Local degradation of the membrane and catalyst support in polymer electrolyte fuel cells

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Local Degradation of the Membrane and Catalyst Support in Polymer Electrolyte Fuel Cells

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presented by

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2013
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Abstract

In the present work, membrane degradation and catalyst support corrosion in polymer electrolyte fuel cells (PEFC) were investigated locally. Because degradation processes are spatially inhomogeneous, particularly in technical cells, this work links fundamental research to the technical applications of PEFCs. The work addresses the loss of the gas separation capability of polymer electrolyte membranes (Chapter 6) and the corrosion of the carbon catalyst support during fuel cell start-up and shutdown (Chapter 7). In each chapter an up-to-date background and the recent results regarding inhomogeneous degradation processes are presented and discussed in order to integrate local effects into current degradation mechanisms. Chapters 3 to 5 describe the experimental setup, accelerated stress tests, characterization techniques and preparation methods. The motivation (Chapter 1), an introduction in PEFC technology (Chapter 2) and the conclusions (Chapter 8) form the framework of the thesis.

A loss of gas separation is the most detrimental failure mode of perfluorosulfonic acid membranes. The gas crossover was analyzed locally by mass spectrometry using a tracer gas concept, which allows for online analysis during fuel cell operation. Local membrane failures were further investigated by synchrotron based X-ray tomographic microscopy and FTIR spectro-microscopy. Due to the improved chemical stability of Nafion NR 211 membranes, chemical membrane thinning was not observed and does not contribute to the increase of the gas crossover. Rather, mechanical formation of small membrane defects (about 10 µm in diameter) is the main degradation process during fuel cell operation. This process is accelerated by imperfections and local defects of the gas diffusion electrodes. Variations in the operating conditions, such as humidity and temperature, cause membrane defects to form nonuniformly across the active area (Chapter 6.2). In the early stages of cell lifetime, the gas crossover through these defects does not affect the cell performance significantly, but it does accelerate local membrane degradation. To study the impact of these local defects, pinholes were implemented artificially in the membrane by focused ion beam (FIB) milling and other techniques (Chapter 5). FIB produces pinholes that are comparable to those formed by natural degradation processes. These membranes were then degraded in different accelerated stress tests to study chemical, mechanical and
thermal degradation processes (Chapter 6.4). From the results that were obtained, an overall degradation mechanism at membrane defects was deduced. The combination of different degradation pathways causes a synergetic effect that exponentially accelerates the degradation at membrane defects. Gas crossover is a key function in this scheme and is controlled by operating conditions and material characteristics, such as humidity, temperature, pressure gradient, GDE porosity and others (Chapter 6.3). Since these parameters vary across the cell area, so does the degradation rate of individual membrane defects.

Carbon supported platinum is the most frequently used catalyst in PEFCs. During fuel cell start-up and shutdown, a high potential can be formed at the cathode that electrochemically oxidizes carbon to carbon dioxide and thus degrades the catalyst. By quantifying the carbon dioxide online in the gas phase of the cathode with mass spectrometry, carbon corrosion was investigated locally, along the channel, at different operating conditions during start-up and shutdown. Both the local and total corrosion rates differ for start-up and shutdown. This is because two different mechanisms, the pseudo-capacitive effect of the platinum electrode and diffusive mass transport limitations, have opposite effects (Chapter 7.2). Their magnitude depends on the operating conditions and the cell design, which thus define the local carbon corrosion rates along the channel. Because of this, the catalyst support degrades nonuniformly across the cell area. This is true not only for inhomogeneous operating conditions, but for homogeneous ones as well (Chapter 7.3). The set of parameters investigated in this work form a basis to evaluate and predict local carbon support corrosion rates during fuel cell start-up and shutdown for different operating conditions.
Zusammenfassung


Die Zunahme der Gasdurchlässigkeit stellt den wichtigsten Alterungsprozess von Perfluorsulfonsäure basierten Membranen dar. Diese wird durch die Zumischung eines Indikatorgases an einem speziell für die lokale Gasanalyse entwickelten Teststand online während dem Betrieb mit einem Massenspektrometer bestimmt. Die lokale Membranalterung wurde zusätzlich mittels synchrotron basierter Röntgentomografie und Infrarotspektroskopie analysiert. Aufgrund der verbesserten chemischen Stabilität der in dieser Arbeit hauptsächlich verwendeten Nafion NR 211 Membran nimmt die Gaspermeation nicht wie erwartet durch die Verringerung der Membran dicke zu. Stattdessen werden vorwiegend kleine Membrandefekte mit Durchmessern von ca. 10 µm während dem Betrieb der Brennstoffzelle durch mechanische Prozesse gebildet, welche durch Inhomogenitäten und Defekte in der Oberflächenstruktur der Gasdiffusionsschichten begünstigt werden. Aufgrund der stark variierenden Bedingungen entlang der Zelle, wie zum Beispiel Feuchtigkeit und Gaszusammensetzung, bilden sich Löcher ungleichmäßig über die Zellfläche verteilt (Kapitel 6.2). Zwar beeinflusst die lokal erhöhte Gasdurchlässigkeit die Zellleistung nur unwesentlich was einen fortlaufenden Betrieb ermöglicht, jedoch werden
Zusammenfassung

Alterungsprozesse lokal an der Membran beschleunigt. Um die lokalen Auswirkungen von Membrandefekten gezielt zu untersuchen, wurden künstliche Löcher mit dafür speziell entwickelten Herstellungsverfahren in die Membran erzeugt (Kapitel 5). Diese sind den natürlich gebildeten Defekten ähnlich und wurden unter geeigneten Versuchsprotokollen beschleunigend gealtert. Dadurch konnten an künstlichen Membrandefekten chemische, mechanische und thermische Alterungsprozesse untersucht werden und in einem vollständigen Degradierungsmechanismus vereinigt werden. Die exponentiell ansteigende Gasedurchlässigkeit lässt sich durch Synergieeffekte der Alterungsprozesse begründen, wobei die lokal erhöhte Gaspermeation eine Schlüsselrolle einnimmt. Sie wird durch die Betriebsbedingungen und durch Materialeigenschaften bestimmt und variiert je nach Feuchtigkeit, Temperatur, Druckgradient und Gaseigenschaft (Kapitel 6.3), was zu lokal unterschiedlichen Lochwachstumsraten entlang der Zelle führt (Kapitel 6.4).

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1 Motivation

Considering the impending shortage of resources, the security of future energy sources is a pivotal research question at the beginning of the 21st century. Besides the exploitation of new resources, efficient energy management and utilization of current resources are two key strategies for fulfilling the increasing energy demand. This energy turnaround must rely on technology that is free of greenhouse gas emissions in order to avoid increasing the socio-ecological impacts of the climate change. In transportation and shipping, the electrification of automotive propulsion systems is a promising technology for mastering these challenges. Semi- or fully electrical propulsion systems can save fuel by the recuperation of braking energy and can reduce air pollution caused by soot particles and exhaust gases, which is of particular concern in large metropolises. In 2012 the most developed technology for electrification is the serial or parallel hybridization of conventional internal combustion engines with batteries. Purely battery-driven automotive systems have only small market shares because the energy density is too low and the cost too high, to allow for a driving range of more than 200 km or for applications in heavy-duty vehicles. A range extender or an additional power supply, such as an internal combustion engine, is still required in most cases. A polymer electrolyte fuel cell (PEFC) can replace internal combustion engines in hybridized, electrified propulsion systems. PEFCs convert fuel (hydrogen) directly into electricity with the highest electrical efficiencies of any current technology. The hybridization not only offers a full electrification and thus simplification of the system, but also increases the efficiency, thus significantly decreasing fuel consumption. In addition, the system has zero emissions, as the only product is water. Therefore, polymer electrolyte fuel cells are a promising technology, though they do require a hydrogen infrastructure.

In order to be competitive with internal combustion engines and to allow for a fast market introduction, fuel cell cost must be reduced and their durability must be increased. Both objectives are linked. An improvement of the durability leads to a reduction in the cost per lifetime. Unlike internal combustion engines, fuel cells have no moving parts, whose lifetimes are limited by abrasion and fatigue. The challenge is rather to find persistent materials that are adapted to the harsh chemical environment in a fuel cell, which includes high potentials in the presence of hydrogen and/or oxygen. The catalyst, its
support and the polymer electrolyte membrane are the most susceptible components for failures. To improve the durability of these components, new materials are being developed and fuel cell operation is being optimized.

One complicating fact is that in fuel cells of technical size, the operating conditions are nonuniform across the cell area, which will obviously lead to nonuniform degradation. Therefore, existing fundamental degradation mechanisms, mostly based on laboratory tests with small cells, must be scaled up to technical sized cells, thus accounting for nonuniform degradation phenomena. The aim of this thesis was therefore to identify and understand degradation processes localized in technical cells and to incorporate these findings into the prevailing degradation mechanisms. Trigger processes of nonuniform degradation were investigated and correlated with nonuniform operating conditions of technical cells. For this purpose, analysis methods with high spatial resolution were developed or adapted. The results ascertain the root cause of inhomogeneous degradation, improve the understanding of membrane and catalyst support degradation mechanisms and enable the elaboration of a comprehensive understanding of degradation mechanisms in technical cells.

The work aims to investigate both the loss of the gas separation capability of polymer electrolyte membranes and the corrosion of the carbon support during fuel cell start-up and shutdown. The loss of gas separation is the most important failure mode of polymer electrolyte membranes because it may lead to a sudden death of the fuel cell, forcing an immediate shutdown of the system. Carbon support corrosion is mainly induced at start-up and shutdown. It is a particularly harmful transient condition, as the high potentials that arise at the cathode can lead to the degradation of the catalyst layer. Both processes, the loss of the gas separation and carbon support corrosion, are two major degradation mechanisms in PEFCs. In this work, they were primarily investigated by local gas phase analysis because the reactants that permeate through the membrane (hydrogen and oxygen) as well as the degradation product of carbon corrosion (carbon dioxide) are all gases. Therefore, a fuel cell hardware connected to a mass spectrometer was used to analyze the gas phase locally and online.
2 Polymer Electrolyte Fuel Cell Basics

2.1 Design and Working Principle

Fuel cells are electric power supplies that convert chemical energy directly into electrical energy and heat. Unlike combustion engines and steam or gas turbine power stations, the electrical energy is generated in a single process, not as sequence of energy conversion processes that is associated with significant losses. The electrical efficiency of fuel cell systems in small size application is already comparable to modern, large-scale power stations with electrical efficiencies of about 60% [1]. Therefore, fuel cells are promising power supplies, especially for small-scale and intermediate needs (0.5–500 kW), such as residential heat and power stations, telecommunication backup power systems and mobile power supplies for military or automobile applications [2]. Depending on the technical and operative requirements, various fuel cell types can be used, such as solid oxide-, molten carbonate-, phosphoric acid-, and polymer electrolyte fuel cells (PEFC), with each system differing in fuel, components and operating conditions. PEFC have been established in portable systems due to their high power density of ≥1.5 W cm\(^{-3}\)\(^{(1)}\), fast start-up and dynamic operation capabilities. They are developed and commercialized by Ballard Power Systems, Plug Power, Hydrogenics, United Technologies Company, NuCellSys, Nedstack, and other companies. In a PEFC, hydrogen is oxidized and oxygen (usually in the form of air) is reduced electrochemically to water at 20–90 °C and 100–300 kPa according to Equation 2.1.

\[
\begin{align*}
\text{Oxidation :} & \quad 2H_2 &\rightarrow 4H^+ + 4e^- \\
\text{Reduction :} & \quad O_2 + 4H^+ + 4e^- &\rightarrow 2H_2O \\
\text{Redox reaction :} & \quad 2H_2 + O_2 &\rightarrow 2H_2O \quad (2.1)
\end{align*}
\]

\(^{(1)}\)Minimum stack power density required for automotive applications as defined in the EU project Autostack.
Figure 2.1 Schematic cross-section of a polymer electrolyte fuel cell, consisting of bipolar plates (BPP), gas diffusion layers (GDL), catalyst layers (CL) and a polymer electrolyte membrane. The electrochemical oxidation of hydrogen and reduction of oxygen takes place at the three-phase boundary (gas, ionomer and catalyst), magnified on the right side.

As depicted in Figure 2.1, oxidation of hydrogen and reduction of oxygen are separated spatially into two half cells, the anode and the cathode. Electric power can be drawn directly from the cell by connecting the anode and cathode via an external electric circuit. To increase the power output, cells are assembled sequentially in a stack. In the following, the main components of a PEFC and their functions are explained.

**Bipolar Plate** Hydrogen and oxygen enter the fuel cell through separate manifolds and are distributed uniformly over the cell area via channels in metallic or composite bipolar plates. The bipolar plates provide mechanical stability, transport reactants and conduct both heat and electrical current within the stack. Metallic bipolar plates, typically made of stainless steel, have good thermal and electrical conductivity, can be mass produced by die cutting and allow for a compact stack design. However, the electrical contact resistance between the metallic plates and the gas diffusion layer is high and must be lowered
2.1 Design and Working Principle

by additional coating. Furthermore, metallic bipolar plates show poor chemical stability under fuel cell conditions, further increasing the contact resistance, and the resulting decomposition products can degrade other fuel cell components [3]. In contrast, composite bipolar plates, made from graphitized carbon and polymer, are corrosion resistant, have low contact resistance and good electrical conductivity. However, the nominal web thickness must be larger than for metallic bipolar plates due to the brittleness of composite plates, thus decreasing the volumetric power density of the stack. Additionally, production processes for composite plates, such as injection molding, have not yet been optimized for mass production [3].

Gas Diffusion Layer From the flow field channels, the gases permeate to the catalyst via the gas diffusion layer (GDL). GDLs are about 150–250 μm thick and are typically made from carbon fibers (diameter 6–10 μm), either woven into clothes or randomly distributed in carbon papers with high porosities of about 40–70% [4,5]. GDLs enable mass transport of reactants (H₂, O₂, liquid water, water vapor) through the voids, while also conducting charge and heat through the solid phase. The through-plane electrical and thermal conductivities are about 300–1400 S m⁻¹ and 0.2–2 W K⁻¹ m⁻¹, respectively [6]. To control water transport, the hydrophobicity of the GDL can be adjusted through impregnation with either polytetrafluoroethylene or fluoroethylene propylene, up to 30 wt.%. For the same reason, a 10–50 μm thick microporous layer (MPL) is often coated on the GDL side facing the catalyst layer. The MPL consists of a porous carbon-polymer composite network that has a higher density than the GDL as well as different wetting behavior. The MPL is also used to improve the electrical contact between the GDL and the catalyst.

Supported Catalyst Platinum and platinum alloys are the state-of-the-art catalysts for hydrogen oxidation and oxygen reduction in PEFCs. Platinum is an expensive noble metal (about 40 € g⁻¹ in 2012). It accounts for about 10–40% of the total fuel cell system cost depending on the lot size (cost estimates for 2010 [7]). To reduce the catalyst cost, the efficiency of platinum utilization is improved by increasing the electrochemical active surface area to about 60–120 m² g(Pt)⁻¹ [8]. Small platinum particles, typically 2–7 nm in diameter, are highly dispersed on high surface area catalyst supports at a loading of about 20–50 wt.%. State-of-the-art catalyst supports, like Ketjenblack EC300J, Vulcan XC-72 or Black Pearls BP2000, are made of carbon due to its high electrical conductivity (Sp²-hybridized carbon), chemical and thermal stability, high surface area (100–800 m² g⁻¹ [9–11]) and low cost [12]. The carbon support consists of microcrystalline
primary particles (20–50 nm in diameter [10, 13]). Primary particles are stacked graphene layers, which have distortions in their structure that define the microcrystallinity [13]. The proportion of amorphous versus crystalline carbon, as well as their distribution within the particle, depends on the raw material and the manufacturing and downstream processes. Catalyst supports made of carbon black, e.g. Vulcan XC-72, generally have more disordered graphene layers towards the center of the particle, as illustrated in Figure 2.2 [13]. The primary particles are agglomerated into three dimensional clusters. Catalyst particles are deposited on the surface of the clusters, as shown by transmission electron microscopy in Figure 7.3A [14] on page 106.

The carbon-supported platinum is mixed with about 20–40 wt.% ionomer to form the catalyst layer (CL) in a PEFC [16]. As depicted in Figure 2.1, electrochemical reactions take place at the three-phase boundary of platinum particles, the ionomer and the gas phase. Protons are transported in the ionomer phase, electrons are transferred by platinum, and reactants are supplied by the gas phase. The catalyst layer can be coated on the GDL-MPL assembly or the polymer electrolyte membrane, which is then termed either a gas diffusion electrode (GDE) or a catalyst coated membrane (CCM), respectively. As the rate of the oxygen reduction reaction is slower than that of the hydrogen oxidation by three orders of magnitude, platinum loading is typically 0.4–0.5 mg(Pt) cm$^{-2}$ at the cathode, but only 0.1–0.2 mg(Pt) cm$^{-2}$ at the anode.

**Figure 2.2** Scheme illustrating the cutaway of a carbon black particle with diminishing order of the graphene layers towards the center. Reprinted from Heidenreich et al. [15] with permission from the Journal of Applied Crystallography.
2.1 Design and Working Principle

**Polymer Electrolyte Membrane**  The polymer electrolyte membrane is 20–100 µm thick and physically separates the two half cell reactions at the anode and cathode. It is electrically insulating and prevents the mixing of the reactants, thus blocking the direct combustion of hydrogen to water. To close the electrical circuit, the polymer must conduct protons. Details of membrane function and degradation are given in Chapter 6.1.1. There are two types of membranes: hydrocarbon- and fluorocarbon-based. The latter are the most widely used due to their superior chemical, mechanical and thermal stability. One common example is perfluorosulfonic acid (PFSA) membranes, such as Nafion (DuPont, USA), Gore-Select (W. L. Gore & Associates, Inc., USA), Aciplex (Asahi Kasei Chemicals Corporation, Japan) and Flemion (Asahi Glass, Japan). Figure 2.3A illustrates the generic, chemical structure of PFSA membranes. It is polytetrafluoroethylene with sulfonic acid groups connected via perfluorovinyl ether side chains. The membranes are functionalized with sulfonic acid groups to be made proton conductive. The sulfonic acid group concentration is expressed as an equivalent weight (EW) that is defined by the polymer dry weight per mole of sulfonic acid groups (Equation 2.2).

\[
EW = \frac{m_{\text{dry}}}{n_{SO^3}}
\]  

(2.2)

Due to the amphiphilic nature of PFSA membranes, the polymer phase separates, as shown in Figure 2.3B. Filling the hydrophilic phase with water provides a proton conductive network. In this work, Nafion was used as it is the best described PFSA membrane and is widely used in the literature. For Nafion, \( n \) is 5–13 (i.e. after 5–13 \(-CF_2-CF_2-\) fragments a side chain is branched), \( m \) is 50–1000 and \( z \) is 1. The molecular weight of PFSA membranes is typically 1–10 \( \times \) 10^5 g mol\(^{-1}\) [17].

![Figure 2.3](image_url) A) Chemical and B) microscopic structure of Nafion membranes. The hydrophobic and hydrophilic fragments of Nafion are phase separated forming a proton conductive network.
2.2 Electrochemical Energy Conversion

2.2.1 Reaction Mechanisms

Hydrogen is oxidized and oxygen is reduced electrochemically to water in a PEFC. At the anode, molecular hydrogen adsorbs onto two adjacent platinum atoms of the catalyst and dissociates due to the released adsorption energy, as shown in the Tafel reaction (Equation 2.3). The hydrogen atoms are then oxidized in the Volmer reaction (Equation 2.4). Hydrogen oxidation according to the Volmer-Tafel mechanism dominates on platinum surface atoms [18]. The catalyst turnover frequency can be expressed as a current density and is a function of the electrode potential. At standard conditions (0.0 V, 1 M $\text{H}_3\text{O}^+$, 25 °C and 100 kPa hydrogen partial pressure), it is about $4 \times 10^{-3}$ A cm$^{-2}$ and is termed the exchange current density $j^o$ [18].

\[
\begin{align*}
H_2,\text{ad} & \rightarrow 2H_{\text{ad}} \quad (2.3) \\
H_{\text{ad}} + H_2O & \rightarrow H_3O^+ + e^- \quad (2.4)
\end{align*}
\]

At the cathode, oxygen is reduced to water on platinum. However, the reaction mechanism is not yet fully understood [18, 19]. Depending on how oxygen is adsorbed on the catalyst, two different reaction pathways are possible, as depicted in Figure 2.4: the four electron and two electron pathway. When molecular oxygen is adsorbed on a single platinum atom through only one oxygen atom, the oxygen molecule does not dissociate. Instead, it is reduced to a hydroperoxyl group and then to hydrogen peroxide in a two electron process (Equation 2.5–2.6). The hydrogen peroxide is subsequently reduced to water in a second two electron process (Equation 2.7). In contrast, when both of the oxygen atoms in O$_2$ adsorb onto a single or two adjacent platinum atoms, the oxygen bond is weakened and the molecule dissociates. The two oxygen atoms are then reduced to water in a four electron process, as shown in Equation 2.8–2.10.

\[
\begin{align*}
\text{O}_2 & \rightarrow O_{2,\text{ad}} \\
2H^- & \rightarrow 2H_{\text{ad}} \\
2H^- + 2H_2O & \rightarrow 4H^+ + 2H_2O
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{O}_2 & \rightarrow 4e^- \\
\text{H}_2\text{O}_2 & \rightarrow H_2O + 2e^- \\
\text{H}_2O & \rightarrow 4H^+ + 4e^-
\end{align*}
\]

**Figure 2.4** Two electron and four electron oxygen reduction mechanism on platinum.
2.2 Electrochemical Energy Conversion

\[ O_{2,ad} + H^+ + e^- \rightarrow HO_{2,ad} \]  \hspace{1cm} (2.5)

\[ HO_{2,ad} + H^+ + e^- \rightarrow H_2O_2 \]  \hspace{1cm} (2.6)

\[ H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \]  \hspace{1cm} (2.7)

\[ O_{2,ad} \rightarrow 2O_{ad} \]  \hspace{1cm} (2.8)

\[ 2O_{ad} + 2H^+ + 2e^- \rightarrow 2OH_{ad} \]  \hspace{1cm} (2.9)

\[ 2OH_{ad} + 2H^+ + 2e^- \rightarrow 2H_2O \]  \hspace{1cm} (2.10)

2.2.2 Thermodynamics

The formation of liquid water has a standard enthalpy (\(\Delta H\)) of -287.3 kJ mol\(^{-1}\). The maximum accessible work however is only -237 kJ mol\(^{-1}\) as defined in Equation 2.11 by the Gibbs free energy (\(\Delta G\)) because the reaction of two mole hydrogen and one mole oxygen to only two mole water decreases the entropy (\(\Delta S\)), the more so if liquid water is formed. Table 2.1 shows \(\Delta H\) and \(\Delta G\) under standard and typical fuel cell conditions. The thermodynamic properties given in line two are usually standardized for PEFCs in the literature, yet for accurate specifications the difference in liquid water and water vapor formation should be considered, particularly when calculating the thermodynamic efficiency. Even though PEFCs operate below 100 °C, water can exit the fuel cell as both liquid water and water vapor, with the ratio depending on the relative humidity of the inlet gases.

The maximum electrical energy that can be harvested is equal to the Gibbs free energy. The maximum cell voltage can thus be calculated according to Equation 2.12, yielding a value of 1.23 V (\(E^\circ\)) at standard conditions for a \(\Delta G\) of -237 kJ mol\(^{-1}\) (see also Table 2.1).

<table>
<thead>
<tr>
<th>Form of product water</th>
<th>(T) / °C</th>
<th>(\Delta H) / kJ mol(^{-1})</th>
<th>(\Delta G) / kJ mol(^{-1})</th>
<th>(\Delta E^\circ) / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>25</td>
<td>-241.8</td>
<td>-228.2</td>
<td>1.18</td>
</tr>
<tr>
<td>Liquid</td>
<td>25</td>
<td>-285.6</td>
<td>-237.0</td>
<td>1.23</td>
</tr>
<tr>
<td>Gas</td>
<td>80</td>
<td>-242.4</td>
<td>-228.8</td>
<td>1.19</td>
</tr>
<tr>
<td>Liquid</td>
<td>80</td>
<td>-283.7</td>
<td>-235.1</td>
<td>1.22</td>
</tr>
</tbody>
</table>
The cell voltage is defined as the difference between electrode potentials of the anode and cathode. As the absolute electrode potential cannot be measured, the standard hydrogen electrode (SHE) potential is used as a reference and is set to 0.0 V by definition. Hence, the anode and cathode electrode potentials are 0.0 V and 1.23 V, respectively, at standard conditions. The potentials can be calculated for non-standard conditions by using the Nernst equation (Equation 2.13).

\[
\Delta G = \Delta H - T \Delta S \quad (2.11)
\]

\[-\Delta G = W_d = Q \cdot E^o = zF n \cdot E^o \]

\[
E^o = \frac{-\Delta G}{zF n} \quad (2.12)
\]

\[
E = E^o + \frac{RT}{zF} \cdot \ln \left( \frac{a_{Ox}}{a_{red}} \right) \quad (2.13)
\]

### 2.2.3 Voltage Losses

During fuel cell operation, the actual cell voltage is less than the electrode potential difference at thermodynamic equilibrium due to open circuit voltage losses \( \eta_{ocv} \), charge transfer losses \( \eta_{CT} \), ohmic losses \( \eta_{ohm} \) and concentration losses \( \eta_{conc} \), as shown in Equation 2.14. The magnitude of the last three loss types increases with the current density, as illustrated by the schematic polarization curve (voltage vs. current density) of Figure 2.5.

\[
U_{cell} = (E^o_{O_2} - E^o_{H_2}) - \eta_{ocv} - \eta_{CT} - \eta_{ohm} - \eta_{conc} \quad (2.14)
\]

**Open Circuit Voltage Losses** The open circuit voltage (OCV) is typically only 0.95–1.05 V, compared to the thermodynamic equilibrium potential difference of 1.23 V, due to the following reasons. In addition to the reduction of oxygen to water, the reduction to hydrogen peroxide and the oxidation of carbon and platinum also define the cathode electrode potential. The resultant mixed potential is further reduced due to hydrogen permeated through the membrane, which is then oxidized at the cathode. Furthermore, the reactant concentrations and the cell temperature usually deviate from the standard condition, which can further increase the voltage loss at open circuit \( \eta_{ocv} \).

**Charge Transfer Losses** When an electrical current is drawn from the cell, it gives rise to an overpotential. This situation is described by the Butler-Volmer equation (Equation 2.15), where \( j \) is the current density, \( j_o \) the exchange current density, \( \eta_{CT} \) the charge
2.2 Electrochemical Energy Conversion

Figure 2.5 Schematic of a polarization curve indicating the major voltage losses: open circuit voltage losses $\eta_{\text{ocv}}$, charge transfer $\eta_{\text{CT}}$, ohmic $\eta_{\text{ohm}}$ and concentration losses $\eta_{\text{conc}}$.

transfer potential, and $\alpha_a$ and $\alpha_c$ the anodic and cathodic transfer coefficient, respectively. With increasing current density, the electrodes are depolarized as compared to the thermodynamic equilibrium potential, thus decreasing the cell voltage. Charge transfer losses at the cathode electrode dominate over those at the anode as the exchange current density of oxygen is a factor of 1000 smaller than that of hydrogen. Charge transfer losses are distinctive at low current densities, as shown in region I of Figure 2.5.

$$j = j_0 \cdot \left[ \exp \left( \frac{\alpha_c z F}{RT} \eta_{\text{CT}} \right) - \exp \left( -\frac{\alpha_a z F}{RT} \eta_{\text{CT}} \right) \right] \quad (2.15)$$

**Ohmic Losses** According to Ohm’s law, the electric resistance of cell components causes a voltage drop ($\eta_{\text{ohm}}$) that increases linearly with the current density. This effect is the main voltage loss at moderate current densities, as shown in region II of Figure 2.5. Typical electric resistances are $\geq 30$ m$\Omega$ cm$^2$ for membranes, 3–14 m$\Omega$ cm$^2$ for gas diffusion layers, 0.01–5 m$\Omega$ cm$^2$ for bipolar plates, $\leq 1$ m$\Omega$ cm$^2$ for cabling$^3$ and 1–150 m$\Omega$ cm$^2$ for the summed contact resistances between the components$^3$. The total electric resistance of a single cell, also termed the high frequency resistance, is typically about 60–70 m$\Omega$ cm$^2$ under well humidified conditions, which causes a cell voltage drop of 60–70 mV at 1 A cm$^{-2}$.

