$\rho_{GDL} c_{GDL}$	beat capacity of CL	$1.61.10^{6}$	$Im^{-3}K^{-1}$	[126]
$O_{CL} = 0_{CL} C_{CL}$	heat capacity of CL	1.01 · 10	$J m \Lambda$	[120]
$C_{mem} =$	heat capacity of membrane	$2.18\cdot 10^6$	$J m^{-3} K^{-1}$	[126]
$ \rho_{mem} c_{mem} $	ı			
$C_g =$	heat capacity of gas	$1 \cdot 10^3$	$J m^{-3} K^{-1}$	[126]
$\rho_g c_g$	here the second states of second second	4 1 0 7 1 0 6	T _3 TZ_1	[400]
$C_w =$	heat capacity of water	$4.187 \cdot 10^{\circ}$	$J m^{-3} K^{-1}$	[126]
$\rho_w c_w$ d	water film thickness	Fa 6 18	m	
$D_{O_i}^i$	oxygen diffusion coefficient in	$5 \cdot 10^{-11}$	$m^2 s^{-1}$	[58]
O_2	ionomer			
$D_{O_2}^w$	oxygen diffusion coefficient in	$2.1 \cdot 10^{-9}$	$m^2 s^{-1}$	
\mathcal{D}^{q}	water		2 -1	[100]
$D_{O_2}^{\circ}$		Eq. 0.40	m-s	[120]
$D^{eff,\Omega}$	effective oxygen diffusion co-	Fa 645	$m^2 s^{-1}$	[128]
D_{O_2}	efficient in gas phase	Eq. 0.10	110 0	[120]
D_v^g	vapor diffusion coefficient in	Eq. 6.51	$m^2 s^{-1}$	
	gas phase			
$D_v^{eff,\Omega}$	effective vapor diffusion coef-	Eq. 6.51	$m^2 s^{-1}$	
50	ficient in gas phase		0 1	
$D_s^{\scriptscriptstyle M}$	water diffusion coefficient in	Eq. 6.37	$m^2 s^{-1}$	
D^i	water diffusion coefficient in	Ea 6 26	$m^2 e^{-1}$	[132]
D_{λ}	ionomer	Lq. 0.20	111 3	
EW	equivalent weight	1.1	kg	[114]
h_{gl}	heat of vaporisa-	$40.7\cdot 10^3$	$J mol^{-1}$	[144]
-	tion/condensation			
H	Henry constant	0.0254	— , 9 1	[70]
$j_{O_2}^{g}$	gaseous oxygen flux	Eq. 6.43	$mol m^{-2} s^{-1}$	

6.4 Modeling Liquid Water and its Transient Effects in a PEMFC

Symbol	Description	Value / Eq.	Unit	Reference
		F A (A	- 0 1	
j_v	vapor flux	Eq. 6.48	$mol m^{-2} s^{-1}$	
j_s	liquid water interstitial velocity	Eq. 6.33	$m s^{-1}$	
j_T	heat flux	Eq. 6.53	$J m^{-2} s^{-1}$	
$j_{p,e}$	charge flux	Eq. 6.20	$A m^{-2}$	
j_{λ}	dissolved water flux	Eq. 6.25	$mol m^{-2} s^{-1}$	
j^a_{gen}	current generation per ag- glomerate	Eq. 6.12	A	
k^a_{ad}	adsorption/desorption rate on anode	Eq. 6.75	s^{-1}	assumed
k_{ads}	adsorption rate	80	s^{-1}	assumed
k_{des}	desorption rate	50	s^{-1}	assumed
k_{eva}	evaporation rate	100	$m s k q^{-1}$	[137]
k_{con}	condensation rate	100	s^{-1}	[137]
k_{u}	water uptake rate	0.1	$mol s k a^{-1} m^{-2}$	assumed
k_r	water release rate	0.1	$mol s kg^{-1} m^{-2}$	assumed
k_0	reaction rate	0.001	s^{-1}	assumed
K^{GDL}_{I}	absolute permeability in GDL	$8.7 \cdot 10^{-12}$	m^2	[127]
K^{CL}_{l}	absolute permeability in CL	$1 \cdot 10^{-13}$	m^2	[127]
K_{rel}	relative permeability	Ea. 6.38		[]
n.	number of transferred elec-	2	_	
	trons	-		
p_c^{Ω}	capillary pressure in domain		Pa	
sat		F ₂ , C 40	D	[4]
p^{sur}	saturation pressure	Eq. 6.42	Pa	[1]
q_{ORR}	source/sink term due to ORR	Eq. 6.23	Am^{-3}	
q_{ad}	source/sink term due to ad-	Eq. 6.29	$mol m^{-3} s^{-1}$	
	sorption/desorption		. 2 1	
q_{ur}	source/sink term due to liquid	Eq. 6.32	$mol m^{-3} s^{-1}$	
	water uptake/release		- 9 1	
q_{ec}	source/sink term due to evap-	Eq. 6.40	$mol m^{-3} s^{-1}$	
<i>a</i> ,	source/sink term of the heat	Eas 6 55-6 59	$I_{m} - 3_{c} - 1$	
$\frac{Yh}{DH}$	rolativo humidity	Eqs. $0.00-0.00$	5 111 5	
GDL/CL			—	· · ·
s_{im} '	Immobile saturation	0.2/0	_	assumed
α	symmetry factor	0.45	—	
α_{drag}	electro-osmotic drag coeffi-	Eq. 6.27	—	
ΔS	enthalpy change	162.2	$J \operatorname{mol}^{-1} K^{-1}$	[126]
Θ_m	contact angle in ionomer	90.02	deg	[37]
	channels			
Θ^{Ω}	contact angle in porous me- dia (GDL/CL)	105/95	deg	

6 Water Management in Polymer Electrolyte Membrane Fuel Cell

Symbol	Description	Value / Eq.	Unit	Reference
κ _{GDL} κ _{CL} κ _{mem}	thermal conductivity of GDL thermal conductivity of CL thermal conductivity of mem- brane	$1.67 \\ 0.67 \\ 0.67$	$W m^{-1} K^{-1} W m^{-1} K^{-1} W m^{-1} K^{-1} $	[126] [126] [126]
κ_{tit}	thermal conductivity of tita-	21.9	$W m^{-1} K^{-1}$	[144]
$\lambda_{eq} \ \mu \ u_g$	equilibrated water content liquid water viscosity molar volume of ideal gas	Eq. 6.30 0.001 $2.2414 \cdot 10^{-2}$	$- kg m^{-1} s^{-1} m^3 mol^{-1}$	[1] [96]
	molar volume of liquid water ionomer density surface tension of water unified conductivity of	$ \begin{array}{r} 1.8015 \cdot 10^{-5} \\ 1980 \\ 0.07 \\ 600 / 650 \\ \end{array} $	$m^3 mol^{-1}$ $kg m^{-3}$ $S m^{-1}$	[114, 112] [96] assumed
0 contact	all electronic conductors normed to BP2	000/030	5 11	assumed
σ^{Ω}	protonic conductivity in domain Ω	Eq. 6.21	$S m^{-1}$	[1]
$\Omega_{O_2}^c$	oxygen transfer coefficient cathode	$2.4\cdot 10^4$	m^{-2}	assumed
Ω_v^c	vapor transfer coefficient cathode	$2.4 \cdot 10^4$	m^{-2}	assumed
Ω_s^c	saturation transfer coefficient cathode	$3 \cdot 10^2$	m^{-2}	assumed
Ω^a_w	water transfer coefficient an- ode	$1 \cdot 10^{-5}$	m^{-2}	assumed
Ω_T	heat transfer coefficient	1150	$J K^{-1} m^{-2} s^{-1}$	assumed
Operating	conditions			
i_{cell} P_{O_2} P $T_{coolant}$ T^a_{DP} T^c_{DP}	current density oxygen partial pressure total pressure coolant temperature anode dew point temperature cathode dew point tempera- ture	0.21 1 313 various various	$A cm^{-2}$ atm atm K K K K	
\dot{V}_a	anode gas flow rate	$50 \\ (8.33 \cdot 10^{-7})$	$\frac{ml min^{-1}}{(m^3 s^{-1})}$	
V_c	cathode gas flow rate	$\frac{100}{(16.66 \cdot 10^{-7})}$	$ml \min^{-1} (m^3 s^{-1}) V$	
U	vollaye		V	

6.5 Enhancing Liquid Water Management by GDL perforation

6.5.1 The Idea of GDL Perforation

Despite the remarkable progress in PEFC science and technology during the past decade, optimum water management within the porous components of the PEFC has not been achieved so far. Droplet and liquid film generation in the channel can be influenced by the contact angle of the channel surface and channel clogging can be managed by appropriate flow field design and gas purge. The build-up and transport of liquid water in the gas diffusion layer depends on the pore size distribution and the contact angle on the micro scale within the pores. Accordingly, the microstructure of GDL materials is a key factor in efficient water management that applies before the water reaches the flowfield. One example of influencing the water management by modification of the porous GDL is the application of a micro porous layer (MPL), which reduces the saturation of the CL at the expense of increased mass transfer resistance [145, 146, 122]. However, the optimization potential within the GDL microstructure is still large with respect to liquid water transport. The pore-flooding phenomenon causes significant mass transport losses and is problematic for efficient reliable operation under dynamic load conditions and high current densities.

Sophisticated measurement techniques for the investigation of liquid water in fuel cells have been developed, and these are detailed discussed in Chapter 6. The capillary pressure-saturation relationship, which is one of the most influential properties of gas diffusion layers for the liquid water transport, is experimentally determined in [147]. Mercury intrusion porosimetry and the method of standard porosimetry are applied and compared. The role of microporous layers and the hydrophilic porosity are discussed.

One way of obtaining a physical visualization of the liquid water transport in GDLs is to apply fluorescence microscopy. Direct observation of the liquid water transport in GDLs was achieved [148]. The results show that the transport in Toray GDLs is a fingering and channeling process. The effect of GDL compression on the water transport behavior was investigated using the same technique [149]. It is concluded that compression can create preferential hydrophilic channels for water due to the microscopic damage induced to the fiber material and its coating.

Despite the deep insight into water transport that is provided by the various experimental techniques, the transfer of the results into improved materials has yet to be achieved.

In this work, the development of a method to tailor a commonly used GDL material for improved transport properties with respect to the two-phase flow of air and water is presented. The idea is based on the Laser perforation technique, which is in strong relationship with the MEA segmentation presented in Chapter 4.

For improving the liquid water removal out of the GDL, two physical properties of the GDL indicate the good potential of the perforation technique:

- Experimental data of Gostick et al. [150] proved by simulation results of Schulz et al. [151] show that the in-plane permeability of liquid water in the GDL is up to twice as much than the through-plane permeability due to the prefered orientation of the carbon fibers (Table 6.4).
- The smaller the pore radius of a hydrophobic porous structure, the higher is the essential water pressure to fill these pores (see capillary-saturation relationship in Eq. 6.34 on page 101).

Therefore, providing well-orientated water transport channels (WTCs) in the GDL structure that have larger radii than the mean pore size distribution can improve the liquid water transport from the catalyst layer towards the flow field. Figure 6.26 shows schematically the concept of the water transport enhancement by GDL perforation. Water is generated by the ORR in the CCL and dragged by the protons from the anode side. The water accumulates in the porous structure of the CL, resulting in an increasing liquid water pressure. The existing pressure gradient forces the water out of the CL into the GDL. Here, the water follows the path with the lowest resistance, which is the path with the highest permeability, the in-plane direction. Several water pathways in smaller pores combine to one pathway in a larger pore in order to reduce the water pressure. At the end the water finds a way out of the GDL but with a high tortuosity. Additionally, the rib structure of the flow field, that generally covers about the half of the GDL area, impedes the water removal since some pathways lead to dead-end, clogging the GDL in this region.

By means of the laser perforation technique, WTCs with a desired radius can be generated on favored local positions. Due to the high in-plane permeability, the WTCs act as water collecting points from the surroundings. The water fills the WTCs and is forced to move towards the flow field where it evaporates or get carried away by the air stream. Therefore the water saturation is reduced, leading to an improved oxygen access to the CL.

This method is applied to produce a novel GDL prototype that is dynamically tested according to a method proposed in [124] and by chronoamperometry within a test fuel cell.

permeability	in-plane		through-plane	
	simulated	measured	simulated	measured
Toray TGP-H090	$11.5 \cdot 10^{-12} m^2$	$15 \cdot 10^{-12} m^2$	$7.4 \cdot 10^{-12} m^2$	$8.99 \cdot 10^{-12} m^2$
SGL10BA	$30.9 \cdot 10^{-12} m^2$	$60 \cdot 10^{-12} m^2$	$21.1 \cdot 10^{-12} m^2$	$37.4 \cdot 10^{-12} m^2$

Table 6.4: Through-plane and in-plane permeabilities of gas diffusion layers determined by
Lattice-Bolzmann flow simulations [151] and measurements [150].



Figure 6.26: Schematic of the liquid water transport with and without water transport channel.

6.5.2 Preparation of the GDL

A standard Toray paper (TGP-H-090, thickness $280 \ \mu m$) is modified by producing large pores for the capillary diffusion of liquid water, so that the water can diffuse without requiring large pressure gradients. Simply spoken, the GDL is perforated to obtain water transport channels (WTCs) with a tortuosity of one. It is assumed that the holes "suck" the water from their neighborhood due to the higher in-plane permeability of liquid water compared to the through-plane permeability [151] and the fact that the capillary pressure is lower in larger pores. By providing large pores, the fingering and channeling mechanism as described in [148] is engineered to improve the performance of the cathode.

A laser beam is used to manufacture the holes by cutting out defined areas of the GDL. Compared to other manufacturing techniques, the laser technique has the advantage of creating a smoothly cut edge. The carbon fibers are not broken by this technique, so the risk of undesired broken fibers pointing toward the MEA surface, which causing pin holes, is eliminated. A second advantage of using a laser beam to melt and burn the carbon fibers is the fact that the material is really removed and not just displaced to the surroundings as it would be if needles or similar preparation techniques were used. Displacement of the fibers would lead to rearrangement of the

surrounded fibers and thus to an undesired decrease of the porosity.

WTCs were cut in the GDL by using a Nd:YAG laser ("Rofin Sinar Laser GmbH") operating at a wavelength of 1064 nm in the near infrared. In the focus of the fixed laser optics, a probe chuck can be moved in the xy-plane by a microstepping motor with a position accuracy of $1 \mu m$.

A Toray TGP-H090 was perforated with 39 holes, each of them having a diameter of approx. $80 \ \mu m$. Figure 6.27(a) shows a SEM image of one hole. It can be seen that the fibers and the binder are really removed, leaving a smooth cut edge. One disadvantage of the laser perforation technique should be mentioned here. If the binder content in the GDL is too high, the binder could melt and cause jamming of the WTC wall. The binder content of the Toray paper used seems to be suitable for this preparation technique. In the assembled cell, the holes were located along the flow channel at a distance of $1 \ mm$ to each other so that the liquid water can be removed directly by the gas stream. Figure 6.27(b) shows a drawing of the flow field (the rib is colored gray) with the position of the WTCs. The cell size compared to the hole diameter is drawn to scale. The ratio of the area of all circles to the entire GDL surface is only 0.005% and is thus negligible concerning the reduction of the contact area for the electron transport.



(a) A hole with a diameter of approx. $80\,\mu m$ has been burnt into the GDL by a laser beam.



(b) Schematic drawing of the position and size of the holes along the flow field.

Figure 6.27: Optimization of the GDL structure with regard to liquid water transport by means of laser perforation.

6.5.3 Characterization of a Modified GDL in a Single Cell

Test Cell and Operating Conditions

The experiments were made with the small test cell in a test bench that are both described in detail in the previous chapters. To investigate the influence of the pore structure of the GDL on the liquid water transport an untreated Toray TGP-H090 paper is compared to a perforated one (section 6.5.2). Since the problem of flooding is typically critical on the cathode side only, the anode GDL remains untreated in all experiments. A Gore[™] PRIMEA[®] Series 5510 membrane electrode assembly (loading $_{c/a}$: $0.4/0.4 \, mq \, cm^{-2}$, thickness: $35 \, \mu m$) was used in both cases. Polarization curves were measured in potentiostatic mode with a scan rate of $10 \, mV \, s^{-1}$ from 900 to 60 mV (forward mode) and from 60 to 900 mV (backward mode). During the experiment the cell impedance (@10 kHz), cathode overpotential, anode overpotential and cell temperature were recorded. The air flow rate was set to $100 \, ml \, min^{-1}$ on the cathode side and the hydrogen flow rate was $50 \, ml \, min^{-1}$ on the anode side. Depending on the experiment, humidified or dry gases were used and are specified directly in the result section for each polarization curve. The fuel cell was cooled by a water cooling circuit with a thermostat ($T_{thermostat} = 40 \,^{\circ}C$) to maintain the temperature of the cell in a defined range. Nevertheless, the cell heated up at high current densities due to ohmic heating, so the cell temperature fluctuated within a range of $\Delta T \approx 4^{\circ}C$ during a voltammetry cycle. Several cycles in succession were operated to ensure reproducibility and to approximate dynamic equilibrium.

Chronoamperometry is used as a second characterization technique with a new assembled cell applying the same operating conditions. The current response and cell impedance induced by voltage steps from 0.8 to 0.5 V, 0.7 to 0.4 V, 0.6 to 0.3 V and backwards are analyzed. A higher coolant flow rate than for the voltammetry experiments was chosen to maintain a comparable temperature evolution between the measurements with and without perforated GDLs.

Experimental Results

Figure 6.28 shows a representative example of one voltage-current curve and the separated overpotentials of the present experimental study. The cell was operated in potentiostatic mode with dry gas streams (case (1)). The cell voltage shows a strong hysteresis between the forward and backward sweeps. Beginning with a relatively dry membrane electrode assembly at $900 \, mV$ the cell voltage decreases fast with increasing load. A steep decline at a current density of $1.6 \, Acm^{-2}$ indicates flooding of the porous media, despite the dry inlet streams. In the backward mode, the cell voltage suffers from the flooding event up to a current density of approx. $1.2 \, Acm^{-2}$, where the voltage-current curve in the backward mode crosses the one in forward mode. From then on, the still higher humidification of the porous media and MEA



Figure 6.28: A typical voltammetry measurement that shows MEA dehydration at high cell voltage and flooding in the limiting current density region which results in two hysteresis loops, shaped like an "eight". The loss mechanisms are separated into cathode, anode and ohmic overpotential.

leads to better performance in the backward mode.

It can be seen that the cathode overpotential η_c (Eq. 4.6) is responsible for the rapid drop at high current density when flooding occurs. The main part of the hysteresis in the low current-density region can be attributed to the ohmic loss η_{Ω} (Eq. 4.1) that clearly highlights the effect of hydration/dehydration. This large difference of the ohmic overpotential between the forward and backward mode is responsible for the change in the activation overpotential at the electrodes for a given cell voltage.

> Voltammetry Experiment Figure 6.29 and 6.30 show the behavior of the cathode and anode overpotential as well as the impedance (@10 kHz) during voltammetry measurements of 10 cycles. Repeatability and dynamic equilibrium are assured. Three different operating conditions were chosen for the experiments:

- case (1): dry inlet gas streams on the cathode and anode side,
- case (2): dry air and humidified hydrogen ($T_{dew \, point}^{H_2} = 37 \,^{\circ}C$),
- case (3): hum. air $(T_{dew \, point}^{air} = 37 \,^{\circ}C)$ and hum. hydrogen $(T_{dew \, point}^{H_2} = 37 \,^{\circ}C)$.

In all three cases, Fig. 6.29 (top) indicates flooding when the limiting current density (i_{lim}) is reached, as characterized by the hysteresis shoulder in the high currentdensity region. The measurement with two dry inlet feed streams shows the highest



Figure 6.29: (top) Cathode and anode overpotentials of voltammetry measurements with an original Toray paper. The influence of the feed streams was investigated: case (1) with dry feed streams, case (2) with the anode feed stream humidified, case (3) with both feed streams humidified. (bottom) The increase of the cell impedance for low current density indicates dehydration of the membrane. The temperature fluctuates between 40.5 and $44 \,^{\circ}C$ during a cycle.

current density ($i_{lim} = 1.6 A cm^{-2}$) which obviously indicates that flooding starts later than in case (2) and (3). While the porous media is flooding, the current density is decreasing with increasing overpotential due to accumulation of water over time in all three cases. The high limiting current density of case (1) is paid by a strong dehydration of the MEA in the low current-density region, indicated by the increasing cell impedance (Fig. 6.29 bottom). In case (2), weak dehydration of the MEA can also be observed whereas in the case of both gas streams being humidified (3), the impedance remains nearly stable at a value of approx. $88 m\Omega cm^2$. The anode losses η_a (Eq. 4.4) are small but not negligible in all cases and reach a maximum value of 100 mV at i_{lim} . The heat of reaction and the ohmic losses are responsible for the heating of the cell by up to $3.5^{\circ}C$ during a cycle.

Figure 6.30 shows the same experiments as Fig. 6.29 but with a perforated cathode GDL. The characteristic of the polarization curve in the high current-density region



Figure 6.30: (top) The measurements with the perforated cathode GDL shows reduced flooding and thus higher limiting current densities. (bottom) Due to a slightly higher cell impedance and higher currents, the temperature increased to $42.5 - 46.5^{\circ}C$.

has clearly changed. The hysteresis loop due to flooding has been minimized. The sudden increase of the cathode overpotential in the limiting current-density region has been reduced, so i_{lim} was reached with the highest overpotential. In all three cases, a boost to higher i_{lim} of 8 - 22% has been achieved. In these measurements, the impedance of the cell with the perforated GDL was significantly higher. It was not possible to reduce the impedance to a level of $88 m\Omega cm^2$ as in the first experiment (Fig. 6.29), not even with fully humidified gas streams. Most likely this impedance shift results from a slightly higher contact resistance. The increased performance loss at the anode (approx. 200 mV (perforated) compared to 100 mV (untreated) at i_{lim}) could be an indication for a poor contact on the anode side. Due to this higher basic impedance and the higher current density, the cell heats up to a temperature $2^{\circ}C$ above the temperature of the first experiment. This fact in turn leads to stronger dehydration of the MEA in the low current-density region in the case of dry reactant gases (1), as validated by the increase of the cell impedance.

In Fig. 6.31, a direct comparison of voltage-current curves (left) and cathode polar-

ization curves (right) is made between the operation with the original and the perforated GDL. For clarity, only the cases (1) and (3) are depicted in the graph. On the left-hand side, the voltage-current curves with the perforated GDL show a higher limiting current density, as discussed before. However, rather a small decline than an improvement of the cell voltage at a given current density is observed. This fact is caused by the above mentioned higher basic impedance and the resulting higher anode losses, lowering the cell voltage. For analyzing the enhancement of the liquid water transport the cathode losses are depicted on the right-hand side of Fig. 6.31. In the low current-density region, the polarization curves of the cell equipped with the original and perforated GDL are identical. Turning to high current densities, the cathode polarization curves of the cell with the unmodified GDL start to suffer from transport limitations earlier and finally show a sudden increase of the overpotential. It is obvious that this increase of the overpotential is missing in the polarization curve with the perforated GDL, indicating a reduced pore flooding.