$^2$Ohmic resistance of 10 m long copper cabling with an electrical conductivity of $59.1 \times 10^6$ A V$^{-1}$ m$^{-1}$ for copper.

$^3$Specifications extracted from technical data sheets of various fuel cell component suppliers.
Concentration Losses  The reactant concentration close to the catalyst surface is lower than the bulk concentration due to mass transport limitations. According to the Nernst equation (Equation 2.13), the cell voltage decreases with decreasing reactant concentration. Particularly when air is used, the oxygen partial pressure decreases significantly as oxygen is depleted. The effect is most pronounced at high current densities, as shown in region III of Figure 2.5. Concentration losses can lower the cell voltage to 0 V, which defines the limiting current density. Mass transport limitations are magnified when liquid water is formed at high current densities as pores in the GDL and catalyst layer are blocked. In this situation, concentration losses $\eta_{conc}$ can also arise when pure oxygen is used.

2.2.4 Electrical Efficiency

As previously pointed out, one of the greatest benefits of using a fuel cell as a power supply for small- and intermediate-scale applications is the high electrical efficiency when compared to heat engines. The electrical efficiency of a fuel cell $\eta_{cell}$ is calculated from the thermodynamic efficiency ($\eta_{th}$), the voltage losses ($\eta_{volt}$) and the fuel utilization ($\eta_{fuel}$), as shown in Equation 2.16.

$$\eta_{cell} = \eta_{th} \cdot \eta_{volt} \cdot \eta_{fuel} \quad (2.16)$$

$$\eta_{th} = \frac{\Delta G}{\Delta H} = \frac{-237 (-228.2^*) \text{kJ mol}^{-1}}{-286 (-241.8^*) \text{kJ mol}^{-1}} = 0.83 \ (0.94^*) \quad (2.17)$$

$$\eta_{volt} = \frac{U_{cell}}{E_{O_2}^0 - E_{H_2}^0} \quad (2.18)$$

$$\eta_{fuel} = \frac{i}{zF\eta_{H_2}} \quad (2.19)$$

The thermodynamic efficiency $\eta_{th}$ is defined as the ratio between the Gibbs free energy and the reaction enthalpy (Equation 2.17). If all water is produced in liquid form, $\eta_{th}$ is 83%, while it increases to 94% if all water is in vapor form(*). As both liquid water and water vapor exit the fuel cell, the real value is somewhere in between these limits. The voltage efficiency $\eta_{volt}$ is calculated by the ratio of the cell voltage to the thermodynamic equilibrium potential difference, as illustrated in Equation 2.18. The fuel utilization factor $\eta_{fuel}$ is defined by the ratio of generated current to supplied hydrogen, as shown in Equation 2.19. $\eta_{fuel}$ takes into consideration that not all fuel reacts electrochemically. Some hydrogen exits the fuel cell at the anode outlet or permeates through the membrane. Finally, peripheric devices, such as an air blower, cooling systems and recirculation pumps, further lower the electrical efficiency of fuel cell systems to about 40% to 60%, depending on the current density, cell design and operating conditions.
3 Fuel Cell Hardware

3.1 Electrochemical Components

In all fuel cell tests, membrane electrode assemblies (MEA) were composed of PFSA membranes with gas diffusion electrodes (GDEs). The properties of both are described in this section. Nafion (DuPont, USA) is currently one of the best PFSA membranes available and was therefore used in this work. Specifically, Nafion NR 211 was chosen as this material has greater resistance to chemical degradation than does Nafion 111 [21]. However, Nafion 111 was utilized in a few experiments that were designed to investigate the membrane degradation mechanism, since the chemical stability of Nafion NR 211 handicapped quantitative analysis of membrane degradation by FTIR spectro-microscopy. Both membranes have an equivalent weight of 1100 g mol⁻¹ and a nominal thickness of 25.4 µm. Further properties are summarized in Table 3.1.

The PFSA membranes were assembled (without hot-pressing) with as-received carbon paper gas diffusion electrodes H400 (Solvicore, Germany) to MEAs. To test the effect of the GDE surface morphology on the durability of the membrane, a carbon cloth gas diffusion electrode (E-Tek Elat, A6 STDSI V2.1) replaced the carbon paper electrode in a few experiments. In the following, the carbon paper is referred to as GDE “P” and the cloth GDE as “C”. The physical properties of the two GDEs are given in Table 3.2.

| Table 3.1 Physical properties of Nafion NR 211 and Nafion 111, as given by Ion Power [22]. |
|---------------------------------|---------------------------------|---------------------------------|
| **Nafion NR 211**               | **Nafion 111**                  |
| Base material                  | PFSA/PTFE copolymer             | PFSA/PTFE copolymer             |
| Chemically stabilized          | Yes                             | No                              |
| Equivalent weight / g mol⁻¹    | 1100                            | 1100                            |
| Nominal thickness / µm          | 25                              | 25                              |
| Proton conductivity* / mS cm⁻¹  | 100                             | 100                             |
| Bulk density / g cm⁻³           | 1.97                            | 1.98                            |

* In liquid water at 25 °C
### Table 3.2 Physical properties of the carbon cloth GDE “C” and the carbon paper GDE “P”.

<table>
<thead>
<tr>
<th></th>
<th>GDE “C”</th>
<th>GDE “P”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base material</td>
<td>Carbon fiber woven Cloth</td>
<td>Carbon fiber Paper</td>
</tr>
<tr>
<td>MPL</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Catalyst loading / mg(Pt) cm$^{-2}$</td>
<td>0.5/0.5</td>
<td>0.1/0.4</td>
</tr>
<tr>
<td>Thickness / µm</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>Crack surface area coverage* (%)</td>
<td>15.9 (± 1.0)</td>
<td>12.0 (± 1.8)</td>
</tr>
<tr>
<td>Mean crack width* / µm</td>
<td>11.4 (± 6.9)</td>
<td>5.4 (± 2.7)</td>
</tr>
</tbody>
</table>

* Optical evaluation from SEM images.

Figures 3.1A and 3.1B show the surface images of the microporous layer (MPL) of the pristine GDE “C” and “P”, analyzed by scanning electron microscopy (SEM). Both MPLs have cracks; the one on the paper based GDE “P” has a mean crack width of 5.4 ± 2.7 µm, which is less than that of the cloth (11.4 ± 6.9 µm). The crack surface coverage of GDE “P” is also 25% lower than for GDE “C”. Both the mean crack width and the crack surface coverage were determined by image segmenting of 0.34 mm$^2$ GDE surface area analyzed by SEM. Unlike with the paper, carbon fibers protrude through the MPL of the cloth. Some of these fibers break, which results in exposed fiber ends. These fiber ends can be seen even in the pristine GDE and are thus not a result of the fuel cell operation.

**Figure 3.1** *Ex situ* scanning electron microscopy images of pristine GDE surfaces. A) GDE “C” (cloth); carbon fibers of the GDE protrude through the MPL. B) GDE “P” (paper, 0.4 mg(Pt) cm$^{-2}$); cracks are present, but no carbon fibers. Reprinted from Kreitmeier et al. [23] with permission from the Journal of Power Sources.
3.2 Fuel Cell Setup

MEAs were tested in a segmented fuel cell of technical size and in a differentially operated micro fuel cell. Figure 3.2 illustrates the fuel cell hardware. Both cells are equipped with fully heated gas transfer lines to allow for online gas phase analysis. A mass spectrometer can be connected to each gas transfer line by two sequentially aligned multi-position valves. This enables online gas analysis in the center flow field channel of the cathode at different positions in the segmented cell and at the cathode inlet and outlet in the micro cell.

Figure 3.3 shows a schematic drawing of the segmented cell. Eleven gas extraction ports are aligned along the center channel, and two integral gas sampling ports are installed in the gas inlet and outlet. Details of the gas transfer lines are described in Section 4.1.2 on page 23. Electrical current is collected by 10-fold segmented aluminum plates coated with...
gold (10 μm). Flow field plates, shown in Figure 3.4, are machined from PVDF bonded carbon plates (Sigracet BMA5, SGL Carbon, Germany). They have a linear flow field (28 channels) with an active area of 200 cm². Channel dimensions are 0.8 × 0.5 × 400 mm³ (width × depth × length), resulting in a total channel cross-section area of 11.2 mm². The channel rib width is 1 mm. To uniformly compress the gas diffusion layers of the MEA to 75–80% of their initial thickness, cell compression was adjusted by Teflon spacers. They had a nominal thickness of 150 μm when the carbon paper GDE was used, and 200 μm when the carbon cloth GDE was used. The cell was assembled with a clamping pressure of 6 N m. The cell temperature was controlled by a thermostat (Haake B5, Thermo Scientific, Germany), circulating temperature controlled water through the aluminum end plates. Inlet gases had a purity of 99.995 vol.%, were set by mass flow controllers (5850S, Brooks Instrument, USA) and were humidified by a bubbler humidification system (see Figure 3.2). The relative humidity of the inlet gases was checked by mass spectrometry. Electrically heated transfer lines prevented the condensation of water vapor between the humidification system and the cell. The cell pressure was controlled by upstream pressure controllers (5866, Brooks Instrument, USA) and monitored additionally by pressure sensors (522954, Bürkert, Germany), which are installed at the inlets and outlets of the cell (see Figure 3.2). Cell potential and current was set by a DC electronic load (ZS3606, Höcherl & Hackl, Germany), and the test bench was controlled by LabView V8.2 (National
3.2 Fuel Cell Setup

The fuel cell setup includes an active area with 28 parallel channels, each 400 mm in length. Gas inlets and outlets are positioned as shown in the figure.

Figure 3.4 Schematic drawing of the flow field plate of the segmented cell. Reproduced from Schuler et al. [24] with permission from the Journal of Power Sources.

Instruments, USA). For the evaluation of the membrane durability, the cell was operated in counterflow mode. For all other experiments, it was run in coflow configuration with the gas extraction ports at the cathode.

A small section of the segmented cell was rebuilt and operated in differential mode, which means that there is an insignificant gradient of the gas concentration between inlet and outlet. Figures 3.5A and 3.5B show a schematic of the micro cell and its flow field, respectively. The cell has an active area of 0.54 cm$^2$ and a linear 3-channel flow field made from 5 µm gold coated Hastelloy C stainless steel with channel dimensions of $0.8 \times 0.5 \times 10$ mm$^3$ (width × depth × length). Current collectors are made of copper plates coated with 10 µm gold over 10 µm nickel. 1 mm thick fluoroelastomer gaskets seal and electrically insulate the cell from the end plates. The cell temperature was controlled by electrically heated end plates (230 V CSN High Performance Heating Cartridges, WISAG, Switzerland), and a DC electronic load of a lower power range (IT8511, ITECH Electronics, China) was used. Furthermore, the differential pressure between anode and cathode outlet was monitored by a differential pressure transducer (Model 230, Setra, USA). Additional hardware and controlling is similar to that of the segmented cell. Likewise, the inlet and outlet of the cathode are equipped with gas extraction lines equivalent to the segmented cell. All experiments were carried out in coflow configuration.
3 Fuel Cell Hardware

3.3 Break In

After assembling the cell, back-pressure testing in nitrogen atmosphere validated the air-tightness of the cell to less than 2 kPa per minute. The cells were conditioned for 48 hours by operating in constant voltage mode at 0.7 V, 80 °C, 150 kPa, and 30% RH using hydrogen and air at a stoichiometry of two for both. When carbon corrosion was investigated, the cells were further conditioned by performing 100 start/stop cycles at a flux of 0.4 NL min⁻¹ (0.6 m s⁻¹), 80 °C, ambient pressure, and 70% RH, where NL refers to a liter at 25 °C and 101.3 kPa. This was shown to improve the reproducibility of carbon corrosion, since the corrosion rate exponentially decays with time, as discussed in Section 7.1.1 on page 103. When testing MEAs with artificially implemented pinholes, the cells were conditioned for approximately 48 hours using 0.05 NL min⁻¹ fully humidified nitrogen for both anode and cathode at 80 °C and 150 kPa. Nitrogen was used to exclude any chemical degradation at the membrane defects.

3.4 Accelerated Stress Tests

As the lifetime of advanced fuel cell components is hundreds or thousands of hours [25], accelerated stress tests (AST) were applied to assess the membrane and catalyst support durability. Experimental details of the ASTs are given in this section. Membrane degradation was accelerated by stress tests adopted from DOE protocols [26]. Operating the
cell with hydrogen and air or oxygen in open circuit mode (OCV) accelerates chemical degradation processes, while cycling the humidity accelerates mechanical degradation processes. The latter was carried out with N\textsubscript{2} when only mechanical degradation processes were accelerated. Table 3.3 summarizes the experimental details of ASTs carried out in the segmented cell to accelerate membrane degradation. The following standard conditions were applied: 0.557 NL min\textsuperscript{−1} hydrogen (99.995 vol.%) and 1.36 NL min\textsuperscript{−1} air in counterflow configuration at 80 °C, 150 kPa and 35% inlet RH. For testing the resistance to mechanical stress, oversaturated N\textsubscript{2} and N\textsubscript{2} with 35% RH were used for the wet and dry sweep of the RH cycling, respectively. A load cycling AST represented dynamic fuel cell operation, accelerating both chemical and mechanical degradation processes simultaneously.

Membrane degradation at artificially implemented pinholes was accelerated in the micro cell under the following standard conditions: 0.18 NL min\textsuperscript{−1} H\textsubscript{2} and 0.02 NL min\textsuperscript{−1} He at the anode and 0.1 NL min\textsuperscript{−1} O\textsubscript{2} at the cathode. All experiments were carried out at 80 °C, 150.5 kPa at the anode and 150 kPa at the cathode, and finished after 200 h or if the gas crossover had doubled. Mechanical stress was induced by cycling the humidity from 0% to 70% RH with intervals of 10 min and 230 min for the dry and wet cycle, respectively. Experimental details of the ASTs are given in Table 3.4.

Catalyst support degradation was accelerated in the segmented cell during start-up and shutdown. Start-up and shutdown were simulated by alternately purging the anode with hydrogen (99.995 vol.%) or synthetic air (80/20 vol.% N\textsubscript{2}/O\textsubscript{2}) at intervals of 4 min, ambient pressure and nominal gas speeds between 0.15 and 2.2 m s\textsuperscript{−1}. During this test, the cathode was continuously purged in coflow configuration with 0.4 NL min\textsuperscript{−1} synthetic air (80/20 vol.% N\textsubscript{2}/O\textsubscript{2}). Experimental details of the ASTs are given in Table 3.5. In this work, the term anode is always used for the hydrogen electrode, even though reduction

<table>
<thead>
<tr>
<th><strong>Table 3.3</strong> Experimental set points of accelerated stress tests carried out in the segmented cell to focus membrane degradation.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical</strong></td>
</tr>
<tr>
<td>Current density / mA cm\textsuperscript{−2}</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
</tr>
<tr>
<td>Cycle number</td>
</tr>
<tr>
<td>Cycle holding time / min</td>
</tr>
<tr>
<td>Operating hours</td>
</tr>
<tr>
<td>Cell temperature / °C</td>
</tr>
<tr>
<td>Cell pressure / kPa</td>
</tr>
</tbody>
</table>

| **Mechanical** |
| Current density / mA cm\textsuperscript{−2} | 0 (N\textsubscript{2}/N\textsubscript{2}) |
| Relative humidity (%) | 0–130 |
| Cycle number | 7500 |
| Cycle holding time / min | 2/2 |
| Operating hours | 500 |
| Cell temperature / °C | 80 |
| Cell pressure / kPa | 150 |

| **Combined** |
| Current density / mA cm\textsuperscript{−2} | 0–300 (H\textsubscript{2}/air) |
| Relative humidity (%) | 0–130 |
| Cycle number | 35 |
| Cycle holding time / min | 0.5/0.5 |
| Operating hours | 500 |
| Cell temperature / °C | 80 |
| Cell pressure / kPa | 150 |
may also occur during start-up and shutdown. This terminology is applied analogously for the cathode. If not noted otherwise, the relative humidity and temperature were set to 70% and 80 °C, respectively, in order to accelerate carbon corrosion but avoid electrode flooding. Synthetic air had to be used to eliminate the natural CO₂ background. This allowed to analyze the carbon corrosion-derived CO₂ with concentrations in the range of 10–500 ppm. No load was applied to the cell to facilitate carbon corrosion. As the carbon corrosion rate decays exponentially with time (Section 7.1.1, page 103), degrading the cell improves the reproducibility of CO₂ emissions. Therefore, all cells were pre-degraded with 100 start/stop cycles at an anode/cathode flow rate of 0.4/0.4 NL min⁻¹. This corresponds to a nominal gas velocity of 0.6 m s⁻¹ across the total channel cross-section of 11.2 mm². Here, the term “nominal” refers to the dry gas. If not mentioned otherwise, all experiments were finished after 500 start/stop cycles at the most.

Table 3.4 Experimental set points of accelerated stress tests carried out in the micro cell to focus membrane degradation at artificially implemented defects.

<table>
<thead>
<tr>
<th></th>
<th>Chemical (♯1)</th>
<th>Mechanical (♯2)</th>
<th>Combined (♯3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density / mA cm⁻²</td>
<td>0 (H₂/O₂)</td>
<td>0 (N₂/N₂)</td>
<td>0 (H₂/O₂)</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>0</td>
<td>0–70</td>
<td>0–70</td>
</tr>
<tr>
<td>Cell temperature / °C</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Cell pressure / kPa</td>
<td>150.5/150</td>
<td>150.5/150</td>
<td>150.5/150</td>
</tr>
<tr>
<td>Cycle holding time / min</td>
<td>None</td>
<td>10/230</td>
<td>10/230</td>
</tr>
<tr>
<td>Operating hours</td>
<td>200</td>
<td>200</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 3.5 Experimental set points of accelerated stress tests carried out in the segmented cell to focus catalyst support degradation during start-up and shutdown.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Current density / mA cm⁻²</td>
<td>0 (H₂/air)</td>
</tr>
<tr>
<td>Nominal gas velocity / m s⁻¹</td>
<td>0.15–2.2 (standard: 0.6)</td>
</tr>
<tr>
<td>Relative humidity (%)</td>
<td>10–80 (standard: 70)</td>
</tr>
<tr>
<td>Cell temperature / °C</td>
<td>35–90 (standard: 80)</td>
</tr>
<tr>
<td>Start/stop cycle number</td>
<td>≤ 500</td>
</tr>
<tr>
<td>Cycle holding time / min</td>
<td>4/4</td>
</tr>
<tr>
<td>Cell pressure</td>
<td>Atmospheric</td>
</tr>
</tbody>
</table>
4 Characterization Techniques

4.1 Gas Phase Analysis using Mass Spectrometry

4.1.1 Theory on Mass Spectrometry

Gas phase analysis is an important method for the investigation of reactions and processes taking place in a PEFC, since the reactants – hydrogen, oxygen and water vapor – and other species of interest are gaseous. The gas phase in fuel cells has been investigated by different analysis techniques, such as oxygen, water or carbon dioxide luminescent dye films [27,28], diode laser absorption spectroscopy [29] and gas extraction systems coupled to a gas chromatograph [30–33] or to a mass spectrometer (MS) [34–39]. The last analysis technique was preferred because it is minimal invasive, has a high temporal resolution (≤ 1 s), a low detection limit (≤ 10 ppm) and is able to detect all fuel cell relevant gas species.

A mass spectrometer is capable of identifying the components of a sample in the gas phase by analyzing the mass/charge ratio of atomic, molecular and molecular fragment ions. A typical instrument consists of a sample injection device, which evaporates the sample if it is not yet gaseous, an ionization chamber, a mass/charge analyzer and a detector. Various types of system components are used depending on the sample and analysis requirements. In the present work, the gas phase sample was analyzed via a quadrupole mass spectrometer equipped with an electron ionization source, illustrated in Figure 4.1.

The sample gas is injected into the ionization chamber of the mass spectrometer through a fused silica capillary (150 µm inner diameter). An resistively heated tungsten filament emits electrons thermally, which are accelerated in an electric field. If they collide with the sample molecules, electrons will be ejected according to Equation 4.1. This technique is called electron ionization (EI). In the ion optic, electric fields focus and accelerate the ionized molecules to transfer them through the mass/charge analyzer to the detector.

\[ M + e^- \rightarrow M^+ + 2e^- \]  
(4.1)
The analyzer is a quadrupole, which consists of two parallel couples of cylindrical metal rods, where a positive direct current (DC) voltage is applied to one pair and a negative DC voltage to the other couple (Figure 4.1; cross-section B). An alternating electrical field is superposed to the DC field so that ions move through the quadrupole with an oscillating trajectory. Depending on the applied AC and DC voltage, only ions with a specific mass/charge ratio can pass the quadrupole, else they collide with one of the metal rods and are discharged. By controlling the AC and DC voltage, the quadrupole system functions as a variable ion filter that only passes ions with the appropriate mass/charge ratio.

Subsequently, the ions are directed to the detector, which records the ion flux in the form of an electrical current. The detector is a single channel electron multiplier, also called a channeltron, which consists of a glassy funnel coated with a high-resistance semiconductor. The high electrical resistance of the device permits a large DC voltage (1400–1600 V) to be applied between the wide and narrow openings of the funnel. When ions strike the funnel, electrons are ejected and then accelerated by the applied electric field. When these electrons strike the channeltron walls, additional electrons are ejected, creating an avalanche of secondary electrons that is collected as a current pulse. In this way, the electron multiplier amplifies the weak ion current created by the ionized molecules. This amplified ion current is plotted against the mass/charge ratio, as shown in the mass spectrum of Figure 4.2A. Most molecules of low molecular weight form intact molecular ions.
with a single positive charge. This simplifies the spectral evaluation as the mass/charge ratio is equal to the molar mass of the analyte. To increase the temporal resolution of the mass spectrometer, ion currents were measured only at mass/charge ratios corresponding to relevant gas species, as illustrated in Figure 4.2B, resulting in scan times between 0.5 s (for investigating carbon corrosion) and 1.0 s (for gas permeation analysis).

Figure 4.2 A) Mass spectrum of air in the range of 1–50 mass/charge ratios. B) Ion currents of selected masses can be measured continuously with a temporal resolution below 1.5 s.

4.1.2 Experimental Setup

A quadrupole mass spectrometer (Prisma 200M1, Pfeiffer, Germany) was directly connected to a fuel cell via fused silica capillaries (Inner diameter 50 µm and 150 µm), which penetrate 0.1–0.3 mm into the center channel of the cathode flow field. The size and length of the capillaries were adjusted in accordance with the pumping speed of the turbomolecular pump to maintain the MS system pressure. 20–45 NmL min⁻¹ gas was extracted continuously and analyzed online by the MS [21]. Since the gas extraction volume is very small during the analysis, the online measurement is not expected to influence the gas flux and gas distribution in the fuel cell [21]. To avoid water condensation and quickly evaporate any liquid water, which may intrude into the capillaries, the capillaries were embedded in stainless steel tubes, which were electrically heated to 120 °C. A multi-position valve allows to switch between 11 capillaries that are aligned along the center channel of the segmented cell, thus providing a spatial resolution of 4 cm. Additionally, the inlets and outlets of both the segmented and micro fuel cell were equipped with gas extraction ports. Dynamic measurements between different gas extraction lines have a response time of 20–30 s due to the dead volume of the gas extraction system. For the same reason, the
MS signal is delayed 20–30 s during online measurements. However, this does not limit the temporal resolution of the online measurement.

The system pressure was monitored with a Pirani/cold-cathode pressure transducer (PKR261, Pfeiffer, Germany). During analysis the pressure was $1–2 \times 10^{-7}$ kPa, which ensures a linear correlation between the sample gas concentration and the ion current. Due to this fact, a one point calibration is sufficient [40]. The MS was calibrated for $N_2$, $O_2$, $H_2O$, $CO_2$, $H_2$ and $He$ with premixed dry calibration gases (Messer, Switzerland) by purging the calibration gas through the fuel cell setup until steady state condition was reached. For water vapor analysis the calibration factor of nitrogen is used as the relative ionization probabilities of the two gases are similar [41], yielding a relative error of less than 2.5% [21]. As the calibration is sensitive to the gas matrix, calibration gases with different concentrations were used depending on the sample gas composition. The system was also calibrated for different absolute pressures of the fuel cell as the calibration is pressure-sensitive. Small pressure differences among the gas extraction lines or along the flow field channel can be neglected because the relative deviation is below 4% as long as the calibration pressure corresponds to the mean pressure of the gas extraction lines [21].

The calibration of the mass spectrometer includes mass scale calibration, background correction (termed zero gas subtraction in the MS software) and the gas specific sensitivity. All gas species were scaled based on the masses of their singly ionized atoms or molecules. Molecular fragments and doubly ionized species were not considered. Zero gas subtraction, which adjusts for the background signal of the MS, was required for residual gas analysis of $CO_2$. The gas extraction system (in particular the multi-position valve) had some small gas leaks, even after advanced fittings were installed (ZF1PK-10 in combination with FS1L.2-5, VICI, Switzerland). This resulted in a $CO_2$ background of approximately 20 ppm, which was corrected by background subtraction. The background signal for $CO_2$ was measured while purging the cell with nitrogen at the relevant pressure. The analysis of the helium permeation did not require zero gas subtraction as the background was below 1 ppm. Except for online measurements, the MS signal was evaluated under steady state conditions for at least 20 consecutive scans. The standard deviation is typically less than 1 ppm for helium and less than 3 ppm for $CO_2$ between 10 ppm and 1000 ppm.

### 4.1.3 Methodology for Gas Permeation Analysis

The electrochemical measurement of the hydrogen crossover is the standard method to analyze gas permeation through the membrane [42]. Permeated hydrogen is assumed to be oxidized quantitatively at the cathode catalyst layer. However, this may not be the case at exposed locations, such as membrane defects. In addition, the electrochemical mea-
4.1 Gas Phase Analysis using Mass Spectrometry

Measurement is carried out in situ, but not online. Similarly, the influence of the gas diffusion electrode as a gas barrier cannot be studied. To overcome these drawbacks, gas permeation was measured by mass spectrometry in this work. The use of a tracer gas enables the online determination of the gas crossover, which is restricted for hydrogen or oxygen as significant amounts are lost by electrochemical reactions at the catalyst layers [24]. Helium (10 vol.%) was added as a tracer to the anode stream, and its permeate concentration was measured in the cathode stream by gas phase analysis at standard fuel cell conditions without applying a load. Helium is an inert gas and is present only at trace amounts in air. This allows for sensitive analysis and simplified interpretation of the experimental data. The helium permeate flux was calculated according to Equation 4.2, where \( \dot{n}_{He} \) is the helium permeate flux (mol s\(^{-1}\)), \( c_{He} \) (vol.%) the measured helium permeate concentration, \( c_{N2} \) (vol.%) and \( c_{oN2} \) (vol.%) the measured and initial nitrogen concentrations in the cathode, \( c_{oHe} \) (vol.%) the measured helium concentration in the anode, \( \dot{V} \) (NL s\(^{-1}\)) the flow rate of the cathode mass flow controller, \( R \) the ideal gas constant (8.3145 J K\(^{-1}\) mol\(^{-1}\)), \( T \) the temperature (298 K) and \( p \) the cell pressure at the cathode (150 kPa). Nitrogen was used here as a reference gas in order to account for changes in the cathode flux due to the humidification, oxygen consumption, water production, water permeation, and others. Small nitrogen losses due to membrane permeation can be neglected [21]. The helium permeate flux was multiplied by \((10/c_{oHe})^*\) to account for changes in the initial helium concentration (10 vol.%) due to the humidification. \( \dot{n}_{He} \) is the average of 20 measurements. The relative standard deviation is typically 3.6% including the propagation of error bars for \( c_{He}, c_{N2} \) and \( \dot{V} \). Deviations in the initial concentration \( c_{oN2}^0 \) are neglected.

\[
\dot{n}_{He} = c_{He} \cdot \frac{c_{oN2}^0}{c_{N2}} \cdot \frac{\dot{V} p}{RT} \cdot \left( \frac{10}{c_{oHe}^*} \right)
\]

(4.2)

In an ideal cell, gas species are transported strictly by diffusion through the polymer and water phases of the membrane. However, the presence of pinholes in the membrane allows for convective gas transport through the defects. To discriminate between diffusive and convective gas transport, the pressure gradient between anode and cathode is systematically varied during analysis. Figure 4.3 shows the two transport mechanisms at constant cathode pressure (150 kPa) and different anode pressure levels. When the anode pressure is lower than the cathode pressure, diffusion is the dominant mode of helium transport. With higher anode pressures, an additional convective flow through pinholes adds to the diffusive crossover. The convective transport of helium from the cathode back to the anode is neglected as the concentration is very low at the cathode (\( \leq 500 \) ppm). Likewise, the dilution of helium on the anode by permeated nitrogen and oxygen is neglected, since the helium concentration is 100–1000 times higher at the anode than the
measured nitrogen and oxygen concentration (100–1000 ppm). The nitrogen and oxygen concentration may be significantly higher very close to defects, but the spatial resolution of the gas permeation analysis hardware is too low to be affected by this.