Figure 6.31: (a) A comparison between the polarization curves of the cell equipped with the non-modified and perforated GDL clearly shows a reduced mass transport limitation for the latter due to reduced saturation of the porous media in the high current density region. The higher basic impedance of the cell with the perforated GDL and the resulting increased temperature prevents a better performance at low current densities due to dehydration. (b) A reduced saturation level of the perforated GDL can be supposed by the characteristic of the separated cathode overpotential.

> Chronoamperometry Investigations concerning the transient behavior of the current response on voltage step changes and the corresponding impedance response are shown in Fig. 6.32-6.34. The cell was operated with dry air and humidified hydrogen ($T_{dew \ point}^{H_2} = 39 \ ^{\circ}C$). Gas flow rates and coolant temperature are equal to the

voltammetry experiments. In Fig. 6.32 the cell voltage was stepped between 0.8 and 0.5 V. The current response is shown on the left-hand side. An overshoot is depicted in both cases whereas the peak current density is approx. $0.2 A cm^{-2}$ higher with the perforated GDL and ends $0.1 A cm^{-2}$ above the original GDL. A higher current density is also observed at 0.8 V. A strong dehydration can be reasoned from the impedance data at 0.8 V, pictured in Fig. 6.32 (right). The water generation by the ORR seems not to be sufficient to prevent dehydration of the ionomer, whereas the dehydration is more pronounced with the original GDL due to the lower current density. The cell impedance drops very fast when applying a cell voltage of 0.5 V.



Figure 6.32: (left) The test cell with perforated GDL shows a significantly higher current density than the cell with the original GDL. (right) The cell impedance shows that water generation by the ORR is not sufficient to prevent dehydration of the ionomer at a cell voltage of 0.8 V.

Figure 6.33 shows the dynamics of the current density and the impedance on a step change from 0.7 to 0.4V and backwards for both cells. The peak current densities are similar to each other but the current decline of the cell with the laser-treated GDL is less strong, resulting in an improvement in the power density by about 15%. Due to the higher current density of the cell with the perforated GDL at a voltage of 0.7V, the water generation is high enough to maintain a stable impedance. By contrast, the dehydration in case of the original GDL leads to a decrease in the current density several seconds after the voltage change. The voltage change from 0.6 to 0.3V and backwards is investigated in Fig. 6.34. Only a small overshoot is recorded in case



Figure 6.33: (left) The current density response with the original GDL shows a strong decay of the peak current density due to pore flooding. (right) The current density range between $0.3 - 0.5 Acm^{-2}$ seems to be a critical value for a stable humidification of the membrane.

of the perforated GDL that results in an improvement of the power density of about 20%. By stepping from 0.3 to 0.6V an undershoot behavior is observed in case of the original GDL. This phenomenon can be explained by a reduction of the saturation level when switching to lower current densites, this in turn leads to a performance improvement over time, until a new equilibrated saturation is reached. Both impedances remain stable at the same value, shown in Fig. 6.34 (right).

Conclusion and Outlook

A customized GDL, structured with water transport channels by laser perforation, was prepared and investigated in a test fuel cell with an active area of $1 cm^2$. The laser-cut holes with a diameter of approx. $80 \ \mu m$ are spaced along the channel at a distance of 1 mm. A comparison with a standard, non-modified GDL shows that the performance of the cell with the perforated GDL suffers less from accumulated liquid water. The cathode overpotential shows less limitation of oxygen transport. An increase in the limiting current density of 8 - 22% with the perforated GDL has been achieved. A comparison of chronoamperometry data shows clearly reduced overshoot behavior, ending in a higher current density value when using the perforated GDL. This high-



Figure 6.34: (left) A pronounced overshoot and undershoot behavior is observed in the current response for the cell with original GDL, whereas only a small overshoot is recorded with the perforated GDL. This clearly indicates a lower saturation level for the latter. (right) The impedances are nearly identical and stable over time.

lights the improvement of less pore flooding and an enhanced water transport in the GDL. The potential to optimize the GDL structure with regard to liquid water transport is still very large since the arrangement of the WTCs and their design has not been optimized yet.

This systematic perforation technique can play an important role in the transition to large fuel cells and stacks, where engineers have to cope with strong in-plane inhomogeneities in humidification, saturation and temperature from inlet to outlet. With respect to the flow field geometry and operating conditions, a tailor-made GDL can be manufactured by the laser perforation technique to compensate for these inhomogeneities by a specific layout of the WTCs.

Another application of the presented perforation technique is for direct methanol fuel cells. Systematic positioning of holes in the GDL can help to remove CO_2 in the gas phase, which is a by-product of the methanol oxidation, and therefore to achieve more stable performance especially in passive systems.



Figure 6.35: A 6-cell stack was used to investigate the effects of GDL perforation on the performance.

6.5.4 Characterization of a Modified GDL in a Fuel Cell Stack

Fuel Cell Stack and Operating Conditions

The performance improvement in the single cell experiments due to a better water removal of the modified GDL motivates the transfer of the laser perforation technique from a single cell to a industrial relevant stack for portable applications. An already existing 6-cell stack (see Fig. 6.35) was chosen for characterizing the influence of GDL perforation concerning flooding phenomena.

The stack consists of graphite compound bipolar plates with an active area of $30.87 \ cm^2$ per cell, in which on both sides, cathode and anode, a double-channel serpentine flow field is milled to deliver the reactants across the active area homogeneously. Similar to the single cell experiments, MEAs from GoreTM (PRIMEA® Series 5510, loading_{c/a}: $0.4/0.4 \ mg \ cm^{-2}$, thickness: $35 \ \mu m$) were assembled. This time, GDLs of type Toray TGP-H060 with a thickness of $190 \ \mu m$ (instead of $280 \ \mu m$, used in the single cell experiments) were investigated since this kind of GDL is originally attached and well characterized for this stack.

Again, only the cathode GDLs were modified by laser treatment. WTCs, with the same diameter of approx. $80 \,\mu m$, are placed beneath the channel along the serpentine flow field with a pitch of $1 \,mm$, leading to approx. 950 holes over the entire GDL area.

The stack temperature is regulated with a controllable fan, blowing through cooling channels that are visible in Fig. 6.35. Such an air cooling system is not able to

achieve a homogeneous temperature distribution throughout the stack. The outer cells (cell #1 and #6) are mostly cooler than the inner cells due to the additional heat dissipation via the end plates and the fact that only one adjacent cell acts as heat source. A further drawback of air cooling compared to water cooling (like in the single cell experiments) is the limited cooling capacity that complicates the temperature control. Thus, in the following experiments either a constant cooling capacity by a constant fan power was adjusted, leading to relatively high temperature differences for high and low load, or the temperature was controlled, leading to some temperature oscillations of $\pm 1^{\circ}$ C caused by the control. The stack temperature was measured by thermo couples on the surface of the bipolar plate in the middle of the stack. On the anode side, the stack was operated in "open end" mode (no recirculation of unutilized hydrogen).

Since the electrochemical interface from Solartron (used in the single cell experiments) is limited to a maximum current of 2A, a potentiostat from Zentro (EL 3000/60/125) with a maximum current capability of 125A and a voltage range up to 60V was used for the stack experiments. Unfortunately it was not possible to measure the stack impedance with this device. A single cell voltage tap is embedded on the stack to assign the monitored flooding event to the specific cells in the stack.

Several characterization techniques on different operating conditions were applied to investigate the influence of the GDL perforation on the water management:

- Constant current load The cell was operated in galvanostatic mode at a constant current of 22 A (approx. 0.65 Acm⁻²) that corresponds to a single cell voltage in the range of 0.5-0.6 V which is the optimal operating point concerning the interplay of power density, efficiency and stability for this stack in a system. In this mode a stable operation is desired with less purge events³. The mass flow controls of air and hydrogen were adjusted to a stoichiometry (λ) of 2.5 on the cathode side and 1.5 on the anode side. Both gases were humidified to a dew point of 35°C (as in all further stack experiments). The stack temperature was controlled to 63°C by the fan.
- **Polarization curve** Starting from OCV, the load was increased stepwise by 2A until the single cell voltages reached a value of about 0.4V. Then the experiment was stopped to prevent irreversible degradation since the voltages became unstable. Every current point was maintained for 5 min. A stoichiometry of $\lambda_{air} = 2.5$ and $\lambda_{H_2} = 1.5$ was chosen. At the beginning of each current step a purge event was initiated. The stack temperature was controlled to 63° C by the fan.

³A purge event is the activation of an air flow pulse to carry out liquid water. Here, the gas flow rates were automatically increased to $\dot{V}_{air} = 15 l min^{-1}$ and $\dot{V}_{H_2} = 3.5 l min^{-1}$ for a period of 5 s by the stack control to avoid large degradation if the deviation between single cell voltages exceed a limit of 120 mV.

- **Chronoamperometry** The stack voltage was stepped between 4.8V and 3.6V. To ensure repeatability 10 cycles were performed, whereby every voltage level was maintained for 200 s. The mass flow rates were set to $\dot{V}_{air} = 4.3 l \min^{-1}$ and $\dot{V}_{H_2} = 1 l \min^{-1}$. Since the temperature control is not able to fix a constant temperature for such high dynamic load changes, a continuous cooling power was adjusted by setting a constant fan velocity. Hence, the stack temperature increased with increasing current density due to increased reaction and ohmic heat. The higher temperature has a promotive effect to prevent flooding events since the saturation pressure increases with temperature, that makes a direct comparison of two relaxation curves with different temperatures difficult.
- **Chronovoltammetry** The stack current was stepped between 10 A and 15 A. 10 cycles were applied, whereby every current level was maintained for 200 s. Again, mass flow rates of $\dot{V}_{air} = 4.3 l min^{-1}$ and $\dot{V}_{H_2} = 1 l min^{-1}$ were adjusted and the same constant fan velocity for cooling as for the chronoamperometry was chosen.

Since a higher current density causes a higher stack temperature which in turn results in an improved ORR and a better oxygen diffusivity due to a lowered saturation of the porous media, a positive amplifying between temperature and current increase is activated that makes the separation of the influence of the GDL perforation and temperature effects difficult. By applying chronovoltammetry, the current density steps are given and hence more or less the heat sources. Therefore, the temperature effects are decoupled from the influence of the GDL perforation with this measurement technique.

Experimental Results

> Constant Current Load As mentioned before the air cooling system is not able to achieve a homogeneous temperature distribution throughout the stack. The existing temperature gradient from the cooler outer cells to the warmer cells inside the stack leads to inhomogeneous humidification conditions since the saturation, correlated with the relative humidity of the air, is a strong function of the temperature. Thus, a temperature variation of few degrees Celcius along the stack can lead to supersaturation of the gases in the outer cells whereby the water pressure is still below the saturation pressure in the inner cells. In the outer cells further evaporation of the generated water is suppressed and condensation of vapor starts leading to liquid water accumulation in the porous media and in the flow field structure. Thus, the outer cells tend to flood rather than the inner cells. Therefore it is expected that the GDL perforation has a huge advantage especially for the outer cells.