Figure 4.3 Concept for distinguishing between diffusive and convective gas permeation in the membrane, adapted from Schuler [21]. A) A higher pressure at the anode induces convective and diffusive helium transport. B) A lower pressure at the anode only allows for diffusive helium transport.

Local Gas Permeation Analysis in the Segmented Cell  Figure 4.4 shows the applied methodology for analyzing the local helium crossover in the segmented cell with a new membrane. The helium concentration is measured locally in the center channel of the cathode at an anode pressure of 140 kPa and 160 kPa (Figure 4.4A). The increase of the helium permeate flux between two local gas sampling ports is plotted for each segment in Figure 4.4B. Since the gas permeation correlates linearly with the partial pressure on the feed side, the diffusive permeate flux can be calculated for 160 kPa by scaling up the diffusive permeate flux of configuration B (140 kPa) with a factor of 160/140. The permeate flux of configuration A is then subtracted from the up-scaled permeate flux of configuration B, yielding the pure convective permeate flux (Figure 4.4C). As expected, the convective gas transport is zero for new membranes. The helium crossover is referred to the active cell area, where the diffusive crossover is given at a partial helium pressure of 14 kPa and the convective permeate flux at a differential pressure between anode and cathode of about 10 kPa. Since the fuel cell was operated in counterflow configuration and the pressure drop along the channel is typically 1.0 kPa and 3.5 kPa at the anode and cathode, respectively, the actual pressure gradient between anode and cathode may have varied between 6.5 kPa and 11 kPa. This was equal in all measurements, so the relative
4.1 Gas Phase Analysis using Mass Spectrometry

evolution of the convective gas crossover along the channel was not affected. One drawback of the tracer gas method is the in-plane gas permeation through the gas diffusion layer, which decreases the spatial resolution. The relative standard deviation of the local diffusive helium crossover is about 9.6% for pristine MEAs.

![Graphs](image)

**Figure 4.4** A) Measured helium concentration in the center channel of the cathode. The cathode pressure is constant at 150 kPa, while the anode pressure is 140 kPa or 160 kPa, respectively. B) The diffusive and total helium crossover are calculated from the derivative of the measured values at 140 kPa and 160 kPa. C) The convective helium crossover is calculated by combining both data sets of B), where the diffusive helium crossover at 140 kPa is linearly extrapolated to the conditions at 160 kPa and then subtracted from the total crossover.
**Gas Permeation Analysis in the Micro Cell** The gas permeation through artificially implemented pinholes was analyzed in the micro cell. The online helium crossover was calculated according to Equation 4.2 from the measured helium concentration. The diffusive and convective helium permeability was determined according to the following protocol. Anode was supplied with 0.18 NL min\(^{-1}\) nitrogen and 0.02 NL min\(^{-1}\) helium and cathode with 0.1 NL min\(^{-1}\) nitrogen at 80 °C, 150 kPa and 0% relative humidity if not noted otherwise. Figure 4.5 shows the helium crossover scaled to an anode helium concentration of 100 vol.%. From the slope of the red trendline in Figure 4.5, the diffusive gas permeability \(B\) is derived and expressed in terms of mol s\(^{-1}\) Pa\(^{-1}\) cm\(^{-2}\) as illustrated in Equation 4.3, where mol s\(^{-1}\) refers to the helium flux (\(\dot{n}\)), Pa refers to the partial pressure difference of the permeating species between anode and cathode (\(\Delta P\)) and cm\(^2\) refers to the active area (\(A\)).

\[
B = \frac{\dot{n}}{\Delta P \cdot A} \tag{4.3}
\]

The convective helium permeability (for 100 vol.% helium at the anode) is determined from slope C between the linearly extrapolated diffusive permeation (red trendline) and the combined permeation (blue trendline). The convective permeability is expressed in terms of mol s\(^{-1}\) Pa\(^{-1}\) per pinhole, but here Pa refers to the differential pressure between anode and cathode. Both the diffusive and convective helium permeability refers to 100 vol.% helium at the anode, whereas the crossover refers to the applied 10 vol.% in the crossover.

![Figure 4.5](image_url)  
*Figure 4.5 Analysis of the convective helium permeability through MEAs with pinhole defects. The red trendline represents the diffusive, the blue one the total helium crossover, and slope C is the convective permeability. To determine the helium permeability, the crossover was scaled to an anode helium concentration of 100 vol.%.*
all experiments if not noted otherwise. The given convective helium permeability is not intrinsic, since the convective gas permeability depends on the gas composition. As the convective gas permeability through pinholes is several factors larger than the diffusive one for the applied absolute pressures, pressure gradients and pinholes’ sizes, the total gas permeation through pinholes is dominated by the convective gas transport, therefore termed as gas crossover through pinholes.

### 4.1.4 Methodology for Carbon Corrosion Analysis

Irreversible carbon corrosion leads to CO$_2$ formation. Therefore, carbon corrosion of the catalyst support can be deduced quantitatively from the measured CO$_2$ concentration in the fuel cell. Carbon corrosion was investigated locally during fuel cell start-up and shutdown by measuring the CO$_2$ concentration in situ and online in the gas phase of the cathode channel during start-up and subsequently during shutdown. This method is preferred over electrochemical methods because the latter cannot discriminate between currents produced by the oxidation of carbon, water or platinum, nor can it distinguish between irreversible and reversible carbon oxidation, i.e. decomposition of the carbon support versus formation of surface oxides [43].

Figure 4.6 illustrates the CO$_2$ signal of the MS for two consecutive start/stop cycles. The CO$_2$ signal has a delay time of about 1 min and a peak tailing of 1–2 min due to the dead volume of the gas extraction system and mass transport limitations in the MPL and GDL [44]. The background corrected CO$_2$ concentration $c$(CO$_2$) is integrated over time and expressed in terms of carbon mass ($m_c$) per fuel cell start-up or shutdown according to Equation 4.4, where $\dot{V}_{\text{cathode}}$ is the cathode flux (0.4 NL min$^{-1}$) at 298 K ($T$) and 101.3 kPa ($p$), $M$ is the molar weight of carbon (12.01 g mol$^{-1}$), and $R$ is the ideal gas constant (8.3145 J K$^{-1}$ mol$^{-1}$).

$$m_c = \dot{V}_{\text{cathode}} \frac{pM}{RT} \cdot \int c$(CO$_2$)dt \quad (4.4)$$

The CO$_2$ concentration was measured online during fuel cell start-up and shutdown for only one of the eleven gas extraction ports that are aligned along the central cathode gas channel (Figure 4.7A). Thus, 11 start/stop cycles were required to obtain full local resolution along the channel. The CO$_2$ concentrations were analyzed in sequence from the extraction port nearest the inlet to the port nearest the outlet. This sequence was then repeated in reverse, and both data sets were combined. This procedure compensates for the decay of the carbon corrosion rate with time, as discussed in Section 7.1.1 on page 103. The analysis sequence was then repeated 3 more times to ensure reliability, resulting in
a total of 88 start/stop cycles for a single experiment. The relative standard deviation of the local carbon loss is 11% on average. Prior to each analysis sequence, 5 start/stop cycles were carried out to minimize the influence of the previous set of measurement on the carbon corrosion rate, as described by Linse et al. [46].

Figure 4.7B shows the carbon loss accumulated along the channel during a start-up (black data set), which is smoothed with a running average filter (green data set) to improve the significance of the specific local carbon losses. The filter applies an unweighted linear regression of three data points. To smooth endpoints, the raw data is extrapolated linearly by one based on the last three data points. The specific local carbon loss is determined for each segment from the increase in carbon mass within the segment and is expressed in terms of µg carbon per cm$^2$ active area and per start/stop cycle. To determine the relative along-the-channel carbon losses, the local values are normalized to the total carbon loss of the complete start/stop cycle.
4.1 Gas Phase Analysis using Mass Spectrometry

Figure 4.7 Methodology for determining local carbon losses using local mass spectrometric analysis of the cathode gas composition. A) schematic view of cell instrumented with 11 gas extraction ports for local CO$_2$ analysis; B) accumulated carbon loss determined from local CO$_2$ measurements and C) specific local carbon loss along the channel calculated from the difference of two adjacent data points in B) and normalized to the respective cell area. Example shown is for start-up. Reprinted from Kreitmeier et al. [45] with permission from The Electrochemical Society.
4 Characterization Techniques

4.2 X-ray Tomographic Microscopy

X-ray tomographic microscopy (XTM) creates a three-dimensional image of an object’s interior. In this research, XTM was used to find and evaluate pinholes or cracks in degraded membranes. XTM has two main advantages compared to other microscopic techniques that utilize visible light or electrons. First, XTM allows for the nondestructive analysis of MEA samples, since it does not require any sample preparation, such as MEA cutting or breaking, that could induce artifacts. Secondly, the three-dimensional structure of the defect that is obtained by XTM can provide additional information about the degradation process. For example, the pinhole shape can indicate a preferred degradation side.

Figure 4.8 shows the measurement setup used at the TOMCAT beamline of the Swiss Light Source. In the present work, XTM was carried out in absorption mode; a monochromatic X-ray beam passes through the sample, and the transmitted X-rays are analyzed. The X-rays are converted to visible light flashes via a scintillator (YAG:Eu 25 µ, Yttrium Aluminum Garnet doped with Europium), magnified by optical lenses, and then detected by a charge coupled device (CCD) camera. Since chemical elements have different X-ray absorption coefficients, the radiogram is a gray scale image. For tomography, the sample is rotated 180° during analysis, thus producing radiograms of different angles, which are

![Figure 4.8](image)

*Figure 4.8 Experimental setup for X-ray tomographic microscopy.*
then used to reconstruct a tomographic data set of the sample by a computer-assisted algorithm. In typical tomographic projections, strongly absorbing areas appear white and weakly absorbing areas dark because the attenuation coefficients are plotted rather than the absorbance. The data set can be segmented manually by gray scale thresholding to produce clear three dimensional views highlighting different material compositions or areas. With this method the average diameter of pinholes was determined by the mean base area of the pinhole ($A = \sqrt{\frac{\pi}{4}}d^2$).

Samples, $2 \times 10 \text{ mm}^2$ in size, were cut out of the degraded MEA with a surgical knife, stored under air at room temperature and analyzed by XTM in the sample holder depicted in Figure 4.8. The sample holder is made of polyamide-imide (brand-name: Torlon), which has a low X-ray attenuation coefficient. XTM was carried out with a monochromatic X-ray beam of either 11 keV or 13.5 keV at a flux of about $6 \times 10^{11}$ photons per second per mm$^2$ (without filtering). The distance between the sample and scintillator was minimized (about 2–5 mm) to reduce X-ray artifacts induced by scattering and diffraction. The PCO.2000 (or PCO.Edge) CCD-camera was used in combination with 10-fold objective lenses. The pixel field is $2048 \times 2048$ resulting in a field of view with a lateral dimension of $1.5 \times 1.5 \text{ mm}^2$ and a pixel size of $0.74 \times 0.74 \text{ µm}^2$. The CCD-camera was read out in unbinned mode with an exposure time of 350 (120) ms for each projection [47]. Prior to analysis, 32 dark and 400 flat scans were recorded as a background and to compensate beam irregularities. A tomogram was reconstructed by 1501 (2001) projections using the gridrec algorithm at the TOMCAT beamline [48].

### 4.3 Fourier Transform Infrared Spectro-Microscopy

In Fourier transform infrared (FTIR) spectroscopy chemical bonds are excited by infrared light to identify functional groups, molecule structures, chemical compounds and sample composition. In the present work, FTIR spectroscopy was used in combination with an optical microscope (FTIR spectro-microscopy) to identify degradation products and their lateral distribution in the vicinity of defects in Nafion membranes.

FTIR spectro-microscopy is a nondestructive analysis method with high spatial resolution ($\leq 100 \text{ µm}^2$). Molecular bonds are excited if the frequency of electromagnetic radiation corresponds to the vibration frequency. The absorption frequency is characteristic for specific chemical bonds, and the intensity is proportional to both the number of bonds and the specific attenuation coefficient, which is related to how efficiently photons can excite the corresponding molecular vibration [49]. Selection rules, deduced from quantum mechanics, determine what energy transitions are allowed and active. IR spectroscopy
measures the IR-transmittance or -absorbance of the sample at different wave numbers, which is plotted in the IR spectrum. For traditional IR spectroscopy the spectral range (typically 400 cm\(^{-1}\) to 4000 cm\(^{-1}\)) is measured sequentially using a monochromator. In contrast, FTIR spectroscopy relies on the simultaneous excitation of all active molecular vibrations by a polychromatic infrared light. The measured signal – the interferogram – is the superposition of all individual energy transitions, which are deconvoluted by Fourier analysis. This method is about \(10^4\) faster than dispersive IR spectroscopy and is therefore more commonly used.

For the present research, FTIR spectro-microscopy was used in transmission mode, i.e. the absorbance is defined as the difference between incident and transmitted signal intensity. However, multi-reflection of the light between the front and backside of the membrane can result in interference fringes impeding the spectrum evaluation, particularly for small peaks [49]. FTIR spectroscopy in reflection mode was tested, but carbon particles that remained on the membrane surface after the GDE was removed were a potential distortion for the surface sensitive analysis. Attenuated total reflectance (ATR) FTIR spectroscopy is widely applied to analyze Nafion membranes [50–53] and was also tested, but chemical mapping via ATR is time-consuming because the ATR crystal must be cleaned before each scan to avoid the propagation of surface contaminants.

Prior to FTIR spectro-microscopy, the membrane sample was prepared according to the following protocol: the GDEs were removed carefully from degraded MEAs with tweezers after a few droplets of a water/ethanol mixture (50/50 vol.%) were placed on the MEA. This solution etches Nafion, thus detaching the GDE. At a higher ethanol concentration the membrane is dissolved and becomes useless for FTIR analysis. Using the water/ethanol mixture does not affect the FTIR spectrum of Nafion. Subsequently, the membrane was rinsed with deionized water, immersed in 0.5 molar aqueous KI solution to exchange protons with potassium ions, dried overnight in a vacuum oven at 80 °C and then stored under air at ambient conditions. A potassium exchanged membrane has a lower water absorption coefficient than the protonic form [54], thus the water background signal is lower during FTIR analysis. Pristine membranes were prepared similarly except the water/ethanol solution was not used.

FTIR spectra were collected on a Bruker Hyperion 3000 IR microscope with a 36-fold optical objective coupled to a Vertex 70v FTIR spectrometer at the IR beamline of the Swiss Light Source. During measurement the visible light was turned on at the microscope to minimize effects induced by temperature fluctuations. The dimensions of the upper and lower aperture were set to 5 × 5 \(\mu\)m\(^2\) and 20 × 20 \(\mu\)m\(^2\), respectively. Spectra, collected as the average of 100 scans with a spectral resolution of 4 cm\(^{-1}\), were recorded from 400 cm\(^{-1}\) to 4000 cm\(^{-1}\) in transmission mode at 25 °C using air as background.
reference, unless noted otherwise. For mapping, the sample was raster-scanned with the background renewed after 20 spectra to compensate for temporal fluctuations of the setup. Data processing was automatized by OPUS 6.5 software (Bruker Optik GmbH, Germany). Spectra were baseline corrected, and the peak area was calculated for setting a local baseline between the manually defined integration limits, which were typically as follows: COC (935–1015 cm$^{-1}$), SO$_3$ (1035–1075 cm$^{-1}$), SO (1380–1425 cm$^{-1}$), SOS (1420–1480 cm$^{-1}$), COOK (1660–1725 cm$^{-1}$) and CO (1740–1800 cm$^{-1}$). Chemical mapping was also compiled and assembled automatically by the software.

To evaluate the reliability of FTIR spectro-microscopy, pristine Nafion 211 was analyzed at 120 different sample spots. The relative standard deviation of the COC and SO$_3$ absorbance is 4.5% and 4.1%, respectively. This is due to inhomogeneities in the chemical composition of Nafion, thickness variations of pristine membranes and deviations in FTIR analysis. Since chemical degradation of Nafion 1XX results in membrane thinning, as discussed in Section 6.1.2 on page 51, differences in the absorbance that are larger than the mean standard deviation do not necessarily correspond to significant changes in the chemical composition of Nafion 1XX. This factor must be considered for accurate data interpretation. Furthermore, the spatial resolution of chemical mapping was evaluated. The pixel size of chemical maps is determined by the smallest aperture dimension, which was limited by the transmitted signal intensity, e.g. 3000–4000 counts per second at an upper aperture dimension of $5 \times 5 \mu m^2$. The spatial resolution is estimated by analyzing a line-profile across an artificially made pinhole with a diameter of 50 $\mu$m. The normalized COC absorbance is zero within the region of the pinhole and about 0.8% in the polymer, as shown in Figure 4.9. Although the pinhole edge extends over an area of about 3 pixels (15 $\mu$m), it is in fact only a few nanometers (as measured by SEM analysis), thus giving a rough estimate of the spatial resolution of FTIR spectro-microscopy. The spatial resolution is limited by diffraction, which may be the reason for the strong deviation in the absorbance at the pinhole boundaries, and by the alignment of the sample, as the contour is distorted for a tilted sample when analyzed two-dimensionally. It was also demonstrated that diffraction at a small pinhole (10 $\mu$m in diameter) and the morphology of the boundary affect the spatial resolution, impeding a general indication for very small features.
IR absorbance of COC (935–1015 cm\(^{-1}\)) of Nafion NR 211 with a 50 µm pinhole artificially implemented by FIB milling. The spatial resolution of the FTIR spectro-microscopy is estimated by a line-profile across the pinhole to be about 3 pixels (15 µm).

4.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is capable of imaging the topography and elemental composition of a specimen surface by analyzing the response of an electron beam that is scanned across the surface. In the present work, GDEs were analyzed to evaluate the surface morphology, and MEA cross-sections were analyzed to determine the thickness variation of the catalyst layer. SEM was preferred to optical microscopy because it has better spatial resolution, i.e. magnifications of more than 500.000 × are possible, a greater depth of field and elemental analysis capabilities.

In a typical SEM an electrically heated tungsten filament produces electrons via thermionic emissions. They are accelerated to 1–40 keV and collimated into an electron beam by electrostatic condenser lenses [55]. An electromagnetic objective focuses the beam to a diameter of about 10 nm, which determines the maximum spatial resolution. The electron beam is deflected in x-y direction in order to systematically scan the specimen, which is also called raster scanning [56]. When electrons interact with the specimen’s atoms, scattered and transmitted electrons, secondary electrons and photons are produced and can be recorded by specific detectors. Each type provides characteristic information about the specimen. For the present research, a secondary electron (SE) detector and a backscattered electron detector (ESB detector from Zeiss) were used. The SE detector records secondary electrons that are produced by the inelastic scattering of primary electrons with the valence electrons of an atom. As secondary electrons have a
4.5 Ion Chromatography

Fluoride ions are a decomposition product of perfluorosulfonic acid membranes and can be detected in the product water of a fuel cell. They thus represent a quantitative indicator for chemical membrane degradation [57, 58]. Fluoride emissions are lower for the Nafion 2XX series than for the Nafion 1XX series due to their better stability towards chemical degradation. Therefore, the fluoride concentration was analyzed by ion chromatography (882 Compact IC plus 1, Metrohm, Switzerland), which has a lower detection limit (≤ 1 ppb) than ion-selective electrodes (≥ 250 ppb). The product water was collected every 24 h...
Characterization Techniques

and 20 µL was injected off-line in the ion chromatograph at room temperature and 8–10 MPa. An eluent flow of 0.7 mL min⁻¹ (1/3.2 millimolar aqueous NaHCO₃/NaCO₃ solution) transported the sample through the ion-selective column (Metrosep A Supp 5 150/4.0 column, Metrohm, Switzerland). Due to the specific ion affinity of the active column material (Polyvinylalcohols with quaternary ammonium groups), analyte ions have specific retention times by which they can be identified. The number of ions in solution is directly proportional to the eluent conductivity, which enables the fluoride concentration to be analyzed by a conductivity detector. To increase the sensitivity, the baseline signal was lowered to 0.8–1.2 µS cm⁻¹ by an integrated sequential suppressor.

The system was calibrated with 7 reference solutions (Fluoride Standard for IC 77365, Fluka Analytical, Switzerland) of different fluoride concentrations in the range from 1 ppb to 10 ppm, thus allowing the integrated peak area of the fluoride signal (µS cm⁻¹ min) to be directly converted into a concentration value (ppb). The sensitivity is less than 1 ppb, and the relative standard deviation is less than 1% for eight consecutive measurements of a 10 ppb fluoride solution. Testing with both internal standards and adding reference solutions to the sample did not reveal any matrix effects in the analysis. The background fluoride concentration of the exhaust water is 70–130 ppb in the segmented cell and 5–20 ppb in the micro cell when purged with fully humidified nitrogen at 80 °C. This background signal is caused by the contamination of the exhaust water by fuel cell components. It corresponds to a virtual fluoride emission rate (FER) of 0–20 ng(F) cm⁻² h⁻¹ for the applied flow settings and relative humidity (0–100%). The BMA5 flow field plates emit fluoride, probably originating from PVDF, which may decompose partly during the production process of the material. Due to the osmotic drag, fluoride ions diffuse out of the material and accumulate in the exhaust water until steady state conditions are reached. Therefore, the BMA5 material (SGL Carbon, Germany) was replaced by PPG 86 (SGL Carbon, Germany), which has no PVDF binder, thus no fluoride emissions were detected. However, bipolar plates made of PPG 86 cannot withstand the compression forces at 80 °C, which is due to the lower glass transition temperature of PPG 86. Due to these difficulties with composite bipolar plates, gold coated stainless steel bipolar plates were used in the micro fuel cell. This lowered but did not eliminate the fluoride background. Polymer additives in the sealant, presumably of the bubbler humidification system, also emit fluoride and organic anions like acetate. Organic anions can impede fluoride analysis by producing overlapping peaks. A longer column, e.g. Metrosep A Supp 5 250/4.0, may improve the evaluation of the fluoride peak in the presence of organic anions. In summary, the exhaust water of the fuel cell is contaminated with fluoride, which limits the fluoride concentration being used as a quantitative indicator for chemical membrane degradation at low emission rates.
4.6 Local Current Density Analysis

The limiting current density was measured locally prior to and after accelerated stress tests (AST) focusing on catalyst support degradation in order to investigate mass transport limitations induced by carbon corrosion [59,60]. For the local limiting current measurements, the anode current collector and bipolar plate were 10-fold segmented and equipped with Hall sensors (LAH 25-NP, LEM, Switzerland), as described previously [21]. The limiting current density, defined as the highest current density of the i/E curve between the open circuit voltage and 0.2 V, was determined according to the following test protocol that was adapted from Carter et al. [60]. The polarization curve was obtained in constant current mode with a current step size of 2.5 mA cm$^{-2}$ and a holding time of 3 s for each point. Curves were recorded at a cell temperature of 60 °C, ambient pressure and 125% RH using 4 NL min$^{-1}$ H$_2$ at the anode and 0.9/9 NL min$^{-1}$ O$_2$/N$_2$ at the cathode. The reported value for the limiting current density is the average of three measurements. The mean relative standard deviation of these measurements was 5.6%.

4.7 Local Temperature Analysis

The temperature was measured locally at membrane defects during fuel cell operation in order to investigate local hotspots, which may cause thermal polymer decomposition. The small size of membrane defects and the good thermal conductivity of the adjacent catalyst layer require the use of a temperature analysis method with high spatial resolution (a few microns). An IR thermal camera has a high spatial resolution, yet the temperature cannot be measured in situ at the membrane as the electrodes absorb infrared light [61,62]. Embedding micro temperature sensors in fuel cell components is widely applied to measure the temperature locally, yet the smallest sensors have a total size of 30–100 µm, which may be still too large [63–66]. He et al. [67] used self-made ultra thin thermistors with a thickness of about 16 µm, which could be used if the manufacturing process was adapted to smaller film widths. Since the high thermal conductivity of temperature sensors might distort the analysis of the local temperature, thermochromic pigments were used in this work to estimate the maximum temperature at membrane defects. The pigments change their color irreversibly at a specific transition temperature. As an example, Figure 4.10 shows thermochromic pigments changing their color from blue (Figure 4.10A) to green (Figure 4.10B) at 215 °C. Pigments with different transition temperatures were placed
Thermochromic pigments were chemically extracted from color changing crayons (Color Change Crayon Kit YO-90307-50, Cole Parmer, USA), consisting of paraffin wax and thermochromic pigments such as lead chromate or inorganic cobalt salts. The crayons were coarsely ground and then dissolved in toluene at 50 °C. The undissolved pigments were transfused and rinsed, first with hexane and then with dichloromethane, followed by careful drying at about 50 °C. This process removes most of the paraffin wax. The isolated pigments were distributed in the vicinity of artificially implemented defects on one side of Nafion 211. The modified membrane and H400 GDEs were assembled with the pigments facing the cathode electrode. The MEA was then operated in the micro fuel cell with H₂/O₂ at OCV at 80 °C, 150 kPa and 0% RH for 60 min without conditioning. The pigment color was analyzed post mortem by an optical microscope (Optiphot, Nikon, Japan), after the anode GDE had been removed carefully with tweezers.

The pigments eventually undergo the color change below the indicated transition temperature after extended exposure times. To account for this effect, pigment particles of the original and changed color were counted manually (30–50 particles in total) to calculate a conversion rate, which was then assigned to a corresponding temperature via a calibration curve. Figure 4.11 shows the conversion rate of color pigments with an indicated transition temperature of 195 °C that were exposed for 60 min at different temperatures. The conversion rate shows a sigmoidal trend with high slopes in the range of 100–120 °C, which dictates the useful temperature range of the pigment. Using four thermochromic pigments with different transition temperatures allows for analyzing peak temperatures in
the range of approximately 100–200 °C.

The pigments do not change their color during fuel cell operation of MEAs without membrane defects at 80 °C, yet high humidity levels weaken the color change, and liquid water can dissolve the pigments. Therefore, all experiments were conducted at 0% RH and repeated three times to ensure good reliability. The conversion rates have an absolute standard deviation of 3% on average, thus the temperature analysis method is expected to produce results within the error bar of ±5 °C as indicated by the manufacturer [69]. The spatial resolution is given by the particle size of the pigment and by the particle to particle distance, which both vary significantly. Therefore, the lateral temperature profile may be evaluated qualitatively but not quantitatively.

![Graph](image)

**Figure 4.11** Calibration curve to determine the temperature at membrane defects using the conversion rate of thermochromic pigments. The figure shows the color change rate for thermochromic pigments with an indicated transition temperature of 195 °C (at an exposure time 1–2 s) exposed to different temperatures for 60 min.
5 Artificial Membrane Defects

Pinholes are formed in polymer electrolyte membranes as a result of degradation processes, as described in Section 6.2 on page 67. The native formation of pinholes is a slow process, and the evolving pinholes differ in size and shape. For systematic analysis of the impact of membrane defects on fuel cell operation and durability, three techniques were therefore developed to implement small (10 µm), reproducible, artificial pinholes in Nafion membranes: (i) electron beam lithography (EBL), (ii) focused ion beam (FIB) and (iii) glass micro-needles. Pinholes were made with EBL (Vistec EBPG5000Plus) at 100 kV, 100 nA and 20 mC cm$^{-2}$, with FIB (Zeiss, NVision40 Dual Beam) at 30 kV, 40 pA and 15 mC cm$^{-2}$ and by using micro-needles (borosilica micro-needle with a 10 µm tip, Hilgenberg, Germany) to perforate the membrane. The artificially implemented pinholes were characterized with X-ray tomographic microscopy and FTIR spectro-microscopy. The tomographic datasets of pinholes implemented by the three methods are shown in Figure 5.1. EBL (Figure 5.1A) and FIB (Figure 5.1B) produce cylindrically shaped pinholes with mean pinhole diameters of 8.3 µm and 9.8 µm, respectively, at a nominal diameter of 10 µm. Both methods can implement pinholes reproducibly with a low deviation in pinhole size.