Figure 6.36 shows the cell voltages of an outer cell (cell #1) and an inner cell (cell #3) at a constant current of 22 A for a period of nearly $30 \min$ for a stack with modified and non-modified GDL. For the sake of clarity not all single cell voltages are shown, but it



Figure 6.36: Stability test of both stacks at a constant load of 22 A shows less cell voltage breaks in case of perforated GDLs than with the original ones. Due to their lower temperature the outer cells suffers more from liquid water than the inner cells which leads to lowered cell voltages. (*Active cell area:* $30.87 cm^2$)

can be stated that cell #3 is representative for all inner cells and that the characteristic of cell #1 is similar to cell #6. In the following only these two representative voltages are analyzed to determine the influence of the two temperature extremes within these cells. Additionally, the measured stack temperature is plotted.

First of all, it can be seen that the cells within the stack with perforated cathodic GDLs (Stack_{perf}) show higher voltages than the cell within the stack with the original GDLs (Stack_{org}). The voltage of the inner cell of the Stack_{perf} shows a stable value of about 0.575 V, compared to 0.53 V of the inner cells of Stack_{org}. Critical are the unstable voltages of the outer cells of both stacks, but again Stack_{perf} shows the higher value. It can be clearly seen that the voltages of the outer cells are responsible for the activation of the air flow pulse by the stack control to prevent a dramatical collapse of the cell voltage. During the shown time of about $30 \min$ four air flow pulses were required to prevent dramatical performance breaks for Stack_{org}, whereas only one pulse after 1400 s was sufficient for Stack_{perf}. This shows that Stack_{perf} suffers less on accumulated liquid water.

The temperatures of both measurements were controlled to 63°C, whereby an alter-

nating temperature of about $\pm 0.5^{\circ}$ C could not be avoided by the temperature control. This small temperature deviation couples with the cell voltages, especially of the voltage of the outer cells, that highlights a high sensitivity of the water management with the temperature in this operating point.

> **Polarization curve** Voltage-current curves of the problematic cell #1 within Stack_{org} and Stack_{perf} are shown in Fig. 6.37.



Figure 6.37: A comparison of polarization curves of cell #1 between Stack_{org} and Stack_{perf} shows clearly a performance and stability improvement in the middle and high current density range by using perforated GDLs.

Two features are evidently, on the one hand the cell voltage of $Stack_{perf}$ decreases slower with increasing curent density than that of $Stack_{org}$ which results in a higher current density. On the other hand the variance of the cell voltages of $Stack_{org}$ are much higher than for $Stack_{perf}$ indicating an improved water management of $Stack_{perf}$. The same data as used for Fig. 6.37 are plotted as voltage-time curve in Fig. 6.38, where some current steps are marked by arrows. In the high current density range the voltage of $Stack_{perf}$ is stable with only a slight decrease over time, whereas the voltage of $Stack_{org}$ exhibits stochastic breaks. Voltage plateaus for the different current steps are not visible for $Stack_{org}$ anymore. This experiments show that the GDL perforation improves the stack performance and stability.



Figure 6.38: The voltage of cell #1 versus time is visualized for both stacks. The curves are marked by arrows at the applied current density steps (in $A cm^{-2}$). The plot shows clearly the periodic instable operation of Stack_{org}, beginning at a current density of $0.45 A cm^{-2}$. Stack_{perf} is nearly stable up to $0.91 A cm^{-2}$.

> Chronoamperometry The current relaxation on a voltage step is investigated for both stacks in Fig. 6.39. The stack voltage was switched between 4.8V and 3.6Vthat corresponds to an average voltage step per single cell of $800 \, mV$ and $600 \, mV$, comparable to the single cell experiments. A distinct enhancement of the current density was achieved especially at low voltages. The characteristics of the relaxation curves are similar to the measurements with the small single cell. A small overshoot is visible on stepping from 4.8 V to 3.6 V which can be explained by a temporally delayed increase of the saturation related to the current increase, resulting in increasing mass transport limitations. The experiments were made with a constant (non-controlled) air cooling, thus the temperature rises about $11^{\circ}C$ (Stack_{org}) and $18^{\circ}C$ (Stack_{perf}). The higher current density of Stack_{perf} causes higher heat production, resulting in a higher stack temperature. The increased temperature in turn improves the reaction kinetics and reduces the saturation by higher evaporation rates. Thus, the direct comparison has to be treated with respect. Nevertheless, the WTCs have a positive influence on the water management and therefore on the fuel cell stack performance because the operating conditions of both experiments were equal.



Figure 6.39: The current response on voltage step changes between 4.8V and 3.6V differ clearly between the stack with untreated and perforated GDLs. Stack_{perf} operates on a higher performance level, especially under high load. It has to be kept in mind that for this characterization technique the higher temperature of Stack_{perf} reduces their significance concerning the prevention of pore flooding.

> Chronovoltammetry To elude the chicken or the egg causality dilemma of current and temperature, a similar experiment was made in galvanostatic mode where the stack current was switched between 10 *A* and 15 *A*. Galvanostatic measurements have the advantage of comparable heat generation because the current determines the ohmic and the reaction heat, that in fuel cells are the main heat sources (see modeling results in Fig. 6.23(b) on page 122). In Fig. 6.40 the cell voltage response on current steps shows a better performance for the Stack_{perf} again. An enhancement of about $50 - 60 \, mV$ was achieved at $15 \, A$. In this experiment a performance improvement due to a temperature effect can be excluded, since the temperature of Stack_{perf} is lower than Stack_{org}. The lower temperature of Stack_{perf} indicates a lower heat generation due to an improved mass transport. Consequently, one can claim that the temperature effect is not the determining influence for the improved performance and thus can be attributed to the GDL perforation by improving the water transport from the CL via the GDL to the channel.



Figure 6.40: Chronovoltammetry measurements show a better performance of $\text{Stack}_{\text{perf}}$. Applying the same current on both stacks leads to a higher temperature of $\text{Stack}_{\text{org}}$ due to higher activation overpotential caused by high oxygen transport limitations which in turn results in a lower cell voltage. Thus, from this experiment the temperature effect for an enhanced water management can be excluded. The improvement results definitely from the GDL perforation. (*Active cell area:* $30.87 \, cm^2$)

Résumé of customized GDL structuring in fuel cell stacks

The restructuring of a cathode GDL by laser perforation technique was effectually transferred from a small test cell (section 6.5.3) to a fuel cell stack with relevant size for portable applications. The shown experimental results of this section reveal that the GDL perforation improves the performance as well as the stability of an operating stack in the medium and high current density range. A reduced pore flooding is definitely verified when using the customized GDLs. The problems caused by an inhomogeneous temperature distribution throughout the cells within the stack, leading to water management problems for the cooler outer cells, is still visible for both stacks. However, the drastic collapses in performance observed in the outer cells of the unmodified stack could be reduced by the GDL perforation leading to less purge events.

By using perforated cathode GDLs, a lowered saturation of the porous media leads to a reduced water back diffusion to the anode side which in turn can increase the time interval between anode purge events. This improves the hydrogen utilization and thus the system efficiency. The more stable operation with the perforated GDLs leads to a easier stack control. The promising outcome of these investigations has given rise to patent the GDL perforation technique [152].

The restructuring of GDLs within the stack was applied with the same strategy as for the single cell. The WTCs were located beneath the channel structure with the same diameter and pitch. Because the hole arrangement, shape and size has not been optimized yet, hidden potential for the water management improvement is assumed by this technique. In-plane inhomogeneities due to temperature, reactant and vapor concentration could be compensated to a certain degree by e.g. graduated WTC pitch or size. The resulting problems of the outer cells due to their lower temperature could be minimized by differentiating the perforating strategy between inner and outer cells. Combining structured GDLs with unstructured or structured MPLs together with selective hydrophobizing/-philizing of some parts of the GDL show promise of achieving an optimized GDL design.



Chapter 7

Summary of Results and Conclusion

The investigations presented in this thesis focus on the dominant loss mechanisms of direct methanol (DMFC) and hydrogen fed polymer electrolyte membrane (PEFC) fuel cells. The main performance losses of DMFCs can be summarized into mixed potential formation caused by internal parasitic currents due to reactant permeation across the membrane, and an incomplete methanol oxidation to carbon monoxide leading to catalyst poisoning. A proper water management is the most challenging task for a stable and efficient operation of a PEFC since the operating window determined by membrane dehydration causing ohmic losses and pore flooding, which is responsible for high mass transport losses, is narrow.

By means of experimental characterization and modeling work, this thesis provides an improved understanding of the highly coupled processes occurring in a fuel cell. Several aspects such as methanol oxidation reaction, mixed potential formation, mass transport in porous media, phase transition, two-phase flow and interface conditions are analyzed with regard to the impact on fuel cell performance and reliability.

Great efforts have been made in embedding a reference electrode inside the fuel cell. A new concept for realizing reference electrodes based on laser ablation technique is presented, tested and used in this work. The well known problem of electrode misalignment due to imprecise preparation is solved by this technique. A new test fuel cell with reference electrodes, which are located close to $(300 \, \mu m)$ the working/counter electrode in their reactant compartment, was developed. The potential of the reference electrodes is able to serve for steady-state experiments as well as for dynamic experiments such as electrochemical impedance spectroscopy. The embedded reference electrodes enable the separation of the overall cell losses into cathode and anode losses.

The undesired cathode mixed potential formation by methanol crossover in DMFCs,

that suppresses the cell voltage, can be avoided by using methanol-tolerant catalysts which do not catalyze the parasitic methonal oxidation but only the desired oxygen reduction. In this work, a promising ruthenium-based catalyst modified with selenium (RuSe_x) was investigated with respect to its selectivity towards the oxygen reduction reaction. The selectivity of this catalyst is proven by current interruption (CI) measurements. It is found that RuSe_x has a lower catalytic activity than the established internal standard platinum (Pt). In spite of the methanol-tolerance of RuSe_x the expected higher open circuit voltage (OCV) was not observed. An anode undershoot of the potential relaxation curve after CI is observed by reference electrode measurements which implies a high deterioration of the anode potential under non-load conditions, responsible for the measured low OCV.

An explanation of this phenomenon is given by a newly developed one-dimensional, time-dependent DMFC model, that accounts for mixed potential formation and CO poisoning. The model captures qualitatively the dynamic of the anode potential after CI. Simulation results show that the insufficient bi-functional mechanism of the PtRu catalyst, which is assumed for the methanol oxidation kinetics, does not provide enough hydroxyl ions for the last oxidation step of CO to CO_2 . Thus, the Pt catalyst sites are nearly completely blocked by CO and thus inactive for further methanol oxidation. Consequently, less oxygen crossover leads to parasitic oxygen reduction reaction (ORR) at the poisoned anode which in turn needs high anode overpotential to counterbalance this undesired ORR.

From these results it can be concluded that further research in anode kinetics and catalyst development have to be done. A faster *CO* oxidation is necessary to avoid catalyst poisoning and therefore to enhance the DMFC performance.

For PEFCs, a good understanding of the formation and transport of liquid water, especially in the gas diffusion layer (GDL), is essential to increase cell performance and enhance durability. Therefore, the wetting properties of GDLs from Toray (TPG-H-090) and Freudenberg (H2315I3) were investigated by ESEM (Environmental Scanning Electron Microscope) imaging and correlated with in-situ potential sweep experiments. Contact angle estimations on the micro scale (fibers) from ESEM images differ strongly from the contact angle measured by the Sessile drop method (GDL surface). Even though the contact angles on the GDL surface are comparable for the Toray and Freudenberg diffusion media (both materials show hydrophobic properties with contact angles in the range of $130 - 140^{\circ}$ C), the Toray paper shows clearly hydrophilic wetting properties on the micro scale. The hydrophilic characteristics of the Toray GDL results in a hysteresis knee in the dynamic voltage-current curves at high current density values. In case of the Freudenberg GDL, no pronounced hysteresis behavior could be observed after detailed investigation of various operating conditions. The flooding events are rather observed in stochastic breakdowns of the current.

The investigations show that the contact angle on the micro scale is the dominant

quality for the liquid water transport.

A one-dimensional, time-dependent, multi-phase PEFC model was developed to improve the understanding of the complex water management. Based on numerous published model descriptions, the presented model was extended by special features reflecting the multi-phase problem. The transport of liquid water in the porous media is driven by capillary forces, modeled by Darcy's law with a modified Leverett-function for the capillary-pressure relationship which accounts for an immobile saturation. As mentioned before, this assumption is verified for a Toray GDL by ESEM imaging. Furthermore, the widely-used assumption of a vanishing saturation at the interface channel \leftrightarrow GDL as boundary condition was dropped and therefore a Cauchy-type boundary condition implemented which correlates the liquid water flux into the channel with the saturation in the GDL. In contrast to the most two-phase flow models, a continuous capillary pressure was used as interior boundary between GDL \leftrightarrow CL, resulting in a discontinuous saturation profile across the interface due to the different material properties of the two porous media. The impact of liquid water in the CL is captured by water film formation around the distributed applomerates, acting as additional diffusion barrier for the oxygen. Furthermore, finite phase transition rates between the three states of water (liquid water, water vapor and dissolved water in the ionomer) are considered.

The simulation results for dynamic current-voltage characteristics are in excellent agreement with measured data. The measured hysteresis loop in the limiting current density region is reproduced by the model and explained by pore flooding. The saturation in the GDL reaches values up to 78% at high current density. The measured cell impedance during a voltage sweep, which is a measure for the time-dependent water content, is in agreement with the simulation over a wide range of operating conditions and current densities.

The model forms a suitable basis for identifying the dominant loss mechanisms in PEFCs at different operating points. Based on the simulation results, suggestions for a better choice of fuel cell components can be made, guidance for their physical properties like pore structure, wettability or thickness can be obtained or simply optimal operating conditions can be found. The latter leads us to the topic of fuel cell control. A good understanding of the response on dynamic load changes is required to control a fuel cell within a stable operating point. This can be realized by implementing the model in a simplified form into a model-based control algorithm.

For improving the liquid water transport in the porous media, the GDL was structured with water transport channels (WTCs) by laser perforation. Investigations of the customized GDL in the test fuel cell showed better performance compared with a standard, non-modified GDL. Polarization curves show an increase in the limiting current density of 8-22% and chronoamperometry measurements show a reduced overshoot behavior. Both results prove that the perforated GDLs suffer less from accumulated liquid water. The potential to optimize the GDL structure with regard to liquid water transport is still very large since the arrangement of the water transport channels and their design has not been optimized yet.

Since a systematic perforation technique can play an important role in the transition to large fuel cells and stacks, where engineers have to cope with strong in-plane inhomogeneities in humidification, saturation and temperature from inlet to outlet, the laser perforation technique was effectually transferred from the test cell to a fuel cell stack with relevant size for portable applications. The experimental results reveal that the GDL perforation improves the performance as well as the stability of an operating stack in the medium and high current density range. A reduced pore flooding is definitely verified when using the customized GDLs. The promising outcome of these investigations has given rise to patent the GDL perforation technique.

With respect to the flow field geometry and operating conditions, a tailor-made GDL can be manufactured by the laser perforation technique to compensate for inhomogeneities in humidity, reactant concentration and temperature by a specific layout of the WTCs (e.g. graduated WTC pitch or size). Combining structured GDLs with customized micro porous layers in conjunction with selective hydrophobizing/-philizing of parts of the GDL would be promising towards an optimized GDL design. Another application of the presented perforation technique is for DMFCs. Systematic positioning of holes in the GDL can help to remove CO_2 in the gas phase, which is a by-product of the methanol oxidation, and therefore lead to a more stable performance especially in passive systems.

Bibliography

- T.E. Springer, T.A. Zawodzinski, and S. Gottesfeld. Polymer electrolyte fuel cell model. *Journal of The Electrochemical Society*, 138(8):2334–2341, 1991.
- [2] R. Greef, R. Peat, L.M. Peter, D. Pletcher, and J. Robinson. *Instrumental Methods in Electrochemistry*. Ellis Horwood Limited, Chichester, West Sussex, England, 1990.
- [3] P. Kurzweil. Brennstoffzellentechnik: Grundlagen, Komponenten, Systeme, Anwendungen. Vieweg+Teubner Verlag, 2003.
- [4] M. Wöhr. Instationäres, thermodynamisches Verhalten der Polymermembran -Brennstoffzelle. VDI Verlag, 2000.
- [5] A. Parthasarathy, B. Davé, S. Srinivasan, and A. J. Appleby. The platinum microelectrode/Nafion interface: an electrochemical impedance spectroscopic analysis of oxygen reduction kinetics and Nafion characteristics. *Journal of The Electrochemical Society*, 139(6):1634–1641, 1992.
- [6] D. Gerteisen, A. Hakenjos, and J.O. Schumacher. AC impedance modelling study on porous electrodes of proton exchange membrane fuel cells using an agglomerate model. *Journal of Power Sources*, 173:346–356, 2007.
- [7] R. Alink, D. Gerteisen, and M. Oszcipok. Degradation effects in polymer electrolyte membrane fuel cell stacks by sub-zero operation - an in situ and ex situ analysis. *Journal of Power Sources*, 182(1):175–187, 2008.
- [8] S.B. Adler, B.T. Henderson, M.A. Wilson, D.M. Taylor, and R.E. Richards. Reference electrode placement and seals in electrochemical oxygen generators. *Solid State Ionics*, 134:35–42, 2000.
- [9] Z. Liu, J.S. Wainright, Huang W., and R.F. Savinell. Positioning the reference electrode in proton exchange membrane fuel cells: calculations of primary and secondary current distribution. *Electrochimica Acta*, 49:923–935, 2004.
- [10] M. Nagata, Y. Itoh, and H. Iwahara. Dependence of observed overvoltages on the positioning of the reference electrode on the solid electrolyte. *Solid State lonics*, 67:215–224, 1994.

- [11] W. He and T. Van Nguyen. Edge effects on reference electrode measurements in PEM fuel cells. *Journal of The Electrochemistry Society*, 151(2):A185–A195, 2004.
- [12] Z. Siroma, R. Kakitsubo, N. Fujiwara, T. Ioroi, S.-I. Yamazaki, and K. Yasuda. Compact dynamic hydrogen electrode unit as a reference electrode for PEM-FCs. *Journal of Power Sources*, 156:284–287, 2006.
- [13] G. Li and P.G. Pickup. Measurement of single electrode potentials and impedances in hydrogen and direct methanol PEM fuel cells. *Electrochimica Acta*, 49:4119–4126, 2004.
- [14] A. Schmitz, S. Wagner, R. Hahn, A. Weil, E. Schneiderlöcher, M. Tranitz, and C. Hebling. MEA segmentation using LASER ablation. *Fuel Cells*, 4(3):1–6, 2004.
- [15] D. Gerteisen. Realising a reference electrode in a polymer electrolyte fuel cell. *Journal of Applied Electrochemistry*, 37(12):1447–1454, 2007.
- [16] K. Wiezell, P. Gode, and G. Lindbergh. Steady-state and EIS investigations of hydrogen electrodes and membranes in polymer electrolyte fuel cells - I. modeling. *Journal of The Electrochemistry Society*, 153(4):A749–A758, 2006.
- [17] K. Wiezell, P. Gode, and G. Lindbergh. Steady-state and EIS investigations of hydrogen electrodes and membranes in polymer electrolyte fuel cells - II. experimental. *Journal of The Electrochemistry Society*, 153(4):A759–A764, 2006.
- [18] T. Iwasita. Chapter 41: Methanol and CO electrooxidation. In W. Vielstich, H. Gaststeiger, and A. Lamm, editors, *Handbook of Fuel Cells*, volume 2, pages 603–624. John Wiley and Sons, Chichester, 2003.
- [19] V. A. Paganin, E. Sitta, T. Iwasita, and W. Vielstich. Methanol crossover effect on the cathode potential of a direct PEM fuel cell. *Journal of Applied Electrochemistry*, 35:1239–1243, 2005.
- [20] H. Dohle, R. Jung, N. Kimiaie, J. Mergel, and M. Müller. Interaction between the diffusion layer and the flow field of polymer electrolyte fuel cells - experiments and simulation studies. *Journal of Power Sources*, 124:371–384, 2003.
- [21] X. Zhao, X. Fan, S. Wang, S. Yang, B. Yi, Q. Xin, and G. Sun. Determination of ionic resistance and optimal composition in the anodic catalyst layers of DMFC using AC impedance. *International Journal of Hydrogen Energy*, 30(2005):1003–1010, 2005.

- [22] V.S. Silva, J. Schirmer, R. Reissner, B. Ruffmann, H. Silva, A. Mendes, L.M. Madeira, and S.P. Nunes. Proton electrolyte membrane properties and direct methanol fuel cell performance - II. fuel cell performance and membrane properties effects. *Journal of Power Sources*, 140:41–49, 2005.
- [23] C. Eickes, P. Piela, J. Davey, and P. Zelenay. Recoverable cathode performance loss in direct methanol fuel cells. *Journal of The Electrochemical Society*, 153(1):A171–A178, 2006.
- [24] K. Lee, O. Savadogo, A. Ishihara, S. Mitsushima, N. Kamiya, and K. Ota. Methanol-tolerant oxygen reduction electrocatalysts based on Pd-3D transition metal alloys for direct methanol fuel cells. *Journal of The Electrochemical Society*, 153(1):A20–A24, 2006.
- [25] U. Krewer and K. Sundmacher. Transfer function analysis of the dynamic behaviour of DMFCs: Response to step changes in cell current. *Journal of Power Sources*, 154:153–170, 2005.
- [26] K. Scott, A.K. Shukla, C.L. Jackson, and W.R.A. Meuleman. A mixed-reactants solid-polymer-electrolyte direct methanol fuel cell. *Journal of Power Sources*, 126:67–75, 2004.
- [27] L. Jörisson, V. Gogel, J. Kerres, and J. Garche. New membranes for direct methanol fuel cells. *Journal of Power Sources*, 105:267–273, 2002.
- [28] R. Jiang. Multilayer structure membranes with sulfonated hydrocarbon methanol barrier for direct methanol fuel cells. *Journal of The Electrochemical Society*, 153(8):A1554–A1561, 2006.
- [29] J. Kallo, J. Kamara, W. Lehnert, and R. von Helmolt. Cell voltage transients of gas-fed direct methanol fuel cell. *Journal of Power Sources*, 127:181–186, 2004.
- [30] H. Tributsch, M. Bron, M. Hilgendorff, H. Schulenburg, I. Dorbandt, V. Eyert, P. Bogdanoff, and S. Fiechter. Methanol-resistant cathodic oxygen reduction catalysts for methanol fuel cells. *Journal of Applied Electrochemistry*, 31:739– 748, 2001.
- [31] R.C. Koffi, C. Coutanceau, E. Garnier, J.-M. Léger, and C. Lamy. Synthesis, characterisation and electrocatalytic behaviour of non-alloyed PtCr methanol tolerant nanoelectrocatalysts for oxygen reduction reaction (ORR). *Electrochimica Acta*, 50:4117–4127, 2005.
- [32] H. Yang, C. Coutanceau, J.-M. Léger, N. Alonso-Vante, and C. Lamy. Methanol tolerant oxygen reduction on carbon-supported Pt-Ni alloy nanoparticles. *Journal of Applied Electrochemistry*, 576:305–313, 2005.