![Figure 5.1](image)

**Figure 5.1** 3D visualization of artificially made pinholes using X-ray tomographic microscopy. Pinholes with a nominal diameter of 10 µm are implemented in Nafion NR 211 membranes with A) electron beam lithography, B) focused ion beam and C) micro-needles. Reproduced from Kreitmeier et al. [70] with permission from the Electrochimica Acta.
and shape, as summarized in Table 5.1. Micro-needles are made of glass by thermoforming and subsequent breaking. The tip is therefore conical, and the resulting pinholes have a rather conical shape (Figure 5.1C). The mean diameter of pinholes made by micro-needles ranges from 10 µm to 20 µm because the micro-needle tips have different diameters due to variations in the production process (±2 µm) and because the penetration depth of the micro-needle into the membrane varies (±0.05–0.1 mm). The penetration depth is controlled by manually adjusting a self-made punching machine. Furthermore, polymer plugs that are punched out by the micro-needle may not fully detach from the membrane, thus acting as a lid for the pinhole when the membrane is assembled into a MEA. In conclusion, the micro-needle method is unreliable and yields reproducible pinhole sizes, so FIB or EBL are preferred as pinhole implementation methods.

The polymer in the vicinity of the pinholes was investigated by FTIR spectroscopy to evaluate possible damage induced by the implementation methods. FTIR spectra of the polymer at the pinholes’ edges (scanning area 5 × 5 µm²) are shown in Figure 5.2B. Besides the typical IR peaks of Nafion for C-O-C (982 cm⁻¹), SO₃ (1072 cm⁻¹), C-F (1100–1300 cm⁻¹) and H₂O (1633 cm⁻¹), additional peaks are observed for pinholes made by EBL. The peaks at 1410 cm⁻¹ and 1460 cm⁻¹ can be assigned to symmetric vibrations in sulfonic anhydride (SO, S-O-S) [53,71], and the ones at 1689 cm⁻¹ and 1772 cm⁻¹ to symmetric vibrations in carboxyl groups (COOK, CO) [53, 72]. These results show that EBL degrades Nafion in the vicinity of the implemented pinholes by condensation of sulfonic acid groups and the formation of carboxyl groups. In the IR spectra of polymer next to pinholes that were made with FIB or micro-needles, no signs of polymer decomposition are observed. The spatial dimension of EBL induced polymer decomposition was investigated by chemically mapping the region surrounding a 50 µm pinhole. Figure 5.2A shows the integrated SO₃ absorbance (1040–1075 cm⁻¹) and integrated COOK absorbance (1655–1730 cm⁻¹) patterns. The polymer is partially decomposed within 65 µm of the pinhole edge. The absorbance of SO₃ and COC (data not shown) declines when approaching

<table>
<thead>
<tr>
<th></th>
<th>EBL</th>
<th>FIB</th>
<th>Micro-needle</th>
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<tbody>
<tr>
<td>Mean pinhole diameter / µm</td>
<td>8.3 ± 0.6</td>
<td>9.8 ± 0.4</td>
<td>15.4 ± 12.4</td>
</tr>
<tr>
<td>Min. pinhole diameter / µm</td>
<td>6.9</td>
<td>9.4</td>
<td>10.1</td>
</tr>
<tr>
<td>Max. pinhole diameter / µm</td>
<td>8.9</td>
<td>10.2</td>
<td>24.5</td>
</tr>
<tr>
<td>Reproducibility of the pinhole size</td>
<td>± 10.9%</td>
<td>± 3.5%</td>
<td>± 29.8%</td>
</tr>
</tbody>
</table>
Figure 5.2 FTIR spectra of Nafion NR 211 membranes with artificially implemented pinholes. A) Maps of integrated SO$_3$ IR absorbance (1040–1075 cm$^{-1}$) and integrated COOK IR absorbance (1655–1730 cm$^{-1}$) in Nafion NR 211 surrounding a 50 µm pinhole, which was implemented by electron beam lithography. B) Local FTIR spectra of a region close to the pinhole, implemented by electron beam lithography (blue), focused ion beam (red) and a micro-needle (black). Adapted from Kreitmeier et al. [70].
the pinhole. Within the pinhole, zero absorbance is measured for all bands. The COOK absorbance reaches a maximum 25 µm away from the pinhole edge and decays in both directions. The integrated absorbance patterns of the SO, CO and SOS groups are similar.

Since both EBL and FIB employ particle beams (gallium ions for FIB and electrons for EBL), they share a common mechanism for material ablation. In this case, the membrane is degraded by collision of the particles with polymer molecules and the subsequent breaking of chemical bonds. The polymer fragments evaporate into the vacuum of the instrument. Due to their low mass, electrons are strongly scattered in the polymer, so even polymer that is not directly in the beam path is also exposed to high energy electrons. The absorbed energy distribution is estimated by a Monte Carlo simulation using the software Casino v2.48. Figure 5.3 shows the calculated absorbed energy in PTFE when a 10 µm pinhole is implemented by a 100 keV electron beam. PTFE is used as model substance for dry Nafton. Less than 75% of the total energy (green line) is absorbed by the creation of the actual pinhole. The rest of the energy may cause partial polymer decomposition in the vicinity of the pinhole. The lateral dimension of the absorbed energy and of the decomposition products observed with FTIR spectro-microscopy differs by a factor of 2–3, but the simulation qualitatively explains the experimental observation. In contrast, gallium ions barely scatter due to their high mass. The lateral deflection of gallium ions with a maximum energy of 90 keV (Ga$^{3+}$, 30 kV acceleration voltage) is less than 60 nm in PTFE according to simulations done with the software package SRIM 2011. This prediction is

![Figure 5.3](image_url)

**Figure 5.3** Simulated absorbed energy distribution of PTFE during the implementation of a 10 µm pinhole by electron beam lithography at 100 keV. Reproduced from Kreitmeier et al. [70] with permission from the Electrochimica Acta.
confirmed by FTIR spectroscopy, which does not show any polymer decomposition next to pinholes implemented by FIB.

In summary, small pinholes with a size comparable to those formed by natural degradation processes (see Section 6.2 on page 67) can be implemented in polymer electrolyte membranes with good reproducibility by both FIB and EBL. The latter is a fast and cheap method, yet polymer next to pinholes is damaged due to electron scattering. Therefore, FIB should be the preferred method for the investigation of pinhole development and growth.
6 Local Polymer Electrolyte Membrane Degradation

6.1 Understanding of Membrane Degradation

6.1.1 Membrane Functionality

Membrane degradation leads to a loss in functionality and limits the service life of the membrane. Therefore, the main membrane functions – gas separation, proton conduction and electrical insulation – and the implications of their losses are described in this section.

The membrane is electrically insulating, separating the two half cell reactions. This allows to extract electrical current from the cell to an external circuit. However, membrane defects, such as cracks or tears, may be formed during the production process, cell assembly or as a result of degradation processes. Carbonaceous material can create a bridge between the anode and cathode through these membrane defects, thus shorting the cell, which decreases the cell performance and seriously compromises its efficiency [73].

The membrane needs to be proton conductive in order to close the electrical circuit. The proton conductivity ranges between 0.01 S cm\(^{-1}\) and 0.1 S cm\(^{-1}\) depending on the membrane and operating conditions [17], so the membrane is typically the highest ohmic resistance in a cell, as discussed in Section 2.2.3 on page 11. As a consequence, degradation processes that decrease the proton conductivity lead to significantly increased ohmic losses and thus reduced cell performance and electric efficiency. The polymer electrolyte membrane consists of two domains. The hydrophobic polytetrafluoroethylene backbone provides morphological, structural, chemical and thermal stability; sulfonic acid groups are inserted as side chains and form a hydrophilic domain, which is the reason why PFSA membranes absorb water. Depending on the amount of sulfonic acid groups, the maximum water uptake ranges between 32 wt.% and 56 wt.% (referred to the dry weight of the membrane) [74]. Due to their opposite polarity, the two domains are nano-separated, thus determining the polymer structure [75]. Proton transport is only possible through connected hydrophilic domains, which are typically only a few nanometers in diameter [17,75]. There are two mechanisms for proton transport in PFSA membranes: the vehicular and the Grotthuss mechanism. The former consists of proton diffusion in the ionic domain,
Local Polymer Electrolyte Membrane Degradation

while the latter occurs through proton hopping via water molecules [73, 76]. Therefore, the proton conductivity is not only determined by the number of sulfonic acid groups, expressed in terms of equivalent weight (EW), but also by the polymer structure and water fraction. Thus, the proton conductivity can be degraded by both the decomposition of sulfonic acid groups or the contamination by cations as well as changes in the polymer morphology and capability to absorb water. To maximize the proton conductivity, the membrane water fraction can be increased (by operating the fuel cell at high humidities), and the membrane thickness can be reduced. However, both of these measures cause an increase in gas crossover [73].

The membrane separates the anode and cathode electrode physically and prevents the mixing of hydrogen and oxygen, which would catalytically combust at the catalyst layer. However, some gas does permeate through the membrane by three different mechanisms: (i) Gas permeates via a solution-diffusion process (molecular diffusion) through the polymer and water phases of the membrane, i.e. the permeability is a product of the gas solubility and diffusivity of the phases [77]. It is not clear in which phase the gas is transported preferentially [78–81]. Although it is most likely transported primarily in the water phase, this does depend on the gas species [77, 78, 80]. (ii) The second transport mechanism is Knudsen diffusion, which occurs in mesopores with pore diameters between $d_{molecule}$ and $\lambda_{mean}$, where $d_{molecule}$ is the molecule diameter and $\lambda_{mean}$ the mean free path of the molecule [21]. The driving force for both molecular and Knudsen diffusion is the partial pressure difference of the gas species between the two sides of the membrane. The diffusive permeability increases with the humidification and temperature, as the polymer morphology changes increasing the gas diffusivity [82–84]. Depending on the temperature (30–95 $^\circ$C), humidity (0–95% RH) and material composition [73], the hydrogen permeability is $5-40 \times 10^{-14}$ mol s$^{-1}$ cm$^{-2}$ kPa$^{-1}$ and the oxygen permeability $2-20 \times 10^{-14}$ mol s$^{-1}$ cm$^{-2}$ kPa$^{-1}$ for pristine membranes without defects. (iii) If the membrane has defects larger than about 0.5 $\mu$m that are open to both sides of the membrane, gas will also permeate the membrane by viscous flow [21]. This process, different from the diffusive gas transport mechanisms, is referred to as convective gas transport and may be a significant gas transport mechanism in degraded membranes. Convective gas transport is driven by the absolute pressure gradient between anode and cathode.

The consequences of gas permeation are as follows. Hydrogen and oxygen permeation reduce the cell performance and efficiency of pristine cells by about 1–3% [85], as the permeated gases react chemically at the catalyst layer without generating any electricity. If the fuel cell is operated with recirculated hydrogen and air, the dilution of hydrogen by permeated nitrogen further reduces the electric efficiency [42]. Furthermore, the chemical reaction of permeated hydrogen and oxygen forms radicals that accelerate chemical poly-
mer decomposition, which in turn causes a dramatic increase in the gas crossover over time, as illustrated in Figure 6.1 [82]. This may be the main reason for the performance decay over long-term operation and is a critical safety issue [86]. The maximum tolerable hydrogen crossover is limited by the lower explosion limit, which is about 4 mol% of hydrogen in air [87]. The US Department of Energy defined a hydrogen crossover of 20 mA cm$^{-2}$ as the end of life criteria [26]. The loss of the gas separation is one of the few sudden failure modes in a fuel cell system that may require an immediate shutdown [88]. Therefore, it is probably the most serious membrane failure. The following sections describe degradation mechanisms of PFSA membranes and their implication on the membrane functionality.

![Figure 6.1 Drawing of the evolution of the gas crossover in a PEFC during operation.](image)

### 6.1.2 Chemical Degradation Mechanisms

Chemical membrane degradation refers to the chemical decomposition of polymer and the contamination of the membrane by cations. Even though PFSA membranes are chemically and thermally very stable due to the high C-F bond strength of about 460 kJ mol$^{-1}$ and the shielding effect of the electronegative fluorine atoms, chemical polymer decomposition is still a major degradation pathway. This is due to the very harsh chemical environment in a PEFC, caused by high moisture, the presence of hydrogen as a reducing agent and oxygen as an oxidizing agent, and electrochemical potentials that can exceed 1 V [58, 89]. As a result, both sulfonic acid groups and bulk material are decomposed chemically, where material losses of about 10 wt.% limit the service life of the membrane [90]. New functional groups are formed, e.g. C-H [50, 91], COOH [51, 92], CO [93], SOS [53, 91, 93–95], creating
weakened sites that accelerate polymer decomposition. Polymer chains are broken, reducing their molecular weight. In total, these processes degrade the physical and chemical properties of the membrane, such as the water absorption capability [96, 97], the proton conductivity [97, 98], the glass transition temperature [99], the tensile strength [100, 101], the elastic modulus [21, 102, 103], the toughness [21, 102, 103] and the membrane thickness [104, 105]. The degradation of these properties is associated with a loss in proton conductivity and gas separation. The latter promotes further degradation processes in turn, as discussed in Section 6.1.3 on page 57.

Cation Contamination Metal cations are formed by the corrosion of cell components such as bipolar plates, tubings and the catalyst. They are leached out by water, contaminating the polymer electrolyte membrane [96,106]. \( \text{Ca}^{2+}, \text{Fe}^{3+}, \text{Cu}^{2+}, \text{Na}^+, \text{K}^+, \text{Mg}^{2+} \) and \( \text{Pt}^{2+} \) have been detected in the membrane after long-term operation [106]. These cations accumulate in the membrane because the Coulomb interaction between metal cations and sulfonic acid groups is stronger than that experienced by lone protons [97]. The cation contamination lowers the ionic conductivity of the membrane, reduces the ORR activity of the catalyst and accelerates chemical polymer decomposition. The ionic conductivity is reduced because the specific conductivity of metal ions is lower than that of protons, mainly due to the absence of the Grotthuss transport mechanism. Additionally, the ionic conductivity decreases as the cationic contaminants lower the membrane hydration for the following reasons. The water absorption capability of the polymer decreases because metal cations are less hydrophilic than protons, and they have a cross-linking effect that limits membrane swelling [97,107]. The weakened water absorption capability will be serious if 50% or more of the protons are replaced by metal cations [96]. Furthermore, the membrane suffers from dehydration when it is contaminated by cations, as the electro-osmotic drag is stronger for cations than protons, an effect that becomes dominant at contamination levels of more than 5% [96]. Contaminant ions at the catalyst/ionomer interface lower the ORR activity of the catalyst for contamination levels of less than 1%. This is because the oxygen gas transport is reduced or the charge transfer reaction is suppressed due to a change in the ionomer morphology [96,107,108]. Finally, cation contaminants accelerate chemical polymer decomposition, as discussed in the next section.

Chemical Polymer Decomposition Hydroxyl radicals decompose the polymer chemically. They lead to the formation of carbon radicals in the polymer and to the unzipping of the polymer chain according to the mechanism shown in Equations 6.1–6.4 [57,58]. Carbon
6.1 Understanding of Membrane Degradation

Radicals can recombine with hydroxyl radicals, generating a metastable fluoroalcohol that undergoes HF elimination to form acyl-fluoride. Acyl-fluoride subsequently undergoes hydrolysis to a carboxyl group. The hydrogen atom of the carboxyl group can be subtracted by a further hydroxyl radical attack. The polymer chain is then decarboxylated to form a more stable carbon radical with the polymer chain shortened by one CF₂ fragment [58]. Both degradation products, CO₂ and HF, have been detected in the gas phase or product water [39, 57, 90]. The analysis of the product water for fluoride has also been established as a standard method to study chemical polymer decomposition [57, 58].

\[ R_f - CF_2 \cdot + \cdot OH \rightarrow R_f - CF_2OH \]  \hspace{1cm} (6.1)

\[ R_f - CF_2OH \rightarrow R_f - COF + HF \]  \hspace{1cm} (6.2)

\[ R_f - COF + H_2O \rightarrow R_f - COOH + HF \]  \hspace{1cm} (6.3)

\[ R_{f-1} - CF_2COOH + \cdot OH \rightarrow R_{f-1} - CF_2\cdot + CO_2 + H_2O \]  \hspace{1cm} (6.4)

Carbon radicals are the starting point of the unzipping polymer chain mechanism and have been detected in the membrane via electron paramagnetic resonance spectroscopy [109, 110]. Carbon radicals can be formed by various processes. Carboxyl end groups may remain from the manufacturing process, enabling the reaction given in Equation 6.4 [58]. Two sulfonic acid groups can condensate according to Equation 6.5. The anhydride was detected by FTIR analysis [90, 91, 93–95].

\[ -CF_2 - SO_3H + HO_3S - CF_2- \rightarrow -CF_2 - SO_2 - O - SO_2 - CF_2 - + H_2O \]  \hspace{1cm} (6.5)

The formation of the sulfonic acid anhydride lowers the proton conductivity, and it may also cause carbon radicals, because the anhydride may further react with another sulfonic acid group, forming a sulfonate ester, which is hydrolyzed to a carboxylic acid, from where reaction 6.4 starts [93]. Hydroxyl radicals can split the C-S bond of the sulfonic acid group [50, 90] or attack the hydrogen-containing terminal bond of the protonated acid group as shown in Equation 6.7. This reaction is most likely at low humidity [111] and followed by the elimination of SO₃. Both of these reactions result in the formation of carbon radicals [99]. The detection of sulfate ions in the product water has confirmed the decomposition of sulfonic acid groups [57, 98]. Furthermore, C-F bonds may be attacked by hydrogen radicals according to Equation 6.6, thus forming carbon radicals [111]. Likewise, tertiary carbon atoms next to the ether group of the side chain have a reduced
bond strength, facilitating the radical attack by hydroxyl radicals \[58,112\]. In both processes, carbon radicals are formed by a polymer chain scission, which fragments, such as CF\(_3\)COOH, HO\(_2\)CCF\(_2\)SO\(_3\)H and HO\(_2\)CCF(CF\(_3\))OCF\(_2\)CF\(_2\)SO\(_3\)H, have been detected in the product water \[58\].

\[
-CF_2- + \cdot H \rightarrow -\dot{C}F - + HF \tag{6.6}
\]
\[
-CF_2 - SO_3H + \cdot OH \rightarrow -CF_2 \cdot + SO_3 + H_2O \tag{6.7}
\]

Hydroxyl radicals have been detected in the membrane using EPR spectroscopy with a combined spin trapping method \[113–115\] and in the exhaust gas using mass spectrometry \[39\]. Gubler et al. \[116\] estimated the radical concentration and the oxidative strength of the respective radical species in a 50 µm thick membrane using a kinetic framework. The radical concentration, expressed as number of radicals per membrane area, was found to be \(2 \times 10^8 \cdot \text{OOH cm}^{-2}\), \(300 \cdot \text{OH cm}^{-2}\) and \(1 \cdot \text{H cm}^{-2}\). The relative oxidative strength follows the trend \(\cdot \text{OH} < \cdot \text{H} < \cdot \text{OOH}\). Quantum mechanical calculations have shown that hydroxyl radicals can be formed directly at the cathode catalyst layer \[117,118\]. But the dominant formation pathway is most likely the indirect formation via hydrogen peroxide \[57,110,119\], which has been detected in the product water \[119\] and in the membrane with a concentration in the order of 1–30 ppm \[120,121\].

Cation contaminants like Fe\(^{2+}\) catalyze the decomposition of hydrogen peroxide to hydroxyl and hydroperoxyl radicals according to Equations 6.8 and 6.9. The recombination of two hydroxyl radicals to hydrogen peroxide is possible but unlikely due to their low concentration \[90\]. As hydrogen peroxide has a longer lifetime than hydroxyl radicals, it may be transported by diffusion and decompose to radicals far away from the production site. Much ongoing debate revolves around whether the polymer is mainly decomposed at the anode \[120\], the cathode \[112,122\] or in the core of the membrane \[105\] because it is still unclear where hydrogen peroxide is formed.

\[
H_2O_2 + M^{2+} \rightarrow HO \cdot + OH^- + M^{3+} \tag{6.8}
\]
\[
H_2O_2 + M^{3+} \rightarrow HO_2 \cdot + H^+ + M^{2+} \tag{6.9}
\]

Figure 6.2 illustrates the chemical and electrochemical formation of hydrogen peroxide in a fuel cell. Hydrogen and oxygen permeate through the membrane and can react chemically to hydrogen peroxide at the cathode catalyst layer (II), at the anode catalyst layer (IV) or in the platinum band region of the membrane (III) \[99\]. Hydrogen peroxide can also
be generated electrochemically by a two electron reduction of oxygen at potentials below 0.695 V, which is catalyzed by both platinum particles and the carbon support [90, 123]. This reaction most likely occurs for oxygen permeating to the anode due to the low potential of that electrode (IV) [57, 124]. Despite the high potential, rotating ring disk electrode experiments on various catalyst types however confirm the electrochemical formation of hydrogen peroxide at the cathode electrode as well, which also correlates with the membrane degradation rate [112]. Chloride and sulfur poisoning of the platinum catalyst may facilitate this reaction path (I) [90, 112, 125].

Chemical polymer decomposition is accelerated under certain fuel cell operating conditions. The degradation rate increases with the gas crossover rate. It is thus directly proportional to the reactant partial pressure and inversely proportional to the membrane thickness [86, 120, 126]. As the gas crossover is highest at OCV due to the elevated partial pressure at the catalyst/membrane interface [57, 90, 127], the highest polymer decomposition rates occur in OCV mode. At low humidity the partial pressure of the reactants is highest, and the low partial pressure of water increases the hydrogen peroxide activity, thus accelerating chemical polymer decomposition [57, 90]. In contrast, high humidities cause more cationic contaminants to leach out and accumulate in the membrane, also facilitating polymer decomposition [124]. Therefore, the effect of the humidity may also depend on the experimental setup, respectively, on the corrosion resistance of fuel cell and system components. Furthermore, high temperatures increase the degradation rate as the reaction kinetics are enhanced [90]. High temperatures, low humidities and OCV are often applied in accelerated stress tests to focus on chemical polymer decomposition [26].

Figure 6.2 Scheme illustrating the four different mechanisms of hydrogen peroxide formation, respectively, radical formation.
6.1.3 Mechanical Degradation Mechanisms

Mechanical membrane degradation refers to membrane failures that are caused by mechanical stress. PFSA membranes are semi-crystalline thermoplastics with moderate elasticity and distinctive plasticity, as illustrated by the stress-strain curve of a recast Nafion NR 211 membrane in Figure 6.3. For pristine PFSA membranes the elastic modulus ranges between 110 MPa and 670 MPa, the ultimate stress between 17 MPa and 36 MPa, and the ultimate strain between 80% and 225%. The visco-elastic properties depend on the humidity, temperature, polymer and fabrication process [21,101,102,128].

Once the mechanical stress exceeds the local yield strength, the membrane integrity degrades irreversibly. Polymer creep is induced in the strain hardening region (Figure 6.3), which decreases the membrane thickness and thereby the cross-section. This accelerates membrane creeping in turn. Crazing sites are induced that can propagate through the membrane and end up as cracks, tears or pinholes at the ultimate stress point (Figure 6.3) [104,129–131]. Both processes, membrane creeping and crack formation, increase the gas crossover. If carbon material bridges the anode and cathode at these membrane defects, the ohmic resistance will be lowered as well. A further consequence of mechanical stress may be the delamination of the catalyst layer [58]. As the visco-elastic properties depend on the stress period and previous history, a given membrane may fail mechanically prior to the expected endurance of a pristine membrane [131]. For instance, chemical

![Stress-strain curve of a recast pristine Nafion NR 211 membrane at 26 °C and 21% RH. Data used from Schuler [21].](image-url)
membrane degradation significantly reduces membrane toughness, leading to membrane failures at lower mechanical stress [101]. This synergetic effect of mechanical and chemical stress may be the most important reason for membrane failures [85, 88, 132].

Mechanical stress can be categorized into humidity-, temperature- and system-induced stresses. The clamping pressure, which is required for cell sealing and reduction of the contact resistance between the GDL and bipolar plates, induces mechanical stress [88]. The nominal clamping pressure is typically between 0.5 MPa and 2 MPa, but can be locally much higher, e.g. under the rib area or at sealing edges [134]. Mechanical stress is also induced by the pressure gradient between anode and cathode, which is up to 20 kPa. Moreover, membrane shearing forces can arise at the edge sealing if the sealant and GDE are not aligned properly [88, 135]. Membrane failures may also result from congenital membrane defects or from an improper fabrication process of the MEA [85]. Humidity induced mechanical stresses are created as follows. Due to its ability to absorb water, the polymer volume changes with the hydration state. Figure 6.4 shows the volume expansion, ranging up to 40%, for various membranes as a function of relative humidity [133]. Fluctuations in the relative humidity, e.g. during load cycling, induce membrane swelling and shrinkage that is associated with mechanical stress [130]. The polymer expansion is not significantly constrained in the through-plane direction as the elastic modulus of the GDE is low (in the order of 0.5 MPa). However, it is constrained in the in-plane direction.

Figure 6.4 Membrane swelling for different membranes as a function of relative humidity, adapted from Mathias et al. [133] with permission from the Electrochemical Society.
due to the high in-plane elastic modulus of the GDE (in the order of 9 GPa). The difference in the mechanical properties of the membrane and GDE causes in-plane stresses that lead to membrane failures [136,137]. In-plane stresses also arise in the polymer under the channel and rib area because the membrane hydration may be different under the rib and channel [138,139].

Since both the mechanical stress and the visco-elastical properties differ locally due to nonuniform membrane hydration, mechanical degradation processes are highly localized. Compressive stresses are distributed nonuniformly across the membrane in the through-plane direction, as the membrane hydration differs significantly across the membrane due to the production of water at the cathode, water back-diffusion and the effect of the electro-osmotic drag [137]. Likewise, an inhomogeneous current density distribution results in nonuniform membrane hydration across the active area [140,141]. Modeling work predicts increased stress at the edge sealing that is induced by the humidity. The temperature-induced volume expansion has a similar effect to that of the water absorption, but it is not as pronounced because the thermal expansion coefficient of PFSA membranes is low [66,137].

### 6.1.4 Thermal Degradation Mechanisms

Thermal membrane degradation refers to temperature-induced processes that change the polymer integrity irreversibly. Temperature-induced mechanical stress due to volume expansion and shrinkage, is part of mechanical membrane degradation. Increasing the temperature beyond the maximum operating temperature of about 90 °C dehydrates the membrane, which may induce the condensation of two sulfonic acid groups [91]. Above the glass transition temperature (approximately 110 °C for Nafion membranes [142]), the polymer chains rearrange considerably, inducing changes in the nanostructure that are associated with increasing crystallinity [142] or the dissociation of ionic clusters [143]. At about 275 °C, Nafion starts to decompose thermally at the sulfonic acid groups; this is accompanied by SO₂ emission [85,144,145], which has also been observed at very low rates for lower temperatures [89]. Further increasing the temperature decomposes the polymer backbone and side chains to polymer fragments, such as CₓFᵧ, CₓFᵧO₂, CₓFᵧHₓ, HF and CO₂ [144].

PEFCs are operated below 100 °C, so extensive thermal membrane degradation can be assumed to be not relevant. However, the catalytic combustion of hydrogen and oxygen that have permeated through the membrane may create local hotspots at platinum particles, inducing thermal decomposition of the ionomer. The gas crossover is too low in pristine membranes for this to occur, but the crossover at defects may be sufficient to
locally initiate this process in degraded membranes [58, 82, 130]. Combustion residues of carbon have been detected next to large, millimeter-sized MEA defects, as shown in Figure 6.21 on page 85. These residues are indicative of high local temperatures, which may have induced thermal polymer decomposition, but how far this applies to smaller defects with diameters of a few tens of microns is still under debate. Modeling work predicts a temperature increase of only a few degrees because the generated heat is effectively dissipated by the carbonaceous material and is also consumed by the evaporation of liquid water [146]. However, the dramatic increase of the gas crossover during long-term operation is often attributed to local hot spots and the associated thermal polymer decomposition without giving any further evidence [39, 130, 147].