- [33] K. Wippermann, B. Richter, K. Klafki, J. Mergel, G. Zehl, I. Dorbandt, P. Bogdanoff, S. Fiechter, and S. Kaytakoglu. Carbon supported Ru-Se as methanol tolerant catalyst for DMFC cathodes. Part II: preparation and characterization of MEAs. *Journal of Applied Electrochemistry*, 37(12):1399–1411, 2007.
- [34] G. Zehl, P. Bogdanoff, I. Dorbandt, S. Fiechter, K. Wippermann, and C. Hartnig. Carbon supported Ru-Se as methanol tolerant catalyst for DMFC cathodes. Part I: preparation and characterization of catalysts. *Journal of Applied Electrochemistry*, 37(12):1475–1484, 2007.
- [35] A. Zawodzinski Thomas, Derouin Charles, Radzinski Susan, J. Sherman Ruth, T. Smith Van, E. Springer Thomas, and Gottesfeld Shimshon. Water uptake by and transport through Nafion 117 membranes. *Journal of The Electrochemical Society*, 140(4):1041–1047, 1993.
- [36] A.Z. Weber and J. Newmann. Transport in polymer-electrolyte membranes. I. Physical model. *Journal of The Electrochemical Society*, 150(7):A1008–A1015, 2003.
- [37] A.Z. Weber and J. Newmann. Transport in polymer-electrolyte membranes. II. Mathematical model. *Journal of The Electrochemical Society*, 151(2):A311– A325, 2004.
- [38] P. Argyropoulos, K. Scott, and W.M. Taama. Dynamic response of the direct methanol fuel cell under variable load conditions. *Journal of Power Sources*, 87:153–161, 2000.
- [39] P. Argyropoulos, K. Scott, and W.M. Taama. The effect of operating conditions on the dynamic response of the direct methanol fuel cell. *Electrochimica Acta*, 45:1983–1998, 2000.
- [40] F. Seland, R. Tunold, and D. A. Harrington. Impedance study of methanol oxidation on platinum electrodes. *Electrochimica Acta*, 51:3827–3840, 2006.
- [41] Z. Jusys, J. Kaiser, and R.J. Behm. Composition and activity of high surface area PtRu catalysts towards adsorbed CO and methanol electrooxidation - a DEMS study. *Electrochimica Acta*, 47(22-23):3693–3706, 2002.
- [42] X.H. Xia, T. Iwasita, F. Ge, and W. Vielstich. Structural effects and reactivity in methanol oxidation on polycrystalline and single crystal platinum. *Electrochimica Acta*, 41(5):711–718, 1996.
- [43] T. Vidakovic, M. Christov, and K. Sundmacher. Rate expression for electrochemical oxidation of methanol on a direct methanol fuel cell anode. *Journal of Electroanalytical Chemistry*, 580(1):105–121, 2005.

- [44] S. Gilman. The mechanism of electrochemical oxidation of carbon monoxide and methanol on platinum. II. the reactant-pair mechanism for electrochemical oxidation of carbon monoxide and methanol. J. Phys. Chem., 68(1):70–80, 1964.
- [45] Hubert A. Gasteiger, Nenad Markovic, Philip N. Ross, and Elton J. Cairns. Methanol electrooxidation on well-characterized platinum-ruthenium bulk alloys. J. Phys. Chem., 97(46):12020–12029, 1993.
- [46] S. Motoo and M. Watanabe. Electrocatalysis by Sn and Ge AD-atoms. *Journal of Electroanalytical Chemistry*, 69:429–431, 1976.
- [47] M. T. M. Koper, J. J. Lukkien, A. P. J. Jansen, and R. A. van Santen. Lattice gas model for CO electrooxidation on Pt-Ru bimetallic surfaces. *J. Phys. Chem. B*, 103(26):5522–5529, 1999.
- [48] E. Christoffersen, P. Liu, A. Ruban, H. L. Skriver, and J. K. Nørskov. Anode materials for low-temperature fuel cells: A density functional theory study. *Journal* of *Catalysis*, 199(1):123–131, 2001.
- [49] B. Hammer and J. K. Nørskov. Electronic factors determining the reactivity of metal surfaces. *Surface Science*, 343(3):211–220, 1995.
- [50] M.R. Shivhare, C.L. Jackson, K. Scott, and E.B. Martin. Simplified model for the direct methanol fuel cell anode. *Journal of Power Sources*, 173:240–248, 2007.
- [51] J. Ge and H. Liu. A three-dimensional mathematical model for liquid-fed direct methanol fuel cells. *Journal of Power Sources*, 160:413–421, 2006.
- [52] W.W. Yang and T.S. Zhao. A two-dimensional, two-phase mass transport model for liquid-feed DMFCs. *Electrochimica Acta*, 52:6125–6140, 2007.
- [53] X. Liu, H. Guo, F. Ye, and C.F. Ma. Water flooding and pressure drop characteristics in flow channels of proton exchange membrane fuel cells. *Electrochimica Acta*, 52(11):3607–3614, 2007.
- [54] E. Vilar and R.A. Dougal. Study of pulsed-current loading of direct methanol fuel cells using a new time-domain model based on bi-functional methanol oxidation kinetics. *Journal of Power Sources*, 169:276–287, 2007.
- [55] T. Frelink, W. Visscher, and J. A. R. van Veen. Measurement of the Ru surface content of electrocodeposited PtRu electrodes with the electrochemical quartz crystal microbalance: Implications for methanol and CO electrooxidation. *Langmuir*, 12(15):3702–3708, 1996.

- [56] K. Scott and P. Argyropoulos. A one dimensional model of a methanol fuel cell anode. *Journal of Power Sources*, 137(2):228–238, 2004.
- [57] M.L. Perry, J. Newman, and E.J. Cairns. Mass transport in gas-diffusion electrodes: a diagnostic tool for fuel-cell cathodes. *Journal of The Electrochemical Society*, 145(1):5–15, 1998.
- [58] F. Jaouen, G. Lindbergh, and G. Sundholm. Investigation of mass-transport limitations in the solid polymer fuel cell cathode - mathematical model. *Journal* of The Electrochemical Society, 149(4):A437–A447, 2002.
- [59] F. Jaouen, G. Lindbergh, and G. Sundholm. Investigation of mass-transport limitations in the solid polymer fuel cell cathode - I. mathematical model. *Journal* of The Electrochemical Society, 149(4):A437–A447, 2002.
- [60] M. Eikerling and A.A. Kornyshev. Modelling the performance of the cathode catalyst layer of polymer electrolyte fuel cells. *Journal of Electroanalytical Chemistry*, 453(1-2):89–106, 1998.
- [61] U. Krewer, A. Kamat, and K. Sundmacher. Understanding the dynamic behaviour of direct methanol fuel cells: response to step changes in cell current. *Journal of Electroanalytical Chemistry*, 609:105–119, 2007.
- [62] M. Watanabe and S. Motoo. Electrocatalysis by ad-atoms : Part III. Enhancement of the oxidation of carbon monoxide on platinum by ruthenium ad-atoms. *Journal of Electroanalytical Chemistry*, 60(3):275–283, 1975.
- [63] S. Gottesfeld and J. Pafford. New approach to the problem of carbon monoxide poisoning in fuel cells operating at low temperatures. *Journal of The Electrochemical Society*, 135(10):2651–2652, 1988.
- [64] S. Eccarius. Approaches to Passive Operation of a Direct Methanol Fuel Cell. PhD thesis, Universität Karlsruhe (TU), 2007.
- [65] J. Ihonen, F. Jaouen, G. Lindbergh, and G. Sundholm. Investigation of masstransport limitations in the solid polymer fuel cell cathode - II. experimental. *Journal of The Electrochemical Society*, 149(4):A448–A454, 2002.
- [66] M. V. Williams, H. R. Kunz, and J. M. Fenton. Influence of convection through gas-diffusion layers on limiting current in PEM FCs using a serpentine flow field. *Journal of the Electrochemical Society*, 151(10):A1617–A1627, 2004.
- [67] B.L. Garcia, V.A. Sethuraman, J.W. Weidner, R.E. White, and R. Dougal. Mathematical model of a direct methanol fuel cell. *Journal of Fuel Cell Science and Technology*, 1:43–48, 2004.

- [68] Sukkee Um, C. Y. Wang, and K. S. Chen. Computational fluid dynamics modeling of proton exchange membrane fuel cells. *Journal of The Electrochemical Society*, 147(12):4485–4493, 2000.
- [69] S. Um and C.-Y. Wang. Computational study of water transport in proton exchange membrane fuel cells. *Journal of Power Sources*, 156:211–223, 2006.
- [70] R. Sander. Compilation of Henry's Law constants for inorganic and organic species of potential importance in environmental chemistry. *http://www.mpch-mainz.mpg.de/ sander/res/henry.html*, 1999.
- [71] Wei Sun, Brant A. Peppley, and Kunal Karan. An improved two-dimensional agglomerate cathode model to study the influence of catalyst layer structural parameters. *Electrochimica Acta*, 50(16-17):3359–3374, 2005.
- [72] A.D. Bosco and M.H. Fronk. US Patent: Fuel cell flooding detection and correction, August 2000 2000.
- [73] F. Barbir, H. Görgün, and X. Wang. Relationship between pressure drop and cell resistance as a diagnostic tool for PEM fuel cells. *Journal of Power Sources*, 141(1):96–101, 2005.
- [74] H. Görgün, M. Arcak, and F. Barbir. An algorithm for estimation of membrane water content in PEM fuel cells. *Journal of Power Sources*, 157(1):389–394, 2006.
- [75] H.P. Ma, H.M. Zhang, J. Hu, Y.H. Cai, and B.L. Yi. Diagnostic tool to detect liquid water removal in the cathode channels of proton exchange membrane fuel cells. *Journal of Power Sources*, 162(1):469–473, 2006.
- [76] Kohei Ito, Kensuke Ashikaga, Hiromitsu Masuda, Toshihiro Oshima, Yasushi Kakimoto, and Kazunari Sasaki. Estimation of flooding in PEMFC gas diffusion layer by differential pressure measurement. *Journal of Power Sources*, 175(2):732–738, 2008.
- [77] W. He, G. Lin, and T.v. Nguyen. Diagnostic tool to detect electrode flooding in proton-exchange-membrane fuel cells. *AIChE Journal*, 49(12):3221–3228, 2002.
- [78] K. Tüber, D. Pócza, and C. Hebling. Visualization of water buildup in the cathode of a transparent PEM fuel cell. *Journal of Power Sources*, 124(2):403–414, 2003.
- [79] F.B. Weng, A. Su, C.Y. Hsu, and C.Y. Lee. Study of water-flooding behaviour in cathode channel of a transparent proton-exchange fuel cell. *Journal of Power Sources*, 157(2):674–680, 2006.
- [80] X. Liu, H. Guo, and C.F. Ma. Water flooding and two-phase flow in cathode channels of proton exchange membrane fuel cells. *Journal of Power Sources*, 156(2):267–280, 2006.
- [81] A. Su, F.B. Weng, C.Y. Hsu, and Y.M. Chen. Studies on flooding in PEM fuel cell cathode channels. *Int J Hydrogen Energy*, 31(8):1031–1039, 2006.
- [82] R.J. Bellows, M.Y. Lin, M. Arif, A.K. Thompson, and D. Jacobson. Neutron imaging technique for in situ measurement of water transport gradients within Nafion in polymer electrolyte fuel cells. *Journal of Electrochemical Society*, 146(3):1099–1103, 1999.
- [83] R. Satjia, D.L. Jacobson, M. Arif, and S.A Werner. In situ neutron imaging technique for evaluation of water management systems in operating PEM fuel cells. *Journal of Power Sources*, 129(2):238–245, 2004.
- [84] N. Pekula, K. Heller, P.A. Chuang, A. Turhan, M.M. Mench, and J.S. Brenizer. Study of water distribution and transport in a polymer electrolyte fuel cell using neutron imaging. *Nucl Instrum Methods Phys Res Sect A*, 542(1-3):134–141, 2005.
- [85] J.J. Kowal, A. Turhan, K. Heller, J.S. Brenizer, and M.M. Mench. Liquid water storage distribution, and removal from diffusion media in PEFCs. *Journal of Electrochemical Society*, 153(10):A1971–1078, 2006.
- [86] Christoph Hartnig, Ingo Manke, Robert Kuhn, Nikolay Kardjilov, John Banhart, and Werner Lehnert. Cross-sectional insight in the water evolution and transport in polymer electrolyte fuel cells. *Applied Physics Letters*, 92(134106), 2008.
- [87] S. Tsushima, K. Teranishi, and S. Hirai. Magnetic resonance imaging of water distribution within a polymer electrolyte membrane in fuel cells. *Electrochem Solid State Lett*, 7:A269–A272, 2004.
- [88] K. Teranishi, S. Tsushima, and S. Hirai. Analysis of water transport in PEFCs by magnetic resonance imaging measurement. *Journal of Electrochemical Society*, 153(4):A664–A668, 2006.
- [89] A. Hakenjos, H. Münter, U. Wittstadt, and C. Hebling. A PEM fuel cell for combined measurement of current and temperature distribution, and flow field flooding. *Journal of Power Sources*, 131:213–216, 2004.
- [90] A. Hakenjos, M. Zobel, and C. Hebling. Spatially resolved measurement of PEM fuel cells. *Journal of Power Sources*, 145(2):307–311, 2005.

- [91] M.M. Mench and C.Y. Wang. In situ current distribution measurements in polymer electrolyte fuel cells. *Journal of Electrochemical Society*, 150(8):A1052– A1059, 2003.
- [92] M. Noponen, J. Ihonen, A. Lundblad, and G. Lindbergh. Current distribution measurements in a PEFC with net flow geometry. *Journal of Applied Electrochemistry*, 34(3):255–262, 2004.
- [93] Ch. Hartnig, I. Manke, N. Kardjilov, A. Hilger, M. Grünerbel, J. Kaczerowski, J. Banhart, and W. Lehnert. Combined neutron radiography and locally resolved current density measurements of operating PEM fuel cells. *Journal of Power Sources*, 176:452–459, 2008.
- [94] I.A. Schneider, D. Kramer, A. Wokaun, and G.G. Scherer. Spatially resolved characterization of PEFCs using simultaneously neutron radiography and locally resolved impedance. *Electrochem. Commun.*, 7(12):1393–1397, 2005.
- [95] P.K. Sinha and C.Y. Wang. Pore-network modeling of liquid water transport in gas diffusion layer of a polymer electrolyte fuel cell. *Electrochimica Acta*, 52:7936–7945, 2007.
- [96] S. Mazumder and J.V. Cole. Rigorous 3-d mathematical modeling of PEM fuel cells - II. model predictions with liquid water transport. *Journal of The Electrochemical Society*, 150(11):A1510–A1517, 2003.
- [97] T. Berning and N. Djilali. A 3d. multiphase, multicomponent model of the cathode and anode of a PEM fuel cell. *Journal of The Electrochemical Society*, 150(12):A1589–A1598, 2003.
- [98] U. Pasaogullari and C.Y. Wang. Two-phase transport and the role of microporous layer in polymer electrolyte fuel cells. *Electrochimica Acta*, 49:4359– 4369, 2004.
- [99] M. Hu, A. Gu, M. Wang, and X. Zhu. Three dimensional, two phase flow mathematical model for PEM fuel cell: Part I. model development. *Energy Conversion* and Management, 45:1861–1882, 2004.
- [100] M. Hu, X. Zhu, M. Wang, A. Gu, and L. Yu. Three dimensional, two phase flow mathematical model for PEM fuel cell: Part II. analysis and discussion of the internal transport mechanisms. *Energy Conversion and Management*, 45:1883–1916, 2004.
- [101] J.J. Baschuk and X. Li. A general formulation for a mathematical PEM fuel cell model. *Journal of Power Sources*, 142:134–153, 2004.

- [102] U. Pasaogullari and C.Y. Wang. Liquid water transport in gas diffusion layer of polymer electrolyte fuel cells. *Journal of The Electrochemistry Society*, 151(3):A399–A406, 2004.
- [103] E. Birgersson, M. Noponen, and M. Vynnycky. Analysis of a two-phase non-isothermal model for a PEFC. *Journal of The Electrochemical Society*, 152(5):A1021–A1034, 2005.
- [104] U. Pasaogullari and C.Y. Wang. Two-phase modeling and flooding prediction of polymer electrolyte fuel cells. *Journal of The Electrochemical Society*, 152(2):A380–A390, 2005.
- [105] K. Steinkamp, J. O. Schumacher, F. Goldsmith, M. Ohlberger, and C. Ziegler. A nonisothermal PEM fuel cell model including two water transport mechanisms in the membrane. *Journal of Fuel Cell Science and Technology*, 5(1):011007, 2008.
- [106] P. Berg, K. Promislow, J. St.Pierre, J. Stumper, and B. Wetton. Water management in PEM fuel cells. *Journal of The Electrochemical Society*, 151(3):A341– A353, 2004.
- [107] G. Lin, W. He, and T. V. Nguyen. Modeling liquid water effects in the gas diffusion and catalyst layers of the cathode of a PEM fuel cell. *Journal of The Electrochemical Society*, 151(12):A1999–A2006, 2004.
- [108] H.K. Hsuen. Performance equations for the cathodes in polymer electrolyte fuel cells with non-uniform water flooding in gas diffusers. *Journal of Power Sources*, 137:183–195, 2004.
- [109] P. Berg, A. Novruzi, and K. Promislow. Analysis of a cathode catalyst layer model for a polymer electrolyte fuel cell. *Chemical Engineering Science*, 61:4316–4331, 2006.
- [110] A. Vorobev, O. Zikanov, and T. Shamim. A computational model of a PEM fuel cell with finite vapor absorption rate. *Journal of Power Sources*, 166:92–103, 2007.
- [111] H. Wu, P. Berg, and X. Li. Non-isothermal transient modeling of water transport in PEM fuel cells. *Journal of Power Sources*, 165:232–243, 2007.
- [112] Y. Wang and C.-Y. Wang. Dynamics of polymer electrolyte fuel cells undergoing load changes. *Electrochimica Acta*, 51:3924–3933, 2006.
- [113] W.-M. Yan, H.-S. Chu, J.-Y. Chen, C.-Y. Soong, and F. Chen. Transient analysis of water transport in PEM fuel cells. *Journal of Power Sources*, 162:1147–1156, 2006.

- [114] F. Chen, M.-H. Chang, and C.-F. Fang. Analysis of water transport in a five-layer model of PEMFC. *Journal of Power Sources*, 164:649–658, 2007.
- [115] M. Eikerling. Water management in cathode catalyst layers of PEM fuel cells a structure-based model. *Journal of The Electrochemical Society*, 153(3):E58– E70, 2006.
- [116] F. Jaouen and G. Lindbergh. Transient techniques for investigating masstransport limitations in gas diffusion electrodes - I. modeling the PEFC cathode. *Journal of The Electrochemical Society*, 150(12):A1699–A1710, 2003.
- [117] R. Madhusudana Rao and R. Rengaswamy. Dynamic characteristics of spherical agglomerate for study of cathode catalyst layers in proton exchange membrane fuel cells (PEMFC). *Journal of Power Sources*, 158:110–123, 2006.
- [118] D. Natarajan and T. V. Nguyen. A two-dimensional, two-phase, multicomponent, transient model for the cathode of a proton exchange membrane fuel cell using conventional gas distributors. *Journal of The Electrochemical Society*, 148(12):A1324–A1335, 2001.
- [119] D. Natarajan and T.V. Nguyen. Three-dimensional effects of liquid water flooding in the cathode of a PEM fuel cell. *Journal of Power Sources*, 115:66–80, 2003.
- [120] N.P. Siegel, M.W. Ellis, D.J. Nelson, and M.R. von Spakovsky. A twodimensional computational model of a PEMFC with liquid water transport. *Journal of Power Sources*, 128:173–184, 2004.
- [121] M. Acosta, C. Merten, G Eigenberger, H. Class, R. Helmig, B. Thoben, and H. Mueller-Steinhagen. Modeling non-isothermal two-phase multicomponent flow in the cathode of PEM fuel cells. *Journal of Power Sources*, 159:1123– 1141, 2006.
- [122] E.C. Kumbur, K.V. Sharp, and M.M. Mench. On the effectiveness of Leverett approach for describing the water transport in fuel cell diffusion media. *Journal of Power Sources*, 168:356–368, 2007.
- [123] J.H. Nam and M. Kaviany. Effective diffusivity and water-saturation distribution in single- and two-layer PEMFC diffusion medium. *International Journal of Heat and Mass Transfer*, 46:4595–4611, 2003.
- [124] C. Ziegler, H.M. Yu, and J.O. Schumacher. Two-phase dynamic modeling of PEMFCs and simulation of cyclo-voltammograms. *J. Electrochem. Soc.*, 152:A1555–A1567, 2005.

- [125] H. M. Yu and C. Ziegler. Transient behavior of a proton exchange membrane fuel cell under dry operation. *Journal of The Electrochemical Society*, 153(3):A570–A575, 2006.
- [126] A.A. Shah, G.-S. Kim, P.C. Sui, and D. Harvey. Transient non-isothermal model of a polymer electrolyte fuel cell. *Journal of Power Sources*, 163:793–806, 2007.
- [127] A.A. Shah, G.-S. Kim, W. Gervais, A. Young, K. Promislow, J. Li, and S. Ye. The effects of water and microstructure on the performance of polymer electrolyte fuel cells. *Journal of Power Sources*, 160:1251–1268, 2006.
- [128] R.B. Bird, W.E. Stewart, and E.N. Lightfoot. *Transport phenomena*. John Wiley and Sons, 2nd edition, 2002.
- [129] B. Andreaus, A.J. McEvoy, and G.G. Scherer. Analysis of performance losses in polymer electrolyte fuel cells at high current densities by impedance spectroscopy. *Electrochimica Acta*, 47:2223–2229, 2002.
- [130] K.C. Neyerlin, H.A. Gasteiger, C.K. Mittelsteadt, J. Jorne, and W. Gu. Effect of relative humidity on oxygen reduction kinetics in a PEMFC. *Journal of The Electrochemical Society*, 152(6):A1073–A1080, 2005.
- [131] E.W. Thiele. Relation between catalytic activity and size of particle. *Industrial and Engineering Chemistry*, 31(7):916–920, 1939.
- [132] Z. Liu, Z. Mao, and C. Wang. A two dimensional partial flooding model for PEMFC. *Journal of Power Sources*, 158:1229–1239, 2006.
- [133] M.T. van Genuchten. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal*, 44:892– 898, 1980.
- [134] R.H. Brooks and A.T. Corey. Hydraulic properties of porous media. *Hydrology Paper*, 3:22–27, 1964.
- [135] J. Bear. *Dynamics of Fluids in Porous Media*. Dover Publications, New York, 1972.
- [136] K. S. Udell. Heat transfer in porous media considering phase change and capillarity - the heat pipe effect. *International Journal of Heat and Mass Transfer*, 28:485–495, 1985.
- [137] W. He, J.S. Yi, and T. Van Nguyen. Two-phase flow model of the cathode of PEM fuel cells using interdigitated flow fields. *AIChE Journal*, 46(10):2053– 2064, 2000.