6.1.5 Mitigation Strategies

To mitigate degradation and thus increase the service life of membranes, two different strategies are pursued: increasing the material stability and decreasing the stress. The chemical stability of membranes is improved by treating the ionomer with fluorine gas in a downstream process. This lowers the concentration of hydrogen-containing end groups, decreasing the fluoride emission rate by a factor of about 25 [58, 124]. The reinforcement of bulk polymer with expanded PTFE, PTFE fibers or cross-linking polymer chains improves the dimensional stability upon hydration changes, thereby enhancing the mechanical stability of membranes [148, 149].

Mechanical stress can be reduced by lowering fluctuations and inhomogeneities in the humidity, temperature and current density; an optimized flow field design avoids membrane dry-out at the inlets, novel bipolar plates provide a uniformly high membrane hydration and effective heat dissipation [150], and an optimized fuel cell operation control minimizes the number of load cycles and time spent operating in OCV mode. The latter does not only mitigate mechanical stress but also chemical polymer decomposition, as described in Section 6.1.2 on page 55. Lowering the hydroxyl radical concentration further mitigates chemical stress, which can be realized as follows. Radical-active substances can be implemented in the membrane, which either trap [57] or decompose the radicals [57, 85, 99]. Using thicker or less permeable membranes, e.g. hydrocarbon based membranes [151] or cross-linked membranes [152], lowers the gas crossover, thereby reducing hydrogen peroxide formation. Mitigating platinum dissolution and precipitation in the membrane by increasing the catalyst stability has a similar effect [148].

Membrane degradation related to cation contamination is reversible. Flushing the fuel cell with pure water while running the cell in electrolysis mode or purging the cell with acid solution can remove cationic contaminants, but both treatments may trigger further
corrosion processes [96]. Despite these improvements, the service life of membranes is still a critical parameter in fuel cell applications that is primarily related to local structural conditions, where simultaneous exposure to both chemical and mechanical stresses exerts a synergetic effect on membrane degradation.

6.1.6 Research Objectives

Gas crossover is the key element of membrane degradation, triggering two out of three possible degradation mechanisms. The hydrogen and oxygen crossover is the primary source of oxygen radical species that chemically decompose the polymer. At the same time, the crossover can initiate thermal membrane degradation if the temperature increases due to permeated hydrogen and oxygen that combust catalytically at the catalyst layer. Because both degradation processes lead to a loss in the gas separation (and thus an enhancement of the gas crossover), a positive feedback loop is created that accelerates the degradation processes. The severity of the accelerated degradation is determined by the interaction of chemical, mechanical and thermal degradation processes, which will depend on the local conditions. This is because parameters that influence these degradation processes, such as mechanical stress, reactant composition, relative humidity and temperature, vary across the active area of a fuel cell of technical size. Hence, membrane failures and the associated gas separation loss are local phenomena and are spatially inhomogeneous.

Post mortem analysis of degraded MEAs with an IR camera shows thermograms with hotspots, indicating local membrane defects that are presumably due to pinhole formation [104, 130]. Using this technique, Vengatesan et al. [130] observed membrane failures at the anode inlet, possibly due to the lower membrane hydration. Membrane failures were also identified at catalyst layer edges by Sompalli et al. [134]. If the cathode catalyst layer extends over the anode catalyst layer in a MEA, the potential will increase to OCV in the overlap region. This was found to enhance chemical polymer decomposition in the overlap region. Stumper et al. [153] observed leakages predominantly at the gas inlets of a 10-cell stack. They used localized polarization curves in combination with OCV profile measurements to calculate local crossover leaks. Likewise, Knights et al. [129] found frequent membrane failures at the gas inlets and attributed them to low humidification and locally increased temperatures. Modeling work from Serincan et al. [137] indicates nonuniform mechanical membrane degradation, such as plastic deformation. The relative humidity of the inlet gases, the relative humidity gradient between anode and cathode, the rib/channel geometry and the current density all affect the water content of the membrane locally. The nonuniform membrane hydration causes mechanical stress, resulting in local failures.
As a conclusion, the gas separation loss must be investigated locally to improve the understanding of the complex interaction between the chemical, mechanical and thermal degradation processes. Analysis methods with spatial resolution are required for accurate measurement and interpretation of changes in the gas separation properties of the membrane. In this work, the gas crossover is investigated locally in the early stages of cell lifetimes in order to identify trigger processes that result in nonuniform degradation. The results shall help to ascertain the root cause of the degradation and improve the understanding of membrane degradation mechanisms that lead to the exponential evolution of the gas crossover shown in Figure 6.1 on page 51.

6.2 The Gas Separation Loss in Technical Cells

MEAs were aged in accelerated stress tests (AST) in the segmented cell of technical size in order to identify the main gas separation loss, and to trigger and investigate processes that result in nonuniform degradation\(^1\). The effects of both mechanical and chemical degradation processes (as well as the combination of the two) were tested by applying relative humidity (RH) cycling, operation in OCV and load cycling in ASTs. Experimental details of the ASTs are given in Table 3.3 on page 19. To test the influence of the gas diffusion electrode (GDE) surface structure, two different types of MEAs were assembled with GDEs of different surface roughness; MEA “C” with a carbon cloth GDE and MEA “P” with a carbon paper GDE. The gas crossover was investigated locally in the early degradation stage by using a tracer gas concept. Dosing the anode gas with 10 vol.% helium at different pressure gradients between anode and cathode allows for in situ analysis of the diffusive and convective helium transport across the membrane (described in Section 4.1.3 on page 26), which yields information about membrane thinning and pinhole formation. The helium crossover refers to a helium partial pressure of 14–16 kPa. Inhomogeneous membrane degradation was further characterized by ex situ XTM, local water vapor analysis and ex situ SEM.

Figures 6.5 and 6.6 show the local evolution of the diffusive and convective helium crossover for MEA “C” (A, B, C) and MEA “P” (D, E) of different ASTs. The initial diffusive helium crossover for new membranes (0 hours) is about $2 \times 10^{-9}$ mol s\(^{-1}\) cm\(^{-2}\) and is homogeneous along the channel. This is characteristic of new intact membranes and corresponds to a mean hydrogen crossover of $8.5 \times 10^{-9}$ mol s\(^{-1}\) cm\(^{-2}\) at 150 kPa partial pressure of hydrogen (corresponding to 1.6 mA cm\(^{-2}\)), assuming a permeability ratio of 2.5 for helium and hydrogen at 80 °C [21].

\(^1\)Results in this chapter have been published in Kreitmeier et al., J. Power Sources 212 (2012) 139–147.
Figure 6.5 The *diffusive* helium crossover as function of channel length for MEA “C” at A) OCV, B) RH cycling and C) load cycling and for MEA “P” at D) RH cycling and E) load cycling. The helium crossover refers to a partial pressure of 14 kPa.
6.2 The Gas Separation Loss in Technical Cells

Figure 6.6 The convective helium crossover as function of channel length for MEA “C” at A) OCV, B) RH cycling and C) load cycling and for MEA “P” at D) RH cycling and E) load cycling. The helium crossover refers to a partial pressure of 16 kPa.
The hydrogen permeation is in agreement with data reported in the literature [154]. The initial \textit{convective} helium crossover of new membranes fluctuates around zero. As expected, there are no detectable pinholes. In the following three subsections, results of the three different ASTs are discussed in detail.

\textbf{Accelerated Chemical Degradation} Chemical membrane degradation can be investigated with an OCV accelerated stress test, such as proposed by the US Department of Energy (DOE) [26]. With this AST no humidity fluctuations are induced, thus avoiding mechanical degradation. As shown in Figure 6.7A, local online water vapor analysis does not reveal any RH fluctuations. The spatial and temporal evolution of the diffusive and convective gas permeation of MEA “C” are illustrated in Figures 6.5A and 6.6A. Neither the helium diffusion nor the membrane thickness, measured with SEM, changed after the 500 h AST. The FER, an indicator used for chemical degradation and polymer decomposition [77], is on average 10.4 ng(F) cm\(^{-2}\) h\(^{-1}\) in this test, which is indistinguishable from the background obtained when operating the cell with nitrogen. Therefore, a measurable chemical degradation of the membrane polymer has not been detected with the applied analysis methods.

In spite of this, the convective gas crossover does increase locally up to \(3.6 \times 10^{-9}\) mol s\(^{-1}\) cm\(^{-2}\) in the cathode \textit{outlet region} at 70\% of the channel length, which corresponds to an increase of \(4 \times 10^{-12}\) mol s\(^{-1}\) cm\(^{-2}\) h\(^{-1}\). Even though extensive chemical polymer decomposition has not been observed, polymer may decompose locally at initial membrane defects due to the elevated gas crossover, which increases the radical formation rate. Preliminary OCV experiments with Nafion 112 show that the convective helium

![Figure 6.7](image_url) **Figure 6.7** \textit{In situ} water vapor analysis in the cathode of the segmented cell during different ASTs. The minimum (red) and maximum (blue cross) relative humidities are shown along the center channel for A) OCV, B) RH cycling and C) load cycling. Reproduced from Kreitmeier et al. [23] with permission from the Journal of Power Sources.
permeation increases nonuniformly at statistically scattered spots indicating that defects are formed randomly distributed across the active area under these conditions [21].

In conclusion, the commonly expected effects of chemically-induced membrane degradation, polymer decomposition and membrane thinning [155], have not been observed for Nafion NR 211 during a 500 h OCV AST. Protecting the polymer backbone by fluorinating the carboxyl end groups reduces the chemical degradation rate, so the Nafion 2XX series materials (end groups fluorinated) have better chemical stability when compared to the 1XX series membranes. However, the convective gas crossover does increase locally over time, indicating that chemical decomposition of the polymer is accelerated at membrane defects.

**Accelerated Mechanical Degradation**  Fluctuations of the water content induce mechanical stress in the membrane through repeated swelling and shrinking. This process can cause membrane creep, cracks and pinholes, thus degrading the gas separation performance of the membrane [155]. To investigate these mechanical degradation processes, accelerated stress tests which cycle the gas humidity were used. Depending on the water storage capacity of the MEA and the cycling frequency, inhomogeneous, transient humidity conditions may be induced in cells with a large active area. This calls for analysis of the local humidity fluctuations, even when using standard protocols. Figure 6.7B illustrates the RH fluctuations measured along the cathode channel of the segmented cell. The RH cycling protocol has been adopted from the DOE protocol [26], with a dry (2 min) and wet (2 min) cycle where the inlet humidity changes between 0% and 130% (oversaturated gas). However, the control measurements show a minimum of only 34% and a maximum of 100% RH at the cathode inlet. During the wet cycle, water droplets condense in the MEA and buffer the relative humidity during the dry cycle. This results in a maximum RH difference of 66% in the cathode gas inlet. Due to the humidity buffering effect of the MEA, the RH fluctuation decreases even more along the channel, almost disappearing in the outlet region. In other words, the MEA acts as a buffer system and significantly dampens the humidity oscillations. A cycling time of 2 min is not sufficient to dry or humidify the cathode outlet region in this cell configuration, leading to a nonuniform RH cycling amplitude along the channel. The effect of this nonuniform RH cycling on the membrane integrity was studied by analyzing the temporal and local evolution of both the diffusive and convective gas permeation. The AST was performed with two different MEA configurations to investigate the effect of the GDE surface roughness on the mechanical degradation rate of the membrane. GDE “C”, based on a carbon fiber cloth, is compared to GDE “P”, based on a carbon fiber paper, which has a smoother surface with fewer and
narrower cracks in the MPL than GDE “C” (details see Table 3.2 on page 14).

Figures 6.5B and 6.5D show the local and temporal evolution of the diffusive helium permeation, while Figures 6.6B and 6.6D show the evolution of the convective helium permeation. The diffusive helium transport through MEA “C” increases over the 500 h test, with average rates of $1.9 \times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2} \text{ h}^{-1}$ in the cathode inlet region (0% to 40% of channel length). The diffusive helium transport for MEA “P” does not change. The diffusive gas transport can increase not only because of chemical membrane thinning, but also from plastic deformation of the membrane, most likely induced by the irregularities of the GDE surface structure. Figures 6.8A and 6.8B illustrate groove formation and membrane creep in MEA “C”. Grooves are formed in the polymer when the sharp edges of cracks in the MPL exert a shear force on the polymer during membrane swelling. At the same time, the polymer counteracts the clamping pressure by creeping into MPL cracks; the larger the crack, the more easily the polymer creeps. Both processes cause local membrane thinning, which increases the diffusiv gas transport through the membrane.

Gas diffusion through MEA “C” increases in the inlet region, which is due to the larger humidity fluctuation and possibly also due to the high humidity, since water acts as a plasticizer for the membrane material. Both humidity fluctuations and a high membrane water content promote membrane creep. Humidity fluctuations lead to the build-up of internal stress [137], while a high membrane water content decreases the Young’s modulus of Nafion [156]. In contrast, gas diffusion through MEA “P” does not increase over time, since plastic deformation of the membrane is less pronounced than for MEA “C”. This is due to the smoother GDE surface, which has fewer and significantly smaller cracks. However, the small size of the cracks in GDE “P” may only slow down plastic deformation, not eliminate it. Regardless, the diffusive gas crossover through MEA “P” does not increase

![Figure 6.8](image.png) Ex situ, post mortem X-ray tomographic microscopy cross-sections of degraded MEAs. A) illustrates a crack in the membrane and B) membrane creep. Reproduced from Kreitmeier et al. [23] with permission from the Journal of Power Sources.
6.2 The Gas Separation Loss in Technical Cells

during the 500 h test.

A similar trend is observed for the local convective crossover over time. The convective helium transport through MEA “C” increases with rates of $0.6 \times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2} \text{ h}^{-1}$ in the cathode inlet region (0% to 60% of channel length) averaged over the 500 h test, while it does not change for MEA “P”. Carbon fiber ends pierce through the MPL of GDE “C” (see Figure 3.1A on page 14) and induce local stress by penetrating into the membrane. This initiates pinhole formation. *Ex situ*, nondestructive, post mortem XTM analysis reveals the presence of such pinholes and the carbon fiber ends associated with them. Figures 6.9A and 6.9B show a MEA cross-section as gray scale image and the corresponding segmented 3D structure of MEA “C” with a pinhole in the membrane, as typically found after applying RH cycling AST. The pinhole has a diameter between 4 µm and 13 µm, and a carbon fiber penetrates into the membrane. Larger humidity fluctuations and possibly the high average humidity also promote pinhole formation in the cathode inlet region, similar to membrane creep.

At least one further mechanism for mechanical pinhole formation exists, since pinholes

![Figure 6.9](image.png)

*Figure 6.9* *Ex situ* X-ray tomographic microscopy of a degraded MEA with a pinhole in the membrane. A) cross-section, B) 3D visualization without the MPL. Reproduced from Kreitmeier *et al.* [23] with permission from the Journal of Power Sources.
are also found in MEA “C” without any nearby fiber ends. Sharp edges of MPL cracks intrude into the membrane during swelling and shrinking and exert shear forces on the polymer. This induces grooves in the membrane, as depicted in Figure 6.8A, which may further evolve into pinholes. Pinholes are not detected in MEA “P” within the 500 h test period because GDE “P” has less cracks and no carbon fiber ends piercing through the MPL. However, pinhole formation may only be slowed down and not eliminated.

**Combined Chemical and Mechanical Degradation at Load Cycling**  This test was employed to investigate the combined effects of chemical and mechanical degradation processes on the membrane durability. Once again, the impact of the GDE surface properties was tested by using MEAs with GDE “C” and GDE “P”. During load cycling, water is produced and it accumulates along the channel, leading to the nonuniform water distribution shown in Figure 6.7C. Despite the alternation between OCV and load, the relative humidity increases almost without fluctuations from 35% to 90% along the cathode channel. This is because the water storage capacity of the GDE compensates for the fluctuating water production within the cycling time of 30 seconds.

The effects of this nonuniform water distribution and of the combined chemical and mechanical degradation processes on the membrane integrity were again studied by analyzing the temporal and local evolution of the diffusive (Figures 6.5C and 6.5E) and convective (Figures 6.6C and 6.6E) helium permeation. The diffusive helium transport through MEA “C” increases with rates of $3.4 \times 10^{-12}$ to $5.4 \times 10^{-12}$ mol s$^{-1}$ cm$^{-2}$ h$^{-1}$ in the cathode outlet region (90% to 100% of channel length). As observed in the RH cycling AST, a high humidity promotes plastic deformation of the membrane, which results in increasing gas diffusion in the cathode outlet region. In MEA “P” the diffusive permeation does not increase during the 500 h test. Plastic deformation is much weaker and is not observed due to the smoother surface of GDE “P”. Furthermore, chemical decomposition of the membrane polymer is not observed by FER analysis. The mean FER of 8.2 ng cm$^{-2}$ h$^{-1}$ is indistinguishable from the background.

The convective helium crossover through MEA “C” increases with rates between $7.3 \times 10^{-12}$ and $8.6 \times 10^{-12}$ mol s$^{-1}$ cm$^{-2}$ h$^{-1}$ (31 $\times$ $10^{-12}$ mol s$^{-1}$ cm$^{-2}$ h$^{-1}$ on average) in the cathode outlet region (60% to 100% of channel length), while changes for MEA “P” are only observed in the integral outlet after 500 h (Figure 6.6E; single markers on the right side), but not in the center channel. The helium crossover increases with a mean rate of $28 \times 10^{-12}$ mol s$^{-1}$ cm$^{-2}$ h$^{-1}$, averaged over 620 h. Even if pinholes are not located in the center channel region, they are usually still detectable along the channel since helium diffusion is fast among adjacent gas channels [21]. Thus, pinholes of MEA “P” are pre-
sumably located in the cathode outlet region of the outer channels, where the remaining residence time of the gas is too short to allow gas diffusion to the center channel. The convective gas crossover probably increases in the cathode outlet region for the same reason as for the diffusive crossover. In addition, a high upstream hydrogen crossover promotes thermal polymer decomposition, as discussed in Section 6.4.2 on page 85.

The convective helium crossover of MEAs with GDE “C” (and also with GDE “P”) increases much faster during load cycling \((31 \times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2} \text{ h}^{-1} \text{ on average})\) than during RH cycling \((0.6–7.2 \times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2} \text{ h}^{-1})\) or during OCV \((4 \times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2} \text{ h}^{-1})\), as summarized in Table 6.1. In other words, chemical and mechanical processes seem to have a synergetic effect that enhances membrane degradation. As outlined by Huang et al. [88], the polymer loses some of its mechanical integrity when it decomposes chemically. Thus, the formation of pinholes and cracks by mechanical processes will be enhanced if chemical degradation occurs simultaneously. In this case, the gas crossover through pinholes accelerates locally the chemical decomposition of the polymer, which in turn enhances mechanical degradation, further boosting the gas crossover. The degradation rates are high for both MEA “C” and MEA “P”, but the temporal onset of the degradation loop is different. Pinholes are formed mechanically in MEA “C” within 200 h, but in MEA “P” not until 500 h due to the smoother surface of GDE “P”. In other words, the synergetic effect of chemical and mechanical degradation processes starts later for MEA “P”.

In conclusion, the diffusive and convective gas transport increases due to membrane creep and due to the formation of cracks and pinholes. These processes are mechanically triggered by the combined effects of the GDE surface morphology, large RH fluctuations in the gas channel and a high membrane humidification. Since the relative humidity and RH fluctuations are inhomogeneous along the channel, the gas crossover develops nonuni-

### Table 6.1 Summary of the mean diffusive and convective helium crossover increase rate, where the diffusive helium crossover refers to a partial pressure of 14 kPa and the convective crossover to a partial pressure of 16 kPa at a pressure gradient between anode and cathode of 10 kPa.

<table>
<thead>
<tr>
<th>GDE material</th>
<th>Diffusive He crossover increase / (\times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2} \text{ h}^{-1})</th>
<th>Convective He crossover increase / (\times 10^{-12} \text{ mol s}^{-1} \text{ cm}^{-2} \text{ h}^{-1})</th>
<th>Relative channel length (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCV</td>
<td>GDE “C” GDE “C” GDE “P”</td>
<td>GDE “C” GDE “P”</td>
<td>70–100 0–50 n. a. 60–100 int. outlet</td>
</tr>
<tr>
<td>RH cycling</td>
<td>0 1.9–4.6 0</td>
<td>0 7.3–86 (831) 28</td>
<td>70–100</td>
</tr>
<tr>
<td>Load cycling</td>
<td>3.4–5.4 0</td>
<td>0 7.3–86 (831) 28</td>
<td>60–100 int. outlet</td>
</tr>
</tbody>
</table>
formly along the channel, i.e. the cell area. Extensive chemical decomposition of the polymer, which induces membrane thinning, is not observed for Nafion NR 211 membranes. However, the mechanical formation of membrane defects is critical for the onset of a synergetic effect of chemical and mechanical processes. This combined degradation accelerates the overall degradation rate and boosts the gas crossover exponentially. This is the root cause for the gas separation loss that limits the service life of membranes. Because of this fact, the local elevated gas crossover and the resulting degradation mechanism at membrane defects were studied extensively and are discussed in the following two chapters.

6.3 Gas Crossover through Pinholes

6.3.1 Diffusive and Convective Gas Permeability

This chapter addresses the gas crossover through membrane defects, which substantially affects the degradation of membranes\(^2\). In order to investigate the gas crossover through membrane defects, pinholes were implemented artificially in Nafion NR 211 by electron beam lithography (EBL), as described in Chapter 5. Although electron scattering damages the polymer surrounding the induced pinholes, EBL was used because it is a fast and inexpensive method. The EBL induced damage is ignored for experiments carried out in this chapter, since these experiments did not focus on pinhole development and growth. The diffusive and convective helium permeability was determined according to the methodology presented in Section 4.1.3 on page 28. For the present experiments, MEAs composed of Nafion NR 211 and H400 GDEs have been prepared with a membrane defect density of 9 pinholes per cm\(^2\) active area, with each pinhole being approximately 10 \(\mu\)m in diameter. Table 6.2 shows the diffusive and convective helium permeabilities for four MEAs. During analysis, nitrogen was flowed through the anode and cathode at 80 \(^\circ\)C, 150 kPa and 0\% RH.

The diffusive helium permeability is on average \(0.52 \pm 0.23 \times 10^{-12}\) mol s\(^{-1}\) Pa\(^{-1}\) cm\(^{-2}\), where Pa refers to the partial pressure. This corresponds to a diffusive helium crossover of \(7.8 \pm 3.4 \times 10^{-9}\) mol s\(^{-1}\) cm\(^{-2}\) at 150 kPa absolute pressure (15 kPa helium partial pressure), compared to about \(2 \times 10^{-9}\) mol s\(^{-1}\) cm\(^{-2}\) for a pristine membrane (see Chapter 6.2). Thus, the diffusive helium crossover through a single 10 \(\mu\)m defect is about \(0.64 \times 10^{-9}\) mol s\(^{-1}\). Gas diffusion through pinholes (diffusion in the gas phase) is a factor \(10^6\) larger than it is through the polymer [157,158]). Therefore, gas diffusion through PFSA membranes increases significantly in the presence of small pinholes, even though

\(^2\)Results shown in this chapter have been published in Kreitmeier et al., Electrochim. Acta 80 (2012) 240–247.
6.3 Gas Crossover through Pinholes

Table 6.2 Reproducibility of the diffusive and convective helium permeability in different MEA samples with a membrane defect density of 9 per cm$^2$ active area each 10 $\mu$m in diameter. The convective permeability refers to a single defect, while the diffusive one to the active area of the membrane.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Convective permeability per defect / $\times 10^{-12}$ mol s$^{-1}$ Pa$^{-1}$</th>
<th>Diffusive permeability / $\times 10^{-12}$ mol s$^{-1}$ Pa$^{-1}$ cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.0</td>
<td>0.77</td>
</tr>
<tr>
<td>2</td>
<td>5.4</td>
<td>0.47</td>
</tr>
<tr>
<td>3</td>
<td>7.8</td>
<td>0.32</td>
</tr>
<tr>
<td>4</td>
<td>6.3</td>
<td>0.37</td>
</tr>
<tr>
<td>Average</td>
<td>6.6 ($\pm$ 15%)</td>
<td>0.52 ($\pm$ 43%)</td>
</tr>
</tbody>
</table>

The pinhole area is only 7 ppm of the total membrane area.

The convective helium permeability through the perforated membranes is on average $59.4 \pm 8.9 \times 10^{-12}$ mol s$^{-1}$ Pa$^{-1}$ cm$^{-2}$, where Pa refers to the differential pressure. This corresponds to a convective helium permeability of $6.6 \pm 1.0 \times 10^{-12}$ mol s$^{-1}$ Pa$^{-1}$ for a single 10 $\mu$m pinhole. Thus, the convective helium crossover through a single 10 $\mu$m defect is about $0.66 \times 10^{-9}$ mol s$^{-1}$ at 1 kPa differential pressure between anode and cathode$^3$. In conclusion, the diffusive and convective gas crossover are in the same range for a 10 $\mu$m pinhole at a pressure gradient of 1 kPa. For larger pinholes or higher pressure gradients gas permeation is dominated by convective gas transport. The total gas crossover through a 10 $\mu$m pinhole is at the given condition about half of the diffusive gas transport through a pristine Nafion NR 211 membrane per 1 cm$^2$ active area.

The reliability of analyzing the diffusive and convective helium permeability in perforated membranes was evaluated on the basis of the standard deviation of the analysis method and the reproducibility of the measurement. The relative standard deviation of the analysis method is 3.9% for the convective and 23.5% for the diffusive helium permeability, as averaged for MEAs with various pinhole sizes at different temperature and RH. The absolute standard deviations of the diffusive and convective helium transport are similar in magnitude, but the relative one is higher for the diffusive transport, since the absolute diffusive helium crossover is much smaller than the convective one at the given conditions. Table 6.2 illustrates the reproducibility of the measurements. The relative standard deviation is 15% for the convective helium permeability, while it is 43% for the diffusive helium permeability. Deviations in the pinhole manufacturing process, the gas

$^3$Note that the convective permeability refers to 100 mol% helium, but the given helium crossover to 10 mol% at the anode.
permeation analysis and the local GDE structure may account for the deviations. The high deviation of the diffusive helium permeability is attributed to the small diffusive helium crossover rates during analysis. Due to the higher accuracy, the convective helium permeability is mainly investigated in this work.