- [138] L. You and H. Liu. A two-phase flow and transport model for the cathode of PEM fuel cells. International Journal of Heat and Mass Transfer, 45:2277– 2287, 2002.
- [139] J.T. Gostick, M.W. Gowler, M.A. Ioannidid, M.D. Pritzker, Y.M. Volfkovich, and A. Sakars. Capillary pressure and hydrophilic porosity in gas diffusion layers for polymer electrolyte fuel cells. *Journal of Power Sources*, 156:375–387, 2006.
- [140] T.E. Springer, T.A. Zawodzinski, M.S. Wilson, and S. Gottesfeld. Characterization of polymer electrolyte fuel cells using ac impedance spectroscopy. *Journal* of The Electrochemical Society, 143(2):587–599, 1996.
- [141] Z.H. Wang, C.-Y. Wang, and K.S. Chen. Two-phase flow and transport in the air cathode of proton exchange membrane fuel cells. *Journal of Power Sources*, 94:40–50, 2001.
- [142] S. Litster and G. McLean. PEM fuel cell electrodes. *Journal of Power Sources*, 130:61–76, 2004.
- [143] P.K. Sinha, C.-Y. Wang, and A. Su. Optimization of gas diffusion media for elevated temperature polymer electrolyte fuel cells. *International Journal of Hydrogen Energy*, 32:886–894, 2007.
- [144] *VDI-Wärmeatlas*. Verein Deutscher Ingenieure, Springer Verlag Berlin Heidelberg, 1988.
- [145] Zhigang Qi and Arthur Kaufman. Improvement of water management by a microporous sublayer for PEM fuel cells. *Journal of Power Sources*, 109(1):38– 46, 2002.
- [146] U. Pasaogullari and C.Y. Wang. Liquid water transport in gas diffusion layer of polymer electrolyte fuel cells. *Journal of The Electrochemistry Society*, 151(3):A399–A406, 2004.
- [147] J.T. Gostick, M.W. Fowler, M.A. Ioannidis, M.D. Pritzker, Y.M. Volfkovitch, and A. Sakars. Capillary pressure and hydrophilic porosity in gas diffusion layers for polymer electrolyte fuel cells. *J. Power Sources*, 156(2):375–387, 2006.
- [148] S. Litster, D. Sinton, and N. Djilali. Ex situ visualization of liquid water transport in PEM fuel cell gas diffusion layers. *J. Power Sources*, 154:95–105, 2006.
- [149] A. Bazylak, D. Sinton, Z.-S. Liu, and N. Djilali. Effect of compression on liquid water transport and microstructure of PEMFC gas diffusion layers. *J. Power Sources*, 163:784–792, 2007.

- [150] J.T. Gostick, M.W. Fowler, M.D. Pritzker, M.A. Ioannidid, and L.M. Behra. Inplane and through-plane gas permeability of carbon fiber electrode backing layers. *Journal of Power Sources*, 162:228–238, 2006.
- [151] V. P. Schulz, J. Becker, A. Wiegmann, P. P. Mukherjee, and C.-Y. Wang. Modeling of two-phase behavior in the gas diffusion medium of PEFCs via full morphology approach. *Journal of the Electrochemical Society*, 154(4):B419–B426, 2007.
- [152] Dietmar Gerteisen. Patent: Verfahren zur Herstellung von Gasdiffusionsschichten, derart hergestellte Gasdiffusionsschichten und diese enthaltende Brennstoffzellen, 15.02.2007 DE102007007533B3 03.07.2008.

Author's publications

Peer-reviewed Journal Articles

Modeling the phenomena of dehydration and flooding of a polymer electrolyte membrane fuel cell *Journal of Power Sources*, Volume 187, Issue 1, 2009, Pages 165-181 D. Gerteisen, T. Heilmann, C. Ziegler

Validity of two-phase polymer electrolyte membrane fuel cell models with respect to the gas diffusion layer *Journal of Power Sources*, Volume 188, Issue 1, 2009, Pages 184-191 C. Ziegler, D. Gerteisen

Degradation effects in polymer electrolyte membrane fuel cell stacks by sub-zero operation - An in situ and ex situ analysis *Journal of Power Sources*, Volume 182, Issue 1, 2008, Pages 175-187 R. Alink, D. Gerteisen, M. Oszcipok

Enhancing liquid water transport by laser perforation of a GDL in a PEM fuel cell *Journal of Power Sources*, Volume 177, Issue 2, 2008, Pages 348-354 D. Gerteisen, T. Heilmann, C. Ziegler

Experimental study of two-phase transients in PEMFCs Journal of the Electrochemical Society, Volume 155, Issue 4, 2008, Pages B349-B355 C. Ziegler, T. Heilmann, D. Gerteisen

AC impedance modelling study on porous electrodes of proton exchange membrane fuel cells using an agglomerate model *Journal of Power Sources*, Volume 173, Issue 1, 2007, Pages 346-356 D. Gerteisen, A. Hakenjos, J.O. Schumacher

Realising a reference electrode in a polymer electrolyte fuel cell by laser ablation *Journal of Applied Electrochemistry*, Volume 37, Issue 12, 2007, Pages 1447-1454 D. Gerteisen

Charakterisierung von porösen Gasdiffusionselektroden in Polymer-Elektrolyt-Brennstoffzellen mit Hilfe der Impedanzspektroskopie in einer Referenzelektrodenanordnung

Technische Mitteilungen, Volume 99, Issue 1/2, 2006, Pages 112-117, ISSN 0040-1439

D. Gerteisen, M. Walter, S. Eccarius

Modelling and simulation of a direct ethanol fuel cell considering multistep electrochemical reactions, transport processes and mixed potentials *Journal of Power Sources*, submitted, 2008 M. Meyer, J. Melke, D. Gerteisen

Conferences

Modelling the Dynamic Effects of Catalyst Poisoning and Mixed Potential Formation in a DMFC *The European FUEL CELL FORUM 2009*, Lucerne, Switzerland D. Gerteisen, M. Meyer

Dynamic modeling of CO poisoning in PBI-based HTPEM fuel cells 6th Symposium on Fuel Cell Modelling and Experimental Validation (MODVAL 6), 2009, Bad Herrenalp, Germany A. Bergmann, D. Gerteisen, T. Kurz

Modelling the Impact of Mixed Potential and Intermediates in a Direct Ethanol Fuel Cell

Proceedings, Fuel Cells Science & Technology 2008, Copenhagen, Denmark, 8./9.10.2008 J. Melke, F. Schmid, M. Meyer, Koch, L., D. Gerteisen

A detailed cathode agglomerate model considering dehydration and flooding effects *10th Grove Fuel Cell Symposium*, London, UK, 25.27.09.2007 D. Gerteisen, T. Heilmann, C. Ziegler Degradation Effects in PEM Fuel Cell Stacks at Sub-Zero-Operation (in In-Situ and Ex-Situ Analysis)

Degradation Workshop (EU), Hersonissos, Crete, Greece, 18.-21.06.2007 C. Hebling, M. Oszcipok, R. Alink, D. Gerteisen

Modeling the influence of water on the electrode performance of a polymer electrolyte fuel cell

Young Scientists Workshop, Victoria, Canada, 4.-5.05.2007 D. Gerteisen, T. Heilmann, C. Ziegler

Predictive fuel cell control strategies based on impedance measurements *Fuel Cell Seminar & Exposition*, Honolulu, Hawaii, 13.-17.11.2006 T. Kurz, J. Steiner, D. Gerteisen, A. Hakenjos, C. Agert, C. Hebling

Characterisation of different flow field geometries for PEM fuel cells *Fuel Cell Science & Technology*, Turino, Italy, 13.-14.09.2006 D. Gerteisen, T. Kurz, A. Hakenjos, W. Hogarth, M. Kornhaas, J. Steiner

Model-Based Analysis of the Current Interrupt Technique for the Characterisation of Porous Gas Diffusion Electrodes in PEM Fuel Cells *Proceedings 3rd European Fuel Cell Forum 2005*, Lucerne, Switzerland, 4.–8.07.2005 D. Gerteisen, A. Hakenjos, J.O. Schumacher

Interpretation of spatially resolved impedance measurement of PEM fuel cells *Proceedings 3rd European PEFC Forum*, Lucerne, Switzerland, 4.–8.07.2005 A. Hakenjos, D. Gerteisen, C. Hebling

Modelling of proton exchange membrane (PEM) fuel cells *Forum Echem*, Applied Electrochemistry, Wien, 2003 J.O. Schumacher, E. Fontes, D. Gerteisen, A. Hakenkos, K. Kühn, M. Ohlberger, A. Schmitz, K. Tüber, C. Ziegler

Investigation of the cathode active layer of PEM fuel cells using AC impedance spectroscopy (2003)

Proceedings 2nd European PEFC Forum 2003, Volume 1, 2003, Lucerne, Switzerland, Pages 271-282

D. Gerteisen, A. Hakenjos, J.O. Schumacher

Oral Presentation

Investigation of multi-phase flow in PEMFC by experimental and modeling work *HyFC Academy School on Fuel Cells and Hydrogen*, Vancouver, Canada, 26.-29.05.2009 D. Gerteisen, R. Alink, C. Hebling

Moderne mathematische Methoden in der Brennstoffzellenforschung *Formel M: Mathematik für Innovation und Energieforschung*, Duisburg, 26.-28.10.2008 D. Gerteisen

Modelling transient effects in a PEM fuel cell considering flooding and dehydration *Fuel Cells Science & Technology 2008: Scientific Advances in Fuel Cell Systems*, Copenhagen, Denmark, 8.–9.10.2008 D. Gerteisen, T. Heilmann, C. Ziegler

A Dynamic Multi-Phase PEM Fuel Cell Model Focused on the Catalyst Layer and Comparison with Polarization Sweep Measurements *5th Symposium on Fuel Cell Modelling and Experimental Validation*, Winterthur, Switzerland, 11.-12.03.2008 D. Gerteisen

Charakterisierung von porösen Gasdiffusionselektroden in Polymer - Elektrolyt - Brennstoffzellen mit Hilfe der Impedanzspektroskopie in einer Referenzelektrodenanordnung

 Symposium – Impedanzspektroskopie Grundlagen und Anwendung, Haus der Technik – Außeninstitut der RWTH Aachen, Germany, 16./17.5.2006
D. Gerteisen, W. Walter

Investigation of the Performance of RuSe Catalyst for the ORR Using a Reference Electrode Measurements Set-up *Workshop O2-RedNet*, Ulm, Germany, 6./7.4.2006 D. Gerteisen, M. Walter, A. Wolff, J. Melke

In-situ Charakterisierungsmethoden für PEMFC und DMFC Netzwerk: H2- und Methanol-PEM-Brennstoffzellen Workshop: Apparative Ausstattung, Messung, Materialcharakterisierung und Parameterbestimmung, Illmenau, 6.-7.03.2006 Dietmar Gerteisen

Patent

Verfahren zur Herstellung von Gasdiffussionsschichten, derart hergestellte Gasdiffusionsschichten und diese enthaltende Brennstoffzellen Patent-Nr. DE102007007533B3, 03.07.2008 Dietmar Gerteisen This thesis deals with the analysis of dominant loss mechanisms in direct methanol fuel cells (DMFC) and hydrogen fed polymer electrolyte membrane fuel cells (PEFC) by means of experimental characterization and modeling work.

The investigations are focused on the water management in PEFCs and mixed potential formation, catalyst poisoning, methanol-selective cathode catalysts in DMFCs.