6.3.2 The Effect of the GDE as Additional Gas Barrier

In new and intact MEAs, the gas crossover between anode and cathode is limited by the membrane. However, if the membrane has defects, the crossover may also be affected locally by the GDE properties. To understand the influence of the GDE, the helium permeability was investigated for membranes with different pinhole sizes, both with and without GDEs. As depicted in Figure 6.10, the convective helium permeability of membrane defects (perforated membrane without GDEs) increases with the defect size, a trend which is best fit by a linear combination of a second and third order power law function shown in Equation 6.10 (Figure 6.10, red trend line), where $B_{He}$ is the convective helium permeability per defect in mol s$^{-1}$ Pa$^{-1}$, and $d$ is the pinhole diameter in micrometer.

$$B_{He} = 1.03 \times 10^{-6} \cdot d^3 + 1.39 \times 10^{-4} \cdot d^2$$

Figure 6.10 Convective helium permeability of pinholes with different sizes at 0% relative humidity and 80 °C for A) Nafion NR 211 and B) Nafion NR 211 assembled with two H400 gas diffusion electrodes. The given permeability refers to a single membrane defect. Reproduced from Kreitmeier et al. [70] with permission from the Electrochimica Acta.
The aspect ratio between the membrane thickness and the pinhole diameter defines the flow type. The aspect ratio is 0.25–25 for pinholes with a diameter of 1–100 µm in a 25 µm thick membrane, so the fluid dynamics are similar to those for an orifice (aspect ratio ≤ 0.5) or short channel (aspect ratio 2–50) [159]. The Reynolds number defines the flow regime: viscous or turbulent flow. Depending on the applied pressure gradient, the pinhole diameter and the GDE porosity, the Reynolds number ranges between 1 and 680 for the experimental values, so the flow regime is in the transition region between viscous and turbulent flow and may be best described by an unsteady laminar flow with both viscous and turbulent dissipation effects [159]. Equations 6.11 and 6.12 show fluid mechanical equations for describing the flow through a short channel in the viscous and turbulent flow regime, respectively. A linear combination of the two results in a second and third order power law function as determined experimentally (Equation 6.10).

\[
\dot{V} = \frac{d^3 \Delta p}{24\eta} \left[1 + \frac{16\delta}{3\pi d}\right]^{-1} \\
\dot{V} = \pi d^2 \sqrt{\frac{\Delta p}{8\rho \xi}}
\]

\[
(6.11) \quad (6.12)
\]

| \dot{V} | Volume flux |
| \Delta p | Pressure gradient |
| \eta | Dynamic viscosity |
| \delta | Membrane thickness |

When the perforated membrane is assembled into a MEA, the convective helium permeability is considerably lower than without the GDE (Figure 6.10), indicating that the gas crossover is limited locally by the GDE rather than by the membrane. In other words, the pinhole diameter has a minor effect on the gas crossover. The convective permeability correlates linearly with the cross-sectional area of the pinhole, as shown in Equation 6.13 (Figure 6.10, blue trend line). The average pore size of microporous and catalyst layers are typically below 200 nm [160, 161], allowing gas transport by combined Knudsen diffusion and viscous flow. The gas transport can be described by the binary friction model, using Knudsen diffusivity and Darcy’s law [161]. Given typical pore sizes, the fraction of Knudsen diffusion is low, so Darcy’s law may be applied as an approximation. This results in the linear correlation between the flux and the cross-sectional area of the pinhole [161]:

\[
B_{He} = 4.93 \times 10^{-6} \cdot \frac{\pi}{4} \cdot d^2
\]

\[(6.13)\]

The GDE, in particular the microporous and catalyst layers, is therefore a significant additional resistance for the gas crossover. It becomes even more important when the transport
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resistance of the membrane is reduced, i.e. with increasing pinhole size. Therefore, local inhomogeneities in the GDE, such as cracks, will affect the convective gas crossover through membrane defects. Decreasing the number of GDE surface defects may reduce the convective gas permeability of the microporous layer and somewhat attenuate the gas separation loss of the membrane, but this needs to be balanced carefully with the reactant transport to and from the catalyst layer.

6.3.3 Effects of Operation Conditions on the Gas Permeability

To understand the impact of fuel cell operating conditions on the gas crossover through membrane defects, the helium permeability was investigated as function of cell temperature and relative humidity. Temperature affects the properties of the ionomer and the gas, and consequently the gas permeability as well. Figure 6.11 illustrates the diffusive and convective helium permeability of a MEA with membrane defects as a function of the temperature at 0% relative humidity. The diffusive helium permeability increases with a mean rate of $13.1 \times 10^{-15}$ mol s$^{-1}$ Pa$^{-1}$ cm$^{-2}$ K$^{-1}$, which is in agreement with data from Catalano et al. [158]. Even though the gas solubility in Nafion decreases with temperature, the

![Figure 6.11](image.png)

Figure 6.11 Convective and diffusive helium permeability of a MEA with a membrane defect density of 9 pinholes per cm$^2$, each 10 µm in diameter, for different temperatures at 0% relative humidity. Note that the diffusive permeability refers to the membrane area and the partial pressure, while the convective one to a single defect and to the differential pressure. Reproduced from Kreitmeier et al. [70] with permission from the Electrochimica Acta.
6.3 Gas Crossover through Pinholes

Permeability actually increases due to the increasing diffusion coefficient. The convective helium permeability shows the opposite trend. It decreases from $4.4 \times 10^{-12} \text{ mol s}^{-1} \text{ Pa}^{-1}$ to $1.9 \times 10^{-12} \text{ mol s}^{-1} \text{ Pa}^{-1}$ per defect as the temperature increases from 40 °C to 100 °C. With increasing temperature, the gas viscosity increases and the density decreases. Both effects reduce the convective permeability, but cannot fully account for the observed decline. It is possible that thermal expansion of the polymer reduces the pinhole diameter and thus the gas crossover.

The relative humidity affects membrane swelling, which in turn will affect the size of pinholes. Therefore, the helium permeability was also investigated as a function of the relative humidity of the feed gases. Figure 6.12 illustrates the diffusive and convective helium permeability of a MEA with membrane defects as a function of the gas humidity at 80 °C. The diffusive permeability increases by 30% when increasing the relative humidity from 30% to 90%, whereas the convective one decreases by 50%. Gas diffusion increases with humidity, since the gas diffusion coefficient of the hydrophilic phase increases with increasing ionic cluster size, which is determined by the membrane water content [78, 79]. Since water acts as a plasticizer, the hydrophobic phase may undergo dimensional changes that also facilitate gas permeation [79]. On the other hand, the convective gas permeability

![Figure 6.12 Convective and diffusive helium permeability of a MEA with a membrane defect density of 9 pinholes per cm$^2$, each 10 µm in diameter, at 80 °C for different membrane humidifications (set by the relative gas humidity). Note that the diffusive permeability refers to the membrane area and the partial pressure, while the convective one to a single defect and to the differential pressure. Reproduced from Kreitmeier et al. [70] with permission from the Electrochimica Acta.](image)

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Local Polymer Electrolyte Membrane Degradation decreases with increasing humidification, since membrane swelling reduces the pinhole size, as illustrated by cross-sections of a perforated membrane shown in Figure 6.13. Membrane swelling was visualized with in situ XTM at room temperature and ambient pressure using a fuel cell setup as described in [162]. When the dry membrane is fully humidified, the mean pinhole diameter shrinks from $9.5 \pm 0.7 \mu m$ (Figure 6.13A) to $8.2 \pm 0.7 \mu m$ (Figure 6.13B). The contrast of the grayscale image in Figure 6.13B is probably lowered by the presence of liquid water in the pinhole.

The convective helium permeability of a defect is completely eliminated at 100% relative humidity, as shown in Figure 6.12, indicating that liquid water fills and seals the pinhole. In fact, when using oversaturated gases, the helium crossover through a $10 \mu m$ pinhole is zero up to a significant pressure gradient of 20 kPa between anode and cathode, as illustrated in Figure 6.14A. At a pressure gradient of 20 kPa the crossover increases immediately. Due to the capillary force of the pinhole, liquid water infiltrates into the hole and seals it as long as the pressure gradient between anode and cathode is below the capillary pressure of the pinhole. Otherwise, liquid water is blown out of the pinhole or the intrusion of liquid water is prevented in the first place. The minimum pressure gradient to do so is labeled the breakthrough pressure. Figure 6.14B shows that the breakthrough pressure decreases with increasing pinhole diameter. In fact, the experimentally determined breakthrough pressures are in excellent agreement with the capillary pressures.

![Figure 6.13](image.png) Figure 6.13 XTM cross-sections of a dry (A) and fully humidified (B) Nafion NR 211 membrane with a $10 \mu m$ artificial pinhole. Membrane swelling decreases the pinhole diameter. Reproduced from Kreitmeier et al. [70] with permission from the Electrochimica Acta.
6.3 Gas Crossover through Pinholes

Figure 6.14 Breakthrough pressure of liquid water for perforated membranes at 80 °C. A) Determination of the breakthrough pressure for a 10 µm pinhole. B) Correlation between the breakthrough pressure and pinhole size. For parameters in the blue area, pinholes are filled with liquid water, otherwise they are open. Reproduced from Kreitmeier et al. [70] with permission from the Electrochimica Acta.

(Figure 6.14B, red trend line), calculated according to Equation 6.14:

\[ P_c = \frac{2\sigma \cos \theta}{r} \]  \hspace{1cm} (6.14)

where \( P_c \) is the capillary pressure, \( \theta \) the contact angle of water (0° for the well wettable polymer), \( r \) the pinhole radius and \( \sigma \) the surface tension of water (0.06268 N m\(^{-1}\) at 80 °C [20]). For pressure gradients and pinhole sizes in the blue region (Figure 6.14B), pinholes are sealed by liquid water; otherwise the pinholes are open.

To verify the sealing ability of liquid water, a pristine MEA without any artificial defects has been degraded in a 500 h accelerated stress test with a load cycling protocol (see Chapter 6.2 on page 68, MEA “C”). The final diffusive and convective helium crossover were \( 2.1 \times 10^{-9} \) mol s\(^{-1}\) cm\(^{-2}\) and \( 5.7 \times 10^{-9} \) mol s\(^{-1}\) cm\(^{-2}\) at 90% relative inlet humidity, 150 kPa absolute pressure, 10 kPa differential pressure and 0 A cm\(^{-2}\). Applying a current density of 0.25 A cm\(^{-2}\) produced enough liquid water to seal most pinholes, and the resulting convective helium crossover dropped to \( 0.11 \times 10^{-9} \) mol s\(^{-1}\) cm\(^{-2}\). In conclusion, the gas crossover of a degraded membrane may be much smaller in operational cells than has been recorded by electrochemical in situ standard measurements as described by Kocha et al. [42], as liquid water can seal pinholes and eliminate the gas crossover through them. For this reason, operating conditions where no or little liquid water is produced electrochemically, such as at OCV or idling, may accelerate chemical polymer decomposition due to the elevated crossover through pinholes. Furthermore, the occurrence of liquid...
water may be a dominant reason for inhomogeneous membrane degradation over the active cell area. Typically, a fuel cell system is operated with nonsaturated inlet gases, so there is no liquid water to seal pinholes in the inlets. However, sufficient liquid water may be generated electrochemically further down the channel so as to seal membrane defects. Therefore, the inlets of a fuel cell may be more prone to membrane failures, as observed by Stumper et al. [153]. Even though a higher humidity reduces or eliminates the gas crossover through pinholes and may slow down chemical polymer decomposition locally, it still promotes mechanical pinhole formation due to the lowered elastic modulus of Nafion with higher water content [23,156]. All in all, humidity has a complex effect on membrane durability that is not yet fully understood.

6.3.4 Cell Performance of MEAs with Defects

Given that the GDE decreases the gas crossover through membrane defects, and also that not all permeated hydrogen may react electrochemically in the catalyst layer, the net effect of the defect on the cell performance was unclear. The cell performance was therefore analyzed for a cell having a significant membrane defect density of 9 pinholes per cm$^2$ active area, with each being 10 $\mu$m in diameter. The convective helium permeability is $5.6 \pm 0.2 \times 10^{-12}$ mol s$^{-1}$ Pa$^{-1}$ per defect, which corresponds to a hydrogen crossover of about 39 mA cm$^{-2}$ at a pressure difference of 10 kPa between anode and cathode. Figure 6.15 shows the fuel cell performances at 150 kPa (H$_2$/air), 100% relative humidity and a cell temperature of 80 $^\circ$C as a function of the pressure gradient (0–100 kPa) and consequently of the gas crossover. When the anode pressure is higher than the cathode pressure, hydrogen permeates by convection from anode to cathode. Up to a pressure gradient of 10 kPa, the hydrogen crossover does not affect the performance (see Figure 6.15A), so small pinholes in the membrane and moderate pressure gradients do not necessarily cause a cell performance drop, which was also observed by Lü et al. [163]. When further increasing the pressure gradient, the cell performance drops in the kinetic and mass transport regimes. When the cathode pressure is higher than the anode pressure (see Figure 6.15B), oxygen permeates by convection from cathode to anode. Interestingly, the cell performance increases with the pressure gradient, despite the increasing permeation. The anode electrode potential probably slightly increases due to the oxygen permeation, so the fuel cell voltage should drop. However, this seems to be offset by the elevated oxygen partial pressure at the cathode, which increases the cathode electrode potential and yields a net increase in the cell voltage.
6.3 Gas Crossover through Pinholes

**Figure 6.15** Polarization curves of a MEA with a membrane defect density of 9 pinholes per cm$^2$ active area, with each pinhole being 10 µm in diameter. Operation with H$_2$/air at 150 kPa, 100% relative humidity and 80 °C cell temperature for different pressure gradients between anode and cathode: A) at higher anode pressure (150–250 kPa); B) at higher cathode pressure (150–250 kPa). Reproduced from Kreitmeier et al. [70] with permission from the Electrochimica Acta.

When the fuel cell is operated with pure oxygen as the cathode gas, no significant effect on the performance is observed for pressure gradients up to 100 kPa, as shown in Figure 6.16. Summing up, the effect of the elevated gas crossover through membrane defects on the cell performance is small and may be neglected for small pinholes, but the gas crossover does accelerate membrane degradation (see Chapter 6.1.2) and extends the pinhole size. This effect is discussed in the following chapter.
6 Local Polymer Electrolyte Membrane Degradation

6.4 Degradation at Membrane Defects

6.4.1 Chemical & Mechanical Degradation

Membrane defects are the main reason for the loss of gas separation, as described in Chapter 6.2. Since the gas crossover significantly accelerates chemical polymer decomposition (as described in Section 6.1.2 on page 53), enhanced degradation is expected at membrane defects. Therefore, degradation processes at membrane defects were systematically investigated in order to generate a database that allows for the elaboration of an overall degradation mechanism.

Chemical Degradation  FTIR spectro-microscopy was applied to study chemical polymer decomposition in the vicinity of membrane defects. Defects were artificially implemented using micro needles in order to avoid any degradation by the implementation process, as described in Chapter 5. The induced pinholes were then degraded for 25 h using AST #3, as defined in Table 3.4 on page 20. Note that this stress test accelerates both chemical and mechanical degradation. Figure 6.17A shows IR spectra of degraded Nafion 111 (black data set) and degraded Nafion 211 (blue data set) next to defects (10 x 10 µm² scan area). Both spectra show the characteristic peaks of the ether group (COC, 983 cm⁻¹),

\footnote{Results shown in this chapter have been submitted to the Journal of the Electrochemical Society and are published in Kreitmeier et al., ECS Trans. 50 (2012) 927–933.}

Figure 6.16 Polarization curves of a MEA with a membrane defect density of 9 pinholes per cm² active area each 10 µm in size. Operation with H₂/O₂ at 150 kPa, 100% relative humidity and 80 °C cell temperature for different pressure gradients between anode and cathode: A) at higher anode pressure (150–250 kPa); B) at higher cathode pressure (150–250 kPa).
sulfonic acid group (SO$_3$, 1060 cm$^{-1}$), fluorocarbon backbone (CF$_2$, 1080–1380 cm$^{-1}$) and absorbed water (H$_2$O, 1628 cm$^{-1}$ and 3350–3700 cm$^{-1}$) [71]. Additional peaks are observed at 1689 cm$^{-1}$ and 1772 cm$^{-1}$, which can be assigned to the carboxyl group (COOK, 1689 cm$^{-1}$; CO, 1772 cm$^{-1}$) [51, 92]. As described in Section 6.1.2 on page 51, the carboxyl group is a key in the unzipping mechanism, and it is therefore used here as indicator for chemical polymer decomposition. Unlike Nafion 111, the COOK absorbance of Nafion 211 is barely recognizable for the given degradation protocol. Nafion 211 is end-group stabilized improving its chemical stability as compared to Nafion 111. Therefore, Nafion 111 was used to further investigate chemical polymer decomposition.

Figure 6.17B illustrates the integrated COOH absorbance for Nafion 111 (1660–1725 cm$^{-1}$) as function of the distance from the edge of the defect. The polymer is decomposed up to a distance of about 150 µm, with the most degradation occurring at 75 µm. No chemical decomposition was detected far away from the pinhole. The COOH concentration can be estimated from the integrated absorbance either by using a calibration method that was previously developed for mixed functionality carboxylate/sulfonate perfluorinated ionomer membranes [164] or by determining the attenuation coefficient of the carboxyl group in perfluorocarboxylate membranes. In the last method, the COOH attenuation coefficient in both ionomers PFSA and perfluorocarboxylate is assumed to be similar [165]. The two estimates from the peak COOK absorbance yield a COOH concentration of about 3.0±0.1% of the equivalent of the sulfonic acid groups in Nafion 111.

![Figure 6.17 A) FTIR spectra of Nafion 211 (blue data set) and Nafion 111 (black data set) next to an artificially implemented pinhole degraded under H$_2$/O$_2$ in OCV mode at 80 °C, 150 kPa and cycling the humidity between 0% and 70% RH. B) Integrated absorbance of the potassium exchanged carboxyl group of Nafion 111 with increasing distance to the pinhole. 0 µm refers to the pinhole edge.](image)
Thus, on average, one carboxyl group is formed in a polymer chain fragment associated with 30 sulfonic acid groups and 30 side chains, respectively. The fact that the COOK band is only observed in the vicinity of the pinhole leads to the question of how chemical membrane degradation is influenced by the hydrogen crossover rate. Therefore, the hydrogen crossover rate was varied by changing the pressure gradient between anode and cathode. Figure 6.18 shows 2D maps of the distribution of the integrated COOK absorbance for membrane defects degraded at AST #3 at a pressure gradient of 0.5 kPa (see Figure 6.18A) and 10 kPa (see Figure 6.18B), respectively. In both cases, the pressure gradient that forces convective hydrogen crossover from the anode to the cathode is assumed to accelerate chemical polymer decomposition at the cathode. The degraded pinholes have dimensions of 100–200 µm and are indicated in Figure 6.18 by a black line. The integrated COOK absorbance is zero in the pinhole, shows a maximum intensity in the vicinity of the pinhole and decays with increasing distance. In both cases, polymer decomposition is highest at the oxygen downstream side. The maximum integrated COOK absorbance is similar for both cases, but the total area of decomposed polymer is larger for the higher pressure gradient, and the maximum intensity is not at the pinhole edge (Figure 6.18B).

**Figure 6.18** 2D-FTIR maps of the integrated COOK absorbance for degraded Nafion 111 membranes at defects. Pinholes were previously implemented artificially by micro-needles and degraded at H₂/O₂, 80 °C, 150 kPa and cycling the humidity from 0–70% RH. A hydrogen crossover was forced through the membrane by a pressure gradient between anode and cathode of A) 0.5 kPa and B) 10 kPa.
In the presence of platinum catalyst, hydrogen and oxygen react to form oxygen radical species, chemically decomposing the polymer. However, as shown in the following section, the catalyst is lost at the cathode near the pinhole, so hydrogen can accumulate in the vicinity of the membrane defect. A reaction zone is formed, the dimensions of which depend on the hydrogen crossover rate and the catalyst availability. Because of this fact, the highest radical formation rate is not necessarily next to the pinhole edge, so the polymer does not decompose in an expanding ring. Instead, larger areas can decompose simultaneously. At the higher pressure gradient (Figure 6.18B), the elevated hydrogen crossover displaces the oxygen at the pinhole, so most radicals are formed about 50 µm away from the pinhole edge. Since significant amounts of the catalyst and the microporous layers are lost at the defect, even a small pressure gradient of the oxygen flux in the flow direction will transport the permeated hydrogen downwards the channel. Thus, the polymer is mainly decomposed in oxygen flow direction.

In conclusion, chemical polymer decomposition is strongly accelerated in the vicinity of pinholes (1–2 pinhole diameters), but does not necessarily achieve the highest rate at the pinhole edge. This is a fundamental finding that is not constricted to Nafion 111. The results may be extrapolated to the more stable Nafion NR 211 membrane, even if the intensity may be significantly lower.

**Figure 6.19** Online helium crossover of MEAs with pinholes in the membrane aged A) under H₂/O₂ in OCV mode accelerating chemical polymer decomposition (see Table 3.4, AST ♯1) and B) under N₂/N₂ and cycling the humidity between 0% and 70% RH with a cycling frequency of 10/230 min (indicated by vertical red lines) accelerating mechanical membrane degradation (see Table 3.4, AST ♯2).
Polymer decomposition close to the pinhole is expected to lead to pinhole growth. However, it is not clear how the pinhole is growing. To test this, the three ASTs shown in Table 3.4 on page 20 (chemical, mechanical and combined) were carried out to age membrane defects while the gas crossover was monitored online as an indicator for the pinhole size (described in Section 4.1.3 on page 28). The ASTs were performed with Nafion NR 211 membranes. Figure 6.19A shows the helium crossover for AST 1, which focuses chemical degradation. The crossover does not increase during the 100 h protocol, indicating that no significant pinhole growth occurs when accelerating only chemical degradation. This was also confirmed by post mortem XTM analysis, which showed that the pinhole diameter had not increased after the AST, as depicted in Figure 6.20.

Figure 6.20 A MEA with a 10 µm artificial pinhole was degraded at H$_2$/O$_2$ in OCV mode at 80 °C, 150 kPa and 70% RH (see Table 3.4, AST 1). Post mortem XTM analysis shows that the pinhole cross-section has not changed after 100 h.

Mechanical Degradation Pinholes are frequently formed by mechanical stress. As previously described in Section 6.1.3 on page 56, fluctuations in the relative humidity induce membrane swelling and shrinkage. In-plane and compressive stresses arise in the polymer and induce crazing sites, which can propagate through the membrane and end up in cracks, tears or pinholes [23, 130, 131]. The effect of mechanical stress on pinhole growth was tested in AST 2 using N$_2$/N$_2$ instead of H$_2$/O$_2$ to exclude any chemical polymer decomposition (see Table 3.4 on page 20). Rather, humidity cycles induced mechanical stress in this AST. Figure 6.19B shows the evolution of the helium crossover. Every 240 min, the cell was dried for 10 min, indicated by the red vertical lines in Figure 6.19B. The initial helium crossover is slightly different as compared to Figure 6.19A, probably due
to the spatially inhomogeneous thickness of the microporous layer, which limits the gas crossover at membrane defects (see Section 6.3.2 on page 72). Also this AST showed that the helium crossover did not increase within the 100 h test when accelerating only mechanical membrane degradation. This was again confirmed by post mortem XTM analysis (data similar to Figure 6.20). In conclusion, neither chemical nor mechanical membrane degradation alone leads to significant pinhole growth during the test duration.

### 6.4.2 Thermal Degradation

Nafion decomposes thermally above 275 °C [89, 144, 145]. Such a temperature is unlikely in a fuel cell operated below 100 °C. However, at membrane defects the hydrogen and oxygen crossover are increased, so permeated hydrogen may combust catalytically at catalyst particles. This can form local hotspots where the temperature is sufficient to decompose Nafion thermally. Evidences for local hotspots can be found in post mortem analysis of failed cells that were operated long-term. Figure 6.21 shows a MEA with a large membrane defect with a size of about 1–2 mm. Hydrogen and carbon were obviously combusted, so the entire GDL material was decomposed in the vicinity of the defect. Since heat is dissipated effectively by the carbon material and consumed by the evaporation of liquid water, the build-up of elevated temperature at minor defects is still under debate [58, 82, 146]. Therefore, the temperature was measured locally at membrane defects during fuel cell operation using thermochromic pigments, as described in Section 4.7 on page 39. The method only gives qualitative results, since the spatial resolution is limited.

![Figure 6.21](image)

*Figure 6.21* The photograph shows a MEA degraded in a technical sized stack during long-term operation. A membrane defect was formed and the GDE material was destroyed in the vicinity of the defect, indicating the presence of local hotspots.
by the particle size of the pigments and by the particle-to-particle distance, which both scatter significantly. Because high humidity interferes with the color transition of the pigments, experiments were carried out at 0% RH. The drawing in Figure 6.22 illustrates the local temperature distribution obtained around a 300 µm pinhole during OCV operation (H₂/O₂) at 80 °C, 150 kPa and a pressure gradient of 30 kPa between anode and cathode. A maximum temperature of about 140 °C is detected close to the pinhole and decaying with distance. Peak temperatures range between 100 °C and 140 °C for various pinhole sizes (0.1–1 mm) and pressure gradients (0.5–30 kPa) (data not shown). Even though the temperature is clearly elevated at membrane defects, it still seems to be too low to allow for thermal polymer decomposition. However, the temperature is above the glass transition temperature of Nafion, which is approximately 110 °C [142]. As a result, it is possible for the polymer chains to restructure and change the nanostructure, leading to increased crystallinity [142] or the dissociation of ionic clusters [143]. The applied temperature analysis method may however underestimate the peak temperature at catalyst particles, since the spatial resolution is too low. Furthermore, catalytic combustion is spatially limited at pinhole edges with agglomerated platinum particles, which may explain why the correlation between pinhole size and peak temperature is not very pronounced.

Because the temperature measurements are not conclusive, degraded membrane defects were analyzed post mortem with XTM. Pinholes, 10 µm in diameter, were implemented in

![Figure 6.22 Illustration of the local temperature profile around a pinhole. A MEA with a 300 µm pinhole was operated in OCV mode at 80 °C, 150 kPa and 0% RH. The temperature was analyzed in the vicinity of the pinhole using thermochromic pigments.](image)
Nafion NR 211 (see Figure 6.23B) and the MEA was degraded with AST $\#3$ for 50 h. As shown in the MEA cross-sections in Figure 6.23, the pinhole grew to a diameter of about 50 $\mu$m, and the cathode catalyst layer and parts of the microporous layer (MPL) next to the pinhole were lost. Catalyst particles agglomerated and were deposited around the pinhole (see Figure 6.23C, bright spots around the pinhole). Catalyst sintering, massive carbon losses and the round shape of the pinhole edges (see also Figure 6.28B), that is presumably caused by polymer melting, are strong indications for a high temperature. In conclusion, membrane defects only a few tens of microns in size allow for permeation of hydrogen that likely combusts catalytically at cathode catalyst particles and forms local hotspots. The elevated temperature induces thermal polymer decomposition and favors catalyst degradation.

![Figure 6.23 MEA cross-sections analyzed post mortem by XTM. A) A pristine MEA. B) MEA with a perforated membrane. C) Degraded MEA with indications for local hotspots: catalyst sintering and massive carbon loss in the MPL and catalyst layer. Reproduced from Kreitmeier et al. [68] with permission from the Electrochemical Society.](image-url)
6.4.3 Synergetic Effect of Chemical, Mechanical and Thermal Degradation

In order to investigate the combined effect of chemical and mechanical stress on pinhole growth, MEAs were aged with AST 3 (see Table 3.4 on page 20). The test was repeated four times to assess reproducibility. Figure 6.24A shows the helium crossover of all tests. A clear effect of the combined chemical and mechanical stress on the crossover is observed, in contrast with observations made when triggering a single parameter only (Figures 6.19A and 6.19B). In the experiment with the combined effect of chemical and mechanical stress, the helium crossover increases exponentially over time, with stepwise jumps in correlation with the humidity cycle. The onset of the crossover jumps and their amplitude vary from experiment to experiment, but the overall characteristics and the average increase of the gas crossover are similar for all experiments. The increasing gas permeation is assigned to pinhole growth. On average, the pinhole diameter expanded from 10 $\mu$m to 31 $\mu$m after 50 h according to post mortem analysis by XTM. Membrane thinning was not observed. The growth rate of pinholes is defined as the operation time required to double the gas crossover with respect to the initial condition (see Figure 6.24B), which is $28.7 \pm 3.9$ h on average ($32$ h for the measurement shown in Figure 6.24B). Hence, differences in the time for doubling the permeation larger than about 8 hours ($2\sigma$) are significant. Parameter variation in single tests can be compared to this base case.

![Figure 6.24](image)

**Figure 6.24** Online helium crossover of MEAs with pinholes in the membrane that was aged during fuel cell operation at $\text{H}_2/\text{O}_2$ in OCV mode, 80 °C, 150 kPa and cycling the humidity between 0% and 70% RH (see Table 3.4, AST 3). A) Reproducibility of helium crossover evolution. B) End of life is determined by the doubling of the helium crossover. Numbers in the figure refer to different degradation mechanisms.
Colored numbers in Figure 6.24B (shown for clarity for a single measurement only) refer to different phases in the degradation mechanism as discussed in section “Combined Degradation Mechanism”: in phase 1 a constant crossover, for phase 2 stepwise jumps at humidity cycles and in phase 3 a significant increase between humidity cycles.

The chemical degradation rate is coupled to the formation rate of oxygen radical species. Although the kinetics of radical formation is not precisely known, it probably depends on the local hydrogen and oxygen concentrations. The radical formation rate should therefore decrease upon lowering the oxygen concentration in the cathode stream as compared to the base case. On the other hand, it should increase with increasing hydrogen crossover when the pressure gradient is increased. Results for testing with AST ≠3 are shown in Figure 6.25. Figure 6.25A compares the evolution of the helium crossover of the base case (H₂/O₂, gray data) with H₂/Air (black data) at the same pressure gradient of 0.5 kPa between anode and cathode. A reduction of the oxygen concentration from 100 vol.% to 21 vol.% is not followed by an increase of the helium crossover within 200 h. This indicates that the pinhole size remained unaffected, as confirmed by XTM analysis. Figure 6.25B compares the evolution of the helium crossover of the base case (0.5 kPa pressure gradient, gray data) to an increased overpressure at the anode of 10 kPa (black data). A higher pressure gradient results in a higher initial gas crossover. At 10 kPa the initial helium crossover increased from $1.0 \times 10^{-8}$ mol s⁻¹ cm⁻² to about $7.5 \times 10^{-8}$ mol s⁻¹ cm⁻². With the higher hydrogen crossover, the degradation rate increases considerably, and the helium crossover doubles after 5 h, as compared to 28 h for the base case. The increased

Figure 6.25 Online helium crossover of MEAs with pinholes in the membrane that was aged during fuel cell operation at H₂/O₂ in OCV mode, 80 °C, 150 kPa and humidity cycles (see Table 3.4, AST ≠3) with A) different oxygen concentration and B) different absolute pressure gradients between anode and cathode.
crossover accelerates the formation of radicals which in turn favors chemical decomposition of the polymer at defect sites. With the above parameter variation (oxygen partial pressure and pressure difference) a change in the pinhole growth rate by at least two orders of magnitude is observed. Thus, the chemical decomposition rate of the polymer is in strong correlation with the pinhole growth rate (in the presence of mechanical stress).

The oxygen flow characteristics at the cathode affect the distribution of permeated hydrogen and therefore the size of the area where chemical polymer decomposition takes place (see Figure 6.18). Its effect on the degradation rate was tested by changing the oxygen flow velocity in the cathode channel. Figure 6.26A compares the evolution of the helium crossover at AST♯3 with two different oxygen flow speeds: 0.28 m s\(^{-1}\) (Figure 6.26A, gray data) versus 1.39 m s\(^{-1}\) (Figure 6.26A, black data). At 1.39 m s\(^{-1}\), the permeation in the cell doubled after 28 h (see also Figure 6.24A), while the helium crossover did not double until 40 h at an oxygen channel velocity of 0.28 m s\(^{-1}\). At low oxygen flux, permeated hydrogen is not distributed very far away from the defect, and chemical polymer decomposition may be spatially limited to areas very close to the pinhole. The overall degradation rate is smaller because the area that decomposes simultaneously is reduced, but the local degradation rate remained unaffected. The absence of gas crossover jumps supports this hypothesis. It indicates that the membrane does not fracture over wide areas of degraded material. This will be further discussed below.

All experiments that have been described so far have been made with hydrogen permeating to the cathode. To test the significance of which side of the membrane is degraded

![Figure 6.26](image-url)

**Figure 6.26** Online helium crossover of MEAs with pinholes in the membrane that was aged during fuel cell operation at H\(_2\)/O\(_2\) in OCV mode, 80 °C, 150 kPa and humidity cycles (see Table 3.4, AST♯3) with A) different oxygen fluxes at the cathode and with B) different pressure directions between anode and cathode.
6.4 Degradation at Membrane Defects

(anode vs. cathode), also the difference between oxygen and hydrogen crossover was studied. Figure 6.26B shows the evolution of the helium crossover for pressure gradients of opposite directions. For the base case when hydrogen permeates to the cathode, the helium crossover doubled after 28 h (Figure 6.26B gray data; 150.5/150 kPa anode/cathode pressure). However, in the case of oxygen permeating to the anode (Figure 6.26B black data; 150/150.5 kPa anode/cathode pressure), the helium crossover only increased by 13% within 170 h. The significant increase in the helium crossover after 232 h is attributed to an exceptional expansion of a single membrane defect, which was detected by XTM analysis and is shown in Figure 6.27. XTM also confirmed that pinholes grow slower when oxygen permeates across the defect than it does for hydrogen. Figure 6.28B shows the cross-section of a MEA degraded with hydrogen crossover, which shows the typical indications for local hotspots: catalyst losses, catalyst agglomeration and a rounded polymer shape. These indicators are not present when oxygen permeates through the pinhole, as shown in Figure 6.28A. Here, pinholes grew only to an average size of 13.2 ± 0.4 µm after 232 h (not considering the exceptional large pinhole shown in Figure 6.27). Etching processes seemed to degrade the polymer around the defect at the anode side. In conclusion, the gas crossover across membrane defects determines which side of the polymer is degraded, which in turn affects the degradation rate. In the case of hydrogen crossover, the catalyst layer and membrane degrade at the cathode, where thermal degradation processes seem to dominate. In contrast, oxygen crossover causes the membrane to degrade at the anode side, where chemical degradation processes seem to be more important.

![Figure 6.27](image)

**Figure 6.27** A MEA with pinholes in the membrane was degraded by operating the fuel cell 232 h at H₂/O₂ in OCV mode, 80 °C, 150 kPa and humidity cycles (see Table 3.4, AST♯3) with the cathode pressure 0.5 kPa higher than the anode pressure. Post mortem XTM analysis shows that one single pinhole became exceptionally large, while other pinholes have grown moderately in size, as depicted in Figure 6.28A.
Figure 6.28 MEAs with pinholes in the membrane were degraded by operating the fuel cell at H$_2$/O$_2$ in OCV mode, 80 °C, 150 kPa and humidity cycles (see Table 3.4, AST $\#3$). A) XTM cross-section of a MEA degraded 232 h with the cathode pressure 0.5 kPa higher than the anode pressure and B) degraded only 50 h with the cathode pressure 0.5 kPa lower than the anode pressure.
6.4 Degradation at Membrane Defects

6.4.4 Combined Degradation Mechanism

From the previous results, an overall picture describing the degradation at membrane defect sites may be postulated and is presented schematically in Figure 6.29. Small membrane defects are formed *mechanically* (phase 0), as described previously in Section 6.2 on page 61. The gas crossover increases locally at these defects, initiating chemical polymer decomposition, as supported by the formation of carboxyl groups. Polymer within 1–2 pinhole diameters becomes fragile and its tensile strength decreases. Pinholes do not grow significantly in this phase (phase 1), and the gas crossover barely increases. When mechanical stress, induced by humidity cycles, exceeds the local tensile strength of the membrane, the polymer fractures. This increases the defect size, and thus the gas crossover. Fracturing is a fast process, as indicated by gas crossover jumps during online measurements (phase 2). The increasing gas crossover in turn accelerates chemical polymer decompo-

![Image of degradation scheme at membrane defects]

**Figure 6.29** Degradation scheme at membrane defects. Reproduced from Kreitmeier et al. [68] with permission from the Electrochemical Society.
sition. This cycle of chemical and mechanical degradation processes expands the defect stepwise and causes a concurrent increase of the gas crossover. When the pinhole has grown to about 15–30 µm, permeated hydrogen combusts catalytically at the cathode, which increases the temperature locally. While a peak temperature of only 140 °C was measured, the local temperature at platinum particles may be much higher, as indicated by catalyst sintering, carbon losses of the MPL and polymer melting (see Figure 6.23C and Figure 6.28B). This may allow for thermal polymer decomposition, which will further expand the defect (phase 3) and thus increase the gas crossover. Chemical, mechanical and thermal degradation thus have a synergetic effect that leads to the overall, exponential increase of the gas crossover.

Several parameters such as pressure gradient between anode and cathode, oxygen concentration or channel velocity affect the defect growth rate. The most striking differences in the general picture are linked to the direction of the gas crossover. Degradation is much faster when hydrogen permeates to the cathode than when oxygen permeates to the anode. Upon hydrogen crossover, the polymer decomposes, the pinhole grows, and thermal degradation processes set in, as can be seen from Figure 6.28B. When oxygen permeates to the anode (pressure gradient inverted), chemical polymer decomposition is the dominant pathway because the electrochemical formation of hydrogen peroxide is facilitated at the low anode potential. Hydrogen peroxide decomposes to oxygen radical species in the presence of cationic contaminants. Typical thermal effects, such as catalyst agglomeration or smooth membrane surfaces, were not observed.

In conclusion, chemical, mechanical and thermal degradation processes have a synergetic effect that leads to the overall degradation mechanism characterized by an exponential increase of the gas crossover. If one of these processes is eliminated or mitigated, the degradation rate decreases significantly. The relevance of the synergetic effect has been verified in long-term durability tests with cells of technical size (see Chapter 6.2).

### 6.4.5 Factors Influencing the Degradation Mechanism

In most of the experiments described above, individual pinholes grow with different rates in the same membrane during the same experiment, with some pinholes not growing at all. Hence, local factors must be present to influence the degradation at these defect sites. Table 6.3 lists the pinhole diameter as analyzed post mortem by XTM after degrading a perforated membrane with 8 pinholes per cm² active area for 50 h with AST♯3 (see Table 3.4). In Table 6.3 the pinholes are listed in the order of their mean diameter, which ranges between 2.5 µm and 142 µm with an average of 31 µm. No correlation between pinhole size and the position within the cell was observed.
6.4 Degradation at Membrane Defects

Table 6.3 Nafion NR 211 membrane with an initial defect density of 8 pinholes per cm² each 10 µm in size was degraded 50 h at H₂/O₂ in OCV mode, 80 °C, 150 kPa and RH cycling between 0% and 70% (see Table 3.4, AST 3). The pinhole diameters are listed as analyzed post mortem by XTM.

<table>
<thead>
<tr>
<th>Pinhole number</th>
<th>Mean diameter / µm</th>
<th>Min. diameter / µm</th>
<th>Max. diameter / µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>0.0</td>
<td>6.4</td>
</tr>
<tr>
<td>2</td>
<td>9.6</td>
<td>8.9</td>
<td>11.4</td>
</tr>
<tr>
<td>3</td>
<td>13.3</td>
<td>12.0</td>
<td>14.1</td>
</tr>
<tr>
<td>4</td>
<td>16.1</td>
<td>14.8</td>
<td>16.8</td>
</tr>
<tr>
<td>5</td>
<td>16.6</td>
<td>14.1</td>
<td>20.7</td>
</tr>
<tr>
<td>6</td>
<td>16.8</td>
<td>12.8</td>
<td>20.6</td>
</tr>
<tr>
<td>7</td>
<td>34.8</td>
<td>24.9</td>
<td>79.9</td>
</tr>
<tr>
<td>8</td>
<td>141.8</td>
<td>114.2</td>
<td>215.1</td>
</tr>
</tbody>
</table>

Membrane defects expand primarily because of fracturing induced by mechanical stress. This explains the distribution in diameter, but cannot explain why some pinholes did not grow (pinhole 2) or even shrink (pinhole 1). Figure 6.30 shows MEA cross-sections of selected pinholes (1, 2, 8) illustrating the different effects. Some pinholes grow fast because of the combined mechanisms including thermal polymer decomposition, as shown in Figure 6.30A for pinhole 8 (see Table 6.3). This is the general case, six out of the eight pinholes were growing. However, it also happens that pinholes do not grow at all. For pinhole 2, a dense carbon agglomerate seems to have sealed the defect and precluded the gas crossover (see Figure 6.30B). Liquid water can seal pinholes in a similar way, as described in Section 6.3.3 on page 74. This eliminates the gas crossover and thus impedes the degradation cycle. The locally elevated gas crossover at membrane defects is a crucial factor of the degradation mechanism. Further factors that influence the gas crossover through pinholes have been described in Chapter 6.3. As shown for pinhole 1, defects can even shrink. This is presumably due to a locally elevated compressive pressure, which causes the polymer to creep into the pinhole (see Figure 6.30C). In this case, the gas crossover through the membrane defect is eliminated, and the self-accelerating degradation loop cannot be initiated. However, creeping of polymer into the defect is not a general rule. Even in the presence of additional mechanical stress (see Figure 6.19B), the gas crossover does not decrease due to polymer creeping into the pinhole. Polymer creep was only observed in regions which seemed to be exposed to elevated compressive stress.

In conclusion, pinholes in the same membrane (in close vicinity, within the same square centimeter) grow with different rates under identical conditions. This is mainly attributed
to the nonuniform surface structure of the catalyst layer. The surface structure determines the effective local gas permeation rate because the GDE material can become the main local gas barrier. Cracks or tears in the catalyst layer facilitate the gas crossover through membrane defects, while carbon agglomerates, a locally dense catalyst layer or locally elevated compressive stress can reduce or eliminate the gas crossover.

Figure 6.30 A MEA with pinholes in the membrane was degraded 50 h at H₂/O₂ in OCV mode, 80 °C, 150 kPa and RH cycling between 0% and 70% (see Table 3.4, AST ♫ 3). Cross-sections of the degraded MEA at different positions within the same sample show A) pinhole growth, B) pinhole blockage by a carbon agglomerate and C) membrane creep.

6.4.6 Effects of Degradation on the Gas Crossover

Inert gases permeate through the membrane and accumulate in the gas channel. In contrast, reactive gases like hydrogen will react at the catalyst layer after permeating. In new and intact MEAs, the permeated hydrogen is oxidized quantitatively at the catalyst layer because the kinetics of hydrogen oxidation are fast, as described in Section 2.2.1 on page 8. This allows for the electrochemical analysis of the hydrogen crossover, as described by Kocha et al. [42]. However, if the gas crossover is locally elevated at membrane defects, and the catalyst layer is degraded at the defect (see Figure 6.23C), then the catalytic activity may not be sufficient to oxidize hydrogen quantitatively. The oxidation rate of permeated hydrogen at the cathode catalyst layer was therefore analyzed by comparing the hydrogen crossover in the presence of oxygen or nitrogen gas in the cathode. In contrast to electrochemical methods, the mass spectrometry based method enables the measurement of the hydrogen crossover at the cathode in the presence of oxygen. Both the helium and hydrogen crossover rates were measured for a perforated MEA prior to and after the degradation protocol. A MEA with a membrane defect density of 7 pinholes per cm² active area, each 10 µm in size, was operated 50 h at AST ♫ 3 (see Table 3.4 on page 20), and the helium and hydrogen crossover was analyzed at 150 kPa absolute pressure and a pressure gradient of 10 kPa between anode and cathode.
Table 6.4 summarizes the helium and hydrogen crossover into oxygen or nitrogen prior to and after the AST. The anode gas was composed of 90 vol.% hydrogen and 10 vol.% helium, yet the ratio of the hydrogen and helium crossover is not 9:1, since the gas permeabilities of hydrogen and helium differ, which also depends on the gas composition at the cathode. Prior to fuel cell operation, the hydrogen crossover is ten times higher when the cathode is purged with nitrogen instead of oxygen. Thus, about 90% of hydrogen that permeates through the defect is oxidized in the cathode catalyst layer during fuel cell operation, but 10% permeates through the GDE and accumulates in the gas channels. After performing the 50 h AST, both the helium and hydrogen crossover increased by a factor of about 10 (in nitrogen). This can be attributed to growth of the pinhole, and the GDE gas permeability presumably also increased locally due to degradation processes. However, when the cathode was purged with oxygen, the hydrogen crossover was half as large as during nitrogen purging. Thus, the conversion rate has decreased from 90% to 50%. This is because large fractions of the catalyst layer are lost at the membrane defect due to thermal degradation processes.

In conclusion, hydrogen that has permeated through membrane defects is not oxidized quantitatively at the cathode electrode. Instead, some hydrogen further permeates through the GDL because the finely distributed catalyst is lost at membrane defects. This is how hydrogen can accumulate in the cathode flow, which may become a serious safety issue in fuel cell systems. Electrochemical analysis methods may thus underestimate the hydrogen crossover in this situation.

Table 6.4

<table>
<thead>
<tr>
<th>Gas crossover</th>
<th>Prior to AST</th>
<th>After AST</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2 ) ( \times 10^{-7} )</td>
<td>( \text{mol s}^{-1} \text{cm}^{-2} )</td>
<td></td>
</tr>
<tr>
<td>in ( \text{N}_2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2 ) crossover</td>
<td>10.4 ± 0.2</td>
<td>105 ± 4.3</td>
</tr>
<tr>
<td>( \text{He} ) crossover</td>
<td>1.6 ± 0.03</td>
<td>15.6 ± 0.9</td>
</tr>
<tr>
<td>in ( \text{O}_2 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2 ) crossover</td>
<td>1.1 ± 0.2</td>
<td>53.7 ± 4.6</td>
</tr>
<tr>
<td>( \text{He} ) crossover</td>
<td>0.8 ± 0.1</td>
<td>12.5 ± 0.6</td>
</tr>
</tbody>
</table>
6 Local Polymer Electrolyte Membrane Degradation

6.5 Conclusions

The effect of chemical, mechanical and combined chemical/mechanical degradation on the gas separation of PFSA membranes was investigated locally in the early stages of fuel cell operation. In this way, trigger processes that lead to nonuniform degradation were identified, and a fundamental understanding of the degradation mechanism was obtained. Using a tracer gas concept, gas permeation through MEAs was analyzed \textit{in situ} in terms of diffusive and convective gas transport. Membrane thinning and pinhole formation were deduced from the temporal evolution of both. The initial gas crossover through the tested MEAs is given by the diffusive gas transport in Nafion NR 211 membranes, which increases due to mechanical, but not chemical membrane thinning. Chemical decomposition of the tested Nafion NR 211 membranes is weak. Mechanical membrane thinning is induced by surface defects of the GDE, which exert shear forces and cause plastic deformation of the polymer. This is accelerated by RH fluctuations in the gas channel and high membrane water content. Due to the spatial nonuniformity of both factors, mechanical membrane thinning is inhomogeneous over the active cell area.

Pinhole formation is by far the major reason for the loss of gas separation for Nafion NR 211 membranes and was therefore investigated in detail. Pinholes, about 10 µm in diameter, are formed mechanically either by carbon fiber endings that originate from the GDE, or by MPL cracks, which exert local stress on the membrane. Areas with high relative humidity and RH fluctuations apply mechanical stress to the membrane, resulting in inhomogeneous pinhole formation over the active cell area. Smooth GDE surfaces delay mechanical pinhole formation and extend the lifetime of membranes. MEAs with few and small membrane defects still provide good cell performance, but the gas crossover is elevated, which accelerates chemical polymer decomposition locally. Therefore, the formation of small pinholes is crucial for the onset of consecutive degradation processes leading to fatal membrane failures.

In order to study the degradation mechanism at membrane defects, artificial pinholes (10 µm in diameter) were implemented in the membrane with focused ion beam milling. Their degradation was investigated in the early stages by online gas permeation analysis, X-ray tomographic microscopy and FTIR spectro-microscopy. The gas crossover is locally elevated at membrane defects, thus accelerating chemical polymer decomposition around the defect via the radical attack mechanism, as indicated by the formation of COOH groups. Local temperatures of above 140 °C were measured at the defect due to
the catalytic combustion of hydrogen. This induces thermal polymer decomposition, mass- 
ive carbon oxidation and catalyst degradation. Since catalyst material is lost, permeated 
hydrogen is not oxidized quantitatively at defects. Instead, it permeates further through 
the catalyst and microporous and gas diffusion layers. Thus, electrochemical hydrogen 
permeation analysis will underestimate the gas crossover for membranes with defects. In 
other words, the electrochemically determined hydrogen crossover is only a limited indicator 
for the health of degraded membranes. This metric can be even more misleading 
if the GDE transport resistance at defects changes, as this can mask or mimic a change 
in membrane's health. As a second consequence, polymer does not only decompose at 
the pinhole edges but will also degrade up to 1–2 pinhole diameters away from the defect, 
with the flow direction being preferential. Chemical degradation processes weaken the 
polymer around defects. The polymer will suddenly fracture, i.e. gas crossover jumps are 
observed, if mechanical stress induced by humidity fluctuations exceeds the local mem- 
brane strength. As described in an overall degradation scheme, chemical, mechanical and 
thermal degradation processes have a synergetic effect on pinhole growth. The combi-
nation of processes accelerates pinhole growth and, in turn, boosts the gas permeation 
exponentially. The elimination or mitigation of only one degradation process slows down 
pinhole growth significantly. Furthermore, degradation processes are side-selective: chem-
ical polymer decomposition dominates when oxygen permeates from the cathode to the 
anode, while thermal polymer decomposition dominates for hydrogen permeating to the 
cathode.

Degradation at pinholes is very nonuniform. Pinholes in the same membrane grow dif-
ferently due to locally different gas crossovers. In order to study the characteristics of the 
gas crossover through small defects, the effect of the GDE and operating conditions on the 
crossover was investigated. The low convective gas permeability of the microporous and 
catalyst layers limits the gas crossover. Local structural features, such as cracks or carbon 
agglomerates of the microporous layer, significantly affect the gas crossover through mem- 
brane defects, and thus degradation processes. Furthermore, the gas crossover is strongly 
influenced by the operating conditions; the higher the temperature or humidity, the lower 
the gas permeability through defects. Depending on the pinhole size and pressure gradient, 
liquid water can seal pinholes and eliminate the convective gas crossover, thereby mitigat-
ing local membrane degradation at defects. A nonuniform liquid water distribution may 
thus be a major reason for inhomogeneous membrane degradation over the active area of 
the cell.
7 Local Catalyst Support Degradation

7.1 Understanding of the Catalyst Support Degradation

7.1.1 Carbon Support Corrosion Mechanism

Carbon is an inexpensive raw material that has high surface areas, good electrical conductivity and chemical stability (see Section 2.1 on page 5). Therefore, it is widely used as catalyst support. However, carbon is not thermodynamically stable under fuel cell conditions. It is oxidized electrochemically to carbon dioxide (CO₂) or carbon monoxide (CO) for potentials that exceed the standard electrode potentials given in Equations 7.1 and 7.2. As the oxidation of CO to CO₂ is thermodynamically favored (Equation 7.3), CO formation is usually an order of magnitude lower than CO₂ formation, and is thus often neglected [36, 166, 167]. Despite the thermodynamic instability, carbon corrosion is usually small in PEFCs, as the oxidation is limited kinetically [168], yet there are detrimental operating conditions that accelerate carbon corrosion. These are discussed later on page 106.

\[
\begin{align*}
C + 2H_2O & \rightleftharpoons CO_2 + 4H^+ + 4e^- \\
E^0 & = 0.207 \text{ vs. SHE} & \quad (7.1) \\
C + H_2O & \rightleftharpoons CO + 2H^+ + 2e^- \\
E^0 & = 0.518 \text{ vs. SHE} & \quad (7.2) \\
CO + H_2O & \rightleftharpoons CO_2 + 2H^+ + 2e^- \\
E^0 & = -0.103 \text{ vs. SHE} & \quad (7.3)
\end{align*}
\]

The detailed mechanism of carbon oxidation has not yet been fully understood. According to Equations 7.4 and 7.5, carbon surface oxides may be formed in an intermediate step, then further oxidized to CO₂. The latter reaction is limited kinetically, therefore higher potentials (above 0.9 V) are required for significant corrosion rates. However, catalysts such as platinum can lower the required potential to about 0.6 V [37, 166]. Platinum oxide groups presumably catalyze the oxidation of carbon surface oxides according to Equations 7.6 and 7.7 [36, 37, 166], by reducing the activation energy for carbon corrosion to 56–67 kJ mol⁻¹ [46, 133, 166]. Carbon surface oxides may act themselves as catalytically active species and promote carbon corrosion by a similar mechanism [46].
7 Local Catalyst Support Degradation

\[
C + H_2O \rightleftharpoons CO_{(ad)} + 2H^+ + 2e^- \quad (7.4)
\]
\[
CO_{(ad)} + H_2O \rightleftharpoons CO_2 + 2H^+ + 2e^- \quad (7.5)
\]
\[
CO_{(ad)} + PtOH_{(ad)} \rightleftharpoons Pt + CO_2 + H^+ + e^- \quad (7.6)
\]
\[
Pt + H_2O \rightleftharpoons PtOH_{(ad)} + H^+ + e^- \quad (7.7)
\]

The rate of carbon corrosion depends on the carbon material and on the operating conditions. Highly graphitized carbon supports have up to 10 times lower corrosion rates than non-graphitized ones, because the BET surface area is smaller, and the corrosion rate decreases with increasing microcrystallinity of the carbon particle [11]. Because the order of the graphene layers diminishes towards the center of a single carbon particle, carbon corrosion is highest in the particle center [11,169]. As carbon corrosion is very sensitive to the operating conditions, their impact on the corrosion rate is discussed in the following paragraphs. The empirical rate law shown in Equation 7.8 quantitatively describes the effect of the electrode potential (\(\varphi\)), temperature (\(T\)), humidity (partial water pressure \(p_w\)) and time (\(t\)) on the carbon corrosion rate (carbon corrosion current \(i_c\)) [10].

\[
i_c = zFk'\left(\frac{p_w}{p_{ref}}\right)^\gamma \cdot \exp\left[-\frac{E_a}{RT}\left(1 - \frac{T}{T_{ref}}\right)\right] \cdot \exp\left(\frac{\alpha_aF}{RT} \cdot \varphi\right) \cdot t^{-m} \quad (7.8)
\]

- \(z\) Number of electrons transferred
- \(F\) Faraday’s constant
- \(k'\) Preexponential rate constant
- \(R\) Ideal gas constant
- \(E_a\) Activation energy
- \(\gamma\) Order dependence of the reactant
- \(\alpha_a\) Anodic transfer coefficient
- \(m\) Time decay exponent

The corrosion rate shows a first order linear dependence on water concentration and an Arrhenius correlation towards the temperature (Equation 7.8) [46, 166]. However, this trend may not exactly translate to an operating fuel cell system, because both humidity and temperature also affect carbon corrosion indirectly by altering the electrode potential. Linse et al. [46] reported a linear dependence of carbon corrosion rate on the relative humidity over a wide range of conditions, except at very low and very high humidities, where carbon corrosion rates deviate due to membrane dry-out and flooding issues, respectively.
Likewise, Kim et al. [170] measured disproportionately high corrosion rates at 100% RH. The rate of carbon corrosion decays with time according to the time decay exponent $m$ (Equation 7.8), which is also shown in Figure 7.1. This effect is caused by decreases in both the total amount of carbon and the fraction of low-ordered graphene layers. Therefore, corrosion rates are only comparable for equivalently degraded catalyst supports.

A high electrode potential is the main driving force of carbon corrosion, which increases exponentially with potential (Equation 7.8) [46]. However, in a fuel cell carbon corrosion is not necessarily fastest at high potentials, as the potential also affects the catalytic activity of platinum. Maintaining high potentials actually decreases carbon corrosion rates over time, as a thick oxide layer is presumably formed on platinum, thus slowing down carbon oxidation [171, 172]. In contrast, repeated cycling to high potentials results in enhanced corrosion rates, as no protective oxide layer can be built up in the short period at high potentials, yet sufficient platinum oxide groups are still formed to catalyze carbon corrosion [166]. Load cycling at lower potentials was also found to accelerate carbon corrosion, as the frequent reduction and oxidation of platinum presumably introduces surface defects that promote carbon corrosion. During the positive-going sweep, oxidized surface groups are likely formed on carbon, which are then converted to adsorbed CO during negative-going sweeps and further oxidized to CO$_2$ within the next positive-going sweep [37, 43, 166].

In conclusion, not only the potential but also the state of the catalyst, which is affected by the previous operational protocol, controls the carbon corrosion rate.

Besides the electrochemical oxidation of carbon, Maass et al. [166] reported that carbon is also oxidized chemically at potentials below 0.3 V due to the production of reactive species. Specifically, hydrogen peroxide can be formed electrochemically by the $2e^- \rightarrow H_2O_2$ reaction.
duction of oxygen at low potentials on supported platinum [19]. Hydrogen peroxide or peroxide radicals oxidize carbon surface atoms, which can be further oxidized to CO$_2$ [166]. Given that the amount of hydrogen peroxide formed is small, and the activation energy for chemical carbon oxidation is relatively high ($\approx 80$ kJ mol$^{-1}$), the chemical corrosion rates are slow.

7.1.2 Consequences of Carbon Support Corrosion

Corrosion of the carbon catalyst support results in decreased cell performance by two different mechanisms. First, mass transport limitations increase, as the catalyst layer increases in density according to the “neck-breaking” mechanism, thus impeding the gas exchange [59,173]. According to this mechanism, carbon corrosion weakens the connections of the carbon particle network, which then collapse due to the compaction force in the MEA. This causes embedding of the catalyst particles and decreases the porosity, as shown by Schulenburg et al. [160] using FIB/SEM serial sectioning and electron tomography. Carbon weight losses of only 5–10 wt.% lead to significant mass transport limitations [11, 133], which are more pronounced under wet conditions, as illustrated in Figure 7.2. Mass transport limitations also arise at high humidity because surface oxides formed on the carbon support decrease the hydrophobicity of the catalyst layer, impeding the removal of electrochemically produced water [174]. Polarization curves at high RH indicate mass transport limitations (Figure 7.2A). Therefore, polarization curves are used to investigate catalyst support degradation, as described in Section 4.6 on page 39.

Carbon corrosion also affects cell performance by decreasing the electrochemically active surface area of platinum, thus reducing the oxygen reduction rate. Due to the catalytic effect of platinum, carbon corrodes the most in the vicinity of the platinum catalyst. The contact between the catalyst particle and the support weakens, leading to the detachment of platinum particles, which become inactive once electrochemical contact is lost [14, 37, 170]. Furthermore, carbon surface atoms oxidize faster at defects than in-plane carbon atoms due to their higher chemical potential (Gibbs-Thomson effect). The reduced surface area promotes the agglomeration of platinum particles, thereby lowering the electrochemical active surface area [14, 170].
7.1 Understanding of the Catalyst Support Degradation

Figure 7.2 Carbon corrosion increases mass transport limitations particularly at high humidity due to a loss in electrode porosity, which is illustrated by hypothetical polarization curves, adapted from Carter et al. [60].

7.1.3 Carbon-Free Catalyst Supports

Despite its deficiency in corrosion resistance, carbon is still the state-of-the-art material for catalyst supports in PEFCs, with no real competitive alternatives as of yet [12, 148]. Most carbon-free supports, such as conductive metal oxides, carbides, nitrides or doped diamonds, do not adequately meet the catalyst support requirements: electrical conductivity above 0.1 S cm$^{-1}$, sufficient porosity (pores sizes larger than 25 nm), surface areas larger than 50 m$^2$ g$^{-1}$ or material costs of less than about 15 € kg$^{-1}$ [12]. In particular, corrosion resistance must be superior, since the corrosion products of carbon-free materials are not gaseous (such as CO$_2$ or CO). The resultant solids accumulate in the cell and may affect the cell performance or durability [43]. Tungsten carbides are promising carbon-free supports, as the electronic structure is similar to platinum, and the supported catalyst shows a high CO tolerance. Unfortunately, carbides and also nitrides are not thermodynamically stable under fuel cell conditions and are eventually oxidized to the corresponding metal oxides [12, 175, 176]. Metal oxides, such as Ti$_4$O$_7$ [177], indium tin oxide [178], NbO$_2$ [179] or SnO$_2$ [180], seem to be the most promising group of carbon-free supports. The substrates induce strong metal-support interactions (SMSI), affecting and potentially enhancing the catalytic activity and durability of the catalyst. Platinum supported on NbO$_2$/C was shown to have three times higher mass activity than commercial platinum supported on carbon [179]. Increased stability was reported for platinum supported on SnO$_2$ during potential cycling [180]. The substrate however must be well adjusted to the catalyst, as the SMSI can also reduce the catalytic activity [12]. An alternative ap-
proach using non-classical catalyst supports is shown by the company 3M. The catalyst is vacuum coated on a nano-structured thin film (NSTF) of crystalline organic pigments and subsequently transferred to the membrane by continuous web processing [181]. Even though the polymer film does not show electronic or ionic conductivity, the catalyst layer thickness (about 1 µm) seems to be sufficiently thin to facilitate charge transport. The NSTF catalysts show superior catalyst activity and utilization, and good stability under fuel cell operating condition, but suffer from cathode flooding [12, 181].

### 7.1.4 Carbon Corrosion in PEFC

Due to the slow kinetics of carbon oxidation in the operational temperature range of a PEFC (20–80 °C), the corrosion rate is low under fuel cell conditions, where electrode potentials are below approximately 1 V. However, in certain cases the potential is elevated significantly, accelerating carbon corrosion and catalyst degradation, and thereby reducing the service life of carbon supported catalysts. Identical-location transmission electron microscopy illustrates the loss of carbon and catalyst particles (Figure 7.3B) after degrading pristine supported catalyst (Figure 7.3A) by simulated fuel cell start-up and shutdowns [14]. The degraded sample displays carbon corrosion, catalyst particle detach-

![Figure 7.3](image)

**Figure 7.3** Identical-location transmission electron microscopy illustrates the degradation of A) pristine carbon supported platinum catalyst. B) After 3600 potential cycles of simulated start-up and shutdown, the sample displays carbon corrosion, catalyst particle detachment, platinum dissolution and platinum particle agglomeration. Dark spots represent platinum particles, and the underlying brighter background represents carbon. Reproduced from Meier et al. [14] with permission from the American Chemical Society.
7.1 Understanding of the Catalyst Support Degradation

ment, platinum dissolution and platinum particle agglomeration. For details in catalyst degradation, the reader is referred to the literature [14, 43, 133, 182–184].

The cathode electrode potential at OCV (≈ 0.95 V) and at idling (≈ 0.9 V) falls into a regime where significant carbon losses are predicted after thousands of operating hours [11]. Similar carbon losses are estimated to occur during load cycling, since dynamic potential sweeps accelerate carbon corrosion, as described on page 101. Higher corrosion rates are observed during fuel starvation. Fast power-up transients, system control failures, flow maldistribution or pressure drop variations may result in global fuel starvation: insufficient hydrogen supply in some cells of a fuel cell stack. If a cell is depleted of hydrogen, the anode potential rises until carbon of the anode catalyst layer and water begin to be oxidized in order to sustain the stack current. Global fuel starvation can result in serious carbon losses in the anode catalyst layer within minutes [11, 148, 182]. Similarly, hydrogen can be depleted locally in the cell due to a gas flow blockage induced by flooding or ice formation during subfreezing start-up, resulting in local fuel starvation [185, 186]. In this case, oxygen permeates through the membrane to the anode and accumulates in the hydrogen depleted regions, forming a hydrogen/oxygen front at the anode. This induces carbon corrosion in the cathode catalyst layer according to the reverse current mechanism shown in Figure 7.4. This mechanism can also arise during fuel cell start-up and shutdown, which is discussed in detail as follows.

7.1.5 Carbon Corrosion during Start-Up and Shutdown

Before start-up, the anode and cathode are usually filled with air, since gas diffusion settles any imbalance between the atmosphere and the anode and cathode compartments, even if they are nominally closed to the environment. When hydrogen is introduced into the air-filled anode for start-up, a hydrogen/air front is formed [11, 46, 187]. It should be noted that this phenomenon also appears during shutdown if the anode is purged with air to remove the remaining hydrogen quickly (for safety reasons). It will even occur without any purging, as air will diffuse from the atmosphere or from the cathode into the hydrogen filled anode [44]. The coexistence of hydrogen and oxygen in the anode induces a high cathode potential by the reverse current mechanism first proposed by Reiser et al. [187]. Thus, carbon in the cathode catalyst layer is electrochemically oxidized.

Figure 7.4 illustrates the reverse current mechanism for the start-up. Introducing hydrogen in region B lowers the anode electrode potential ($\varphi_a^B$) to about 0 V with the cathode electrode potential ($\varphi_c^B$) at about 0.95 V. The corresponding electrode potentials of region A ($\varphi_a^A$, $\varphi_c^A$) are equal due to the high in-plane electrical conductivity of the GDE. The potential difference between anode and cathode of 0.95 V is the typical open circuit voltage
of a PEFC. The membrane potential, defined by the proton concentration, is about 0 V in region B ($\varphi_m^B$) according to the standard electrode potential of hydrogen at the anode electrode. Since oxygen is still present in the anode of region A, $\varphi_m^A$ is approximately -1 V according to the mixed electrode potential of oxygen. Due to the low in-plane proton conductance of the membrane, $\varphi_m^A$ and $\varphi_m^B$ are not equalized. Thus, the Galvani potential difference between $\varphi_m^A$ and $\varphi_m^A$ is about 1 V, whereas it is about 1.9 V between $\varphi_m^A$ and $\varphi_m^C$. However, measurements on real cells yield potentials of only about 1.3–1.7 V due to kinetic and ohmic losses [188–190]. The high Galvani potential difference induces the oxidation of water, carbon and platinum at the cathode electrode in region A. Since in region A the protons are formed at the cathode and consumed at the anode by the oxygen reduction reaction, the current is reversed as compared to normal fuel cell operation. Thus, the effect is termed the “reverse current” mechanism [187].

The oxidation or reduction of platinum influences carbon corrosion by the so-called pseudo-capacitive effect. This can be explained by the cyclic voltammogram of a platinum electrode, as shown in Figure 7.5. Platinum is oxidized to platinum hydroxide above potentials of about 0.7 V according to Equation 7.9, and then further oxidized to platinum oxide and platinum dioxide according to Equations 7.10 and 7.11. Decreasing the potential reduces the platinum in turn. The higher the upper potential, the more platinum is oxidized and subsequently reduced, as indicated by the increasing peak area of the oxide reduction (see Figure 7.5). During shutdown, the anode is filled with air, which

Figure 7.4 Carbon corrosion mechanism during fuel cell start-up and shutdown. For detailed explanation see text.
7.1 Understanding of the Catalyst Support Degradation

Figure 7.5 The cyclic voltammograms of a platinum electrode show platinum oxidation and reduction as a function of the upper potential. The potential was cycled with a scan rate of 100 mV s\(^{-1}\) on a glassy carbon disk electrode with a platinum loading of 60 µg cm\(^{-2}\) in 0.1 M HClO\(_4\) (argon saturated\(^1\)).

oxidizes the platinum at the anode (Equation 7.9). Simultaneously, the reverse current mechanism increases the potential at the cathode, oxidizing the platinum according to Equations 7.10 and 7.11. Platinum oxidation at both the anode and the cathode forms protons, which increase the membrane potential. Thus, the Galvani potential difference between the electrolyte and the cathode electrode is reduced, which mitigates carbon corrosion. During start-up, platinum is oxidized at the cathode, just as for shutdown, but is reduced at the anode according to Equation 7.12. The reactions are still a net source of protons, as the catalyst loading is typically higher for the cathode than for the anode. However, less protons are formed and thus the Galvani potential difference between the electrolyte and the cathode electrode is reduced less as compared to shutdown. Therefore, carbon corrosion is reduced more during shutdown than during start-up. This induces inhomogeneous carbon losses along the flow field as explained later in Chapter 7.2.1.

\(^1\)Data were provided gratefully by Josef C. Meier from the Max Planck Institut für Eisenforschung.
The reverse current mechanism is widely accepted in the literature and has been experimentally verified [10, 166, 188–191]. Siroma et al. [191] validated the mechanism by measuring the local current and voltage distribution in a 97-fold segmented cell. Tang et al. [190] used a dual cell configuration to measure the current flow between region A and B of Figure 7.4. They calculated a Galvani potential difference between electrolyte and cathode electrode of 1.75 V in region A. The potential difference was measured using internal reference electrodes [188, 189, 192]. Maass et al. [166] correlated the cathode potential to different carbon corrosion mechanisms and elaborated the complex interaction of potential limits, exposure time and degradation states.

\[
P tH + H_2O \rightarrow PtOH + 2H^+ + 2e^- \tag{7.9}
\]

\[
P tOH \rightarrow PtO + H^+ + e^- \tag{7.10}
\]

\[
P tO + H_2O \rightarrow PtO_2 + 2H^+ + 2e^- \tag{7.11}
\]

\[
P tOH + 2H^+ + 2e^- \rightarrow PtH + H_2O \tag{7.12}
\]

7.1.6 Mitigation Strategies

Several strategies have been developed to mitigate carbon corrosion during start-up and shutdown by using advanced materials, optimizing operating conditions or modifying the fuel cell system. To obtain corrosion resistant carbon, the proportion of graphitic layers with high crystallinity is increased by heat treatment at temperatures above 2000 °C. These highly graphitized carbon supports have lower corrosion rates, but also lower specific surface areas, thus reducing the catalyst mass activity [10, 193]. Less platinum can be deposited on the carbon surface, which is counterbalanced by a thicker catalyst layer. However, the increasing ohmic and transport losses reduce the platinum mass activity [193]. Further, the usage of catalyst alloys can reduce carbon corrosion. Pt/Ir alloys have a low activity for the oxygen reduction reaction and can be used at the anode to reduce the reverse current and the carbon oxidation current, respectively [194]. Pt/Ru alloys may be used at the cathode to enhance the oxygen evolution reaction, so the oxidation of water is enhanced relative to carbon oxidation [195].

Selecting appropriate operating conditions during start-up and shutdown can also mitigate carbon corrosion. A high purging gas velocity accelerates the gas exchange and reduces the exposure time to the detrimental potentials [196, 197]. However, this may require a larger air blower that is oversized for normal fuel cell operation. Lowering the
temperature [198] or humidity [170,173] reduces carbon corrosion, but both strategies are not suitable for fast shutdowns, as cooling and drying of the stack is a slow process.

Carbon corrosion can be slowed down by modifying the fuel cell system. If the cells are shunted by an ohmic resistor during start-up and shutdown, the electrode potential will be reduced at the cathode, thereby reducing carbon corrosion. Perry et al. [193] demonstrated a decrease in the loss of performance from 100 µV per start/stop cycle to 4 µV per cycle when applying an external load. However, the application on the stack level is difficult because the reverse current must be equal in all cells. Either each cell needs to be shunted by separate resistors or the manifold must be optimized to distribute the gases in each cell uniformly and simultaneously during start-up and shutdown [193]. Moreover, the hydrogen or oxygen concentration can be minimized to reduce the carbon corrosion rate [46]. Before purging with air, the oxygen concentration can be lowered by an upstream burner [199], a gas separation process or other techniques. The oxygen or hydrogen partial pressure can also be reduced electrochemically in the fuel cell before shutdown. Finally, air may be replaced by nitrogen, which would require an additional nitrogen tank or a nitrogen generator [199]. Despite the variety of mitigation strategies, carbon support corrosion is still a major concern, as most strategies mitigate but do not eliminate the degradation of the catalyst support.

**7.1.7 Research Objective**

Most studies on carbon corrosion during start-up and shutdown were carried out in laboratory fuel cells with active areas of 25–50 cm². However, the scale-up of these results to technical size cells requires careful consideration, as carbon corrosion rates vary with the position in the flow field [28,200]. Models have predicted nonuniform corrosion rates, which were partially validated by local analysis of the reverse current, the limiting current density decline and the catalyst loss via SEM imaging [187,201,202]. However, a systematic understanding of the local corrosion rate is still missing.

Therefore, in this work the catalyst support degradation was investigated *locally* in a fuel cell of technical size during start-up and shutdown. Start/stop cycles were simulated by purging the anode alternately with hydrogen or air, and carbon corrosion was analyzed locally by measuring the CO₂ concentration along the cathode channel with mass spectrometry. In this way, a fundamental understanding of *local* carbon corrosion and the influence of the major operating conditions can be elaborated upon.
7.2 Results and Discussion of Local Carbon Support Corrosion

7.2.1 Local Carbon Support Corrosion - Fundamentals

Carbon support corrosion was deduced quantitatively from the measured CO$_2$ concentration in the fuel cell as described in Section 4.1.4 on page 29. Experimental details are given in Chapter 3. The formation of CO$_2$ (as well as CO) via corrosion processes at the MPL, GDL and bipolar plates are assumed to be insignificant under the investigated conditions [36, 46, 166]. Likewise, the amount of CO$_2$ formed at the cathode and permeated through the membrane to the anode is small because the absolute concentration of CO$_2$ is less than about 1000 ppm at the cathode. Thus, these processes only slightly affect the CO$_2$ concentration in the cathode channel and are neglected in the present analysis [46].

Carbon corrosion is nonuniform along the gas channel during start-up and shutdown because the magnitude and duration of the detrimental potential at the cathode show considerable spatial variations. Figure 7.6A shows the local carbon losses for start-up and shutdown (shown as the sum of start and stop) for the standard accelerated stress test given in Table 3.5 on page 20. For start-up, the carbon corrosion rate increases from the inlet to the outlet because the cathode potential rises with ongoing gas exchange. The area of the detrimental potential (region A in Figure 7.4) decreases, while the area of region B increases, resulting in a higher current density in region A and thus in a higher (over-) potential. The outlet is also exposed the longest to the detrimental potential, as the hydrogen/air front moves from the inlet to the outlet. The situation is reversed for the shutdown, where the magnitude and duration of the detrimental potential are highest at

![Figure 7.6](image-url)

**Figure 7.6** Local carbon losses per start/stop cycle during start-up and shutdown – a comparison of experimental data with modeling work from Gu et al. [201]. A) experimentally determined carbon loss at 80 °C, ambient pressure, 70% RH and a nominal anode gas velocity of 0.6 m s$^{-1}$; B) model of the local carbon loss [201]; C) ratio of the limiting current after (EOL) and prior (BOL) to start/stop cycles. Reproduced from Kreitmeier et al. [45] with permission from the Electrochemical Society.
7.2 Results and Discussion of Local Carbon Support Corrosion

the inlet. Combining start-up and shutdown results in moderate carbon losses in the center of the flow field and large ones at inlet and outlet. For the given conditions the losses are highest at the outlet, moderate at the inlet and lowest in the center (Figure 7.6A).

These findings based on the CO$_2$ measurements were confirmed by analyzing the catalyst layer thickness at different positions along the channel by SEM imaging of MEA cross-sections. Figure 7.7 shows representative MEA cross-sections for a pristine MEA (A) and the degraded MEA at the inlet (B), center (C) and outlet (D). The cathode catalyst layer thickness was averaged at different positions; while it is 11.4$\pm$3.0 $\mu$m for a pristine MEA, it is reduced to 3.7$\pm$1.1 $\mu$m for the degraded MEA at the inlet, 6.4$\pm$1.4 $\mu$m at the center and 2.0$\pm$1.6 $\mu$m at the outlet. The reduction in the catalyst layer thickness, induced by carbon loss and subsequent collapse of the layer, qualitatively agrees with the local carbon loss data obtained from mass spectrometry. Gu et al. [201] have modeled local carbon losses during start-up and shutdown. When the pseudo-capacitive effect is incorporated, their model also predicts higher carbon losses at the outlet than inlet and a carbon loss ratio between shutdown and start-up of 0.6 as shown in Figure 7.6B. This agrees very well with the present experimental work, which was carried out at similar conditions. This indicates that the pseudo-capacitive effect is likely to be a driving force for the difference in carbon loss between start-up and shutdown, resulting in significantly different local carbon losses at the inlet and outlet. This general picture may not hold for all conditions, as higher corrosion rates have also been observed for shutdown [46,203], so additional parameters probably affect the relative ratio of carbon corrosion at start-up and shutdown.

![Figure 7.7 MEA cross-sections visualizing carbon loss by the reduction of catalyst layer thickness; A) pristine MEA; degraded MEA B) at the cell inlet, C) at the center and D) at the cell outlet. MEA was degraded at 70% RH, ambient pressure and at a nominal gas velocity of 0.3 m s$^{-1}$ for 500 cycles. Reproduced from Kreitmeier et al. [45] with permission from the Electrochemical Society.](image-url)
It is known that carbon corrosion depends on the gas exchange rate, which is in turn affected by the purging gas velocity [196, 197]. However, the gas exchange rate is also determined by the diffusive gas transport within the GDL, microporous and catalyst layers, as demonstrated by the fact that the gas exchange takes much longer than predicted by the purging gas velocity alone [204]. Schneider et al. [205] have shown that the local potential and in-plane current density differ for fuel cell start-up and shutdown due to diffusive gas transport limitations. To investigate the effect of diffusive mass transport on the start/stop ratio and the local differences of carbon loss, carbon corrosion was analyzed while purging the anode with either helox (80/20 vol.% He/O\textsubscript{2}) or synthetic air (80/20 vol.% N\textsubscript{2}/O\textsubscript{2}). Figure 7.8A shows that the carbon loss during start-up and shutdown is always less for helox than for air. The ratio between helox and air is 0.5–0.7 for start-up and 0.2–0.4 for shutdown and decreases with gas velocity because at high gas speeds the overall gas exchange rate is limited by the diffusion in the GDE rather than the purging gas velocity. Moreover, increasing the diffusive gas transport by using helox lowers the corrosion rate for shutdown more than for start-up. This indicates that there are more severe mass transport limitations during shutdown, where the transport of oxygen is the limiting factor. Indeed, the oxygen diffusion coefficient in helox versus synthetic air is greater by a factor of 3.7 (D_{O2He}/D_{O2N2} = 0.74/0.2 cm\textsuperscript{2}s\textsuperscript{-1} = 3.7), whereas the coefficient for hydrogen only increases by a factor of 2.1 (D_{H2He}/D_{H2N2} = 1.59/0.74 cm\textsuperscript{2}s\textsuperscript{-1} = 2.1) when calculated at 25 \degree C and 100 kPa [206]. Therefore, reduction in mass transport limitations mitigates the carbon corrosion rates for shutdown more than for start-up. As a result, carbon losses are reduced more at the inlet than at the outlet when using helox (Figure 7.8B), thus increasing the relative losses at the outlet while decreasing them at

![Figure 7.8](image-url)

**Figure 7.8** Carbon losses per start/stop cycle when purging the anode with synthetic air and helox at 80 \degree C, ambient pressure and 70% RH; A) ratio of the total carbon loss between helox and air for different purging gas velocities; B) local absolute and C) relative carbon losses for helox and air at a nominal purging gas velocity of 0.6 m s\textsuperscript{-1}. Reproduced from Kreitmeier et al. [45] with permission from the Electrochemical Society.
the inlet (Figure 7.8C). However, hydrogen diffusion is still faster than oxygen diffusion, so the diffusive gas exchange rate should be higher during start-up than during shutdown, which should lead to lower absolute corrosion rates during start-up. In opposition to the pseudo-capacitive effect, diffusive mass transport limitations should thus lead to higher corrosion rates during shutdown than start-up. However, this was not observed in these experiments. Certainly the influence of diffusive mass transport on the start/stop ratio depends on the flow field design parameters (such as rib width), on material characteristics (such as gas permeabilities of the GDL, microporous and catalyst layers) and on operating conditions (liquid water fraction in the porous structures, temperature, gas composition, etc.). Likewise, the influence of the pseudo-capacitive effect on the start/stop ratio also depends on material characteristics, e.g. the catalyst loading at anode and cathode, and operating conditions (RH, temperature, etc.).

The pseudo-capacitance of the electrode and the diffusive mass transport have opposite effects on the carbon corrosion ratio between start-up and shutdown. The cumulative addition of both effects results in the final start/stop ratio. As an example, the effect of the rib width of flow fields on the carbon corrosion during start-up and shutdown is

![Figure 7.9](image-url)

**Figure 7.9** Influence of the pseudo-capacitive effect and diffusive mass transport on the carbon corrosion ratio between start-up and shutdown. A) a small rib width and B) large rib width affect the diffusive mass transport, but not the pseudo-capacitance of the platinum electrode. The combination of the two effects may lead to either higher carbon corrosion during start-up (A) or shutdown (B). Reproduced from Kreitmeier et al. [45] with permission from the Electrochemical Society.
illustrated in Figure 7.9. The pseudo-capacitive effect is independent of the rib width, while diffusive mass transport limitations are smaller for narrow ribs and larger for wide ribs, leading to respectively lower (Figure 7.9A) or higher (Figure 7.9B) corrosion rates during shutdown. In this work, the rib width is relatively small (1 mm), amplifying the effect of the pseudo-capacitance over that of the diffusive mass transport. This is supported by the fact that carbon corrosion is smaller for shutdown than for start-up in most experiments, similar to the scheme in Figure 7.9A. Depending on the experimental design (MEA characteristics and flow field structures), start/stop corrosion ratios vary, resulting in inconsistent literature data [13, 44, 46, 170, 201]. A quantitative model incorporating both the pseudo-capacitive effect and the effect of diffusive mass transport limitations may help to improve the mechanistic understanding of the carbon corrosion ratio between start-up and shutdown.

The along-the-channel variation of the local carbon corrosion rates has the following consequences: first of all, the fuel cell performance decreases in a spatially inhomogeneous manner. As reported by Schulenburg *et al.* [160], the microstructure of the catalyst support becomes unstable with advanced carbon corrosion. As the carbon particles collapse, the density of the catalyst support increases, limiting mass transport and thus lowering cell performance [60]. To show the spatial effect of such mass transport limitations, the limiting current density was also analyzed locally. Figure 7.6C shows the limiting current density ratio between end of life (EOL) and beginning of life (BOL) after applying 500 start/stop cycles in the standard accelerated stress test (see Table 3.5 on page 20) at a nominal gas velocity of 0.3 m s$^{-1}$. The limiting current density profile (Figure 7.6C) is consistent with the local carbon loss profile (Figure 7.6A); the current density decline is highest at the outlet, with intermediate losses at the inlet and the least decline in the center. This result is also in agreement with literature data [60].

Second, the local carbon corrosion rates decrease unevenly with time. Carbon corrosion modifies the material characteristics and thereby the corrosion rate of a given carbon particle: the higher the fraction of graphitized carbon, the lower the corrosion rate (see Section 7.1.1 on page 102). Because less graphitized carbon degrades faster, graphitized phases may accumulate in a particle, decreasing its corrosion rate with advancing degradation. This will particularly be relevant at the inlet and outlet. Figure 7.10 shows the temporal evolution of the local carbon loss during the standard accelerated stress test. As the number of start/stop cycles increases, the carbon loss per cycle decreases more at the inlet and outlet than in the center, i.e. carbon corrosion is shifted towards the center of the flow field, possibly resulting in a more uniform carbon loss along the channel. This means that carbon corrosion during start-up and shutdown is not only the greatest for a
7.2 Results and Discussion of Local Carbon Support Corrosion

Figure 7.10 Local carbon losses for one start/stop cycle after cycle number given in the plot at 80 °C, ambient pressure, 70% RH and a nominal gas velocity of 0.6 m s\(^{-1}\). Reproduced from Kreitmeier et al. [45] with permission from the Electrochemical Society.

new cell, but it is also the least homogeneous. After 2500 start/stop cycles the carbon loss rate becomes almost uniform along the entire channel. The total carbon loss is estimated at about 0.2 mg cm\(^{-2}\), which corresponds to approximately 50% of the carbon in the catalyst layer.

Third, experimental restrictions may be deduced: the carbon corrosion rate depends on both position along the channel and the extent of carbon degradation. In order to properly interpret the local corrosion rate, experiments must be performed with the entire catalyst layer at a consistent level of degradation. Therefore, in this work all interpretations were restricted to the data between 100 and 500 start/stop cycles, for which the trend of the local carbon loss did not show significant changes.

7.2.2 Effect of Operating Conditions on Local Carbon Support Corrosion

Operating conditions affect the carbon corrosion rate as well as its ratio between start-up and shutdown [13, 46], indicating that the relative local corrosion rates might also be affected. Local carbon corrosion was therefore analyzed for different relative humidities, cell temperatures and purging gas velocities. Figure 7.11 shows the local carbon loss for different RHs at standard conditions (see Table 3.5 on page 20). Both carbon and platinum oxidation (pseudo-capacitive effect) increase with the humidity (see Figure 7.4). At low humidity levels, the availability of water is rate limiting, and carbon corrosion increases
linearly with the humidity [46]. This is because the rate limiting step show a first order dependence on water (see Equation 7.5 on page 102). Since the pseudo-capacitive effect is suppressed due to the low humidity, the effect of the diffusive mass transport dominates, and carbon corrosion is slightly higher for shutdown than for start-up. This phenomenon was also observed by Borup et al. [13]. The absolute and relative carbon losses are somewhat higher at the inlet in comparison to the outlet at 10% RH, as shown in Figures. 7.11B and 7.11C. With increasing humidity, it is the cathode potential rather than the humidity that controls the corrosion rate, thus weakening the humidity dependence of the corrosion rate (Figure 7.11A). Simultaneously, the platinum oxidation rate increases with humidity [170], which also reduces the carbon corrosion rate, especially during shutdown (pseudo-capacitive effect). Therefore, the corrosion rate increases more slowly during shutdown with increasing humidity than it does during start-up (Figure 7.11A). Because of this, less corrosion occurs in the inlet than in the outlet, as illustrated in Figure 7.11B. Hence, increasing RH decreases the relative carbon losses at the inlet (Figure 7.11C).

All previous experiments have been conducted with a uniform gas humidity along the channel, but the humidity distribution is inhomogeneous under real operating conditions [24, 30], a condition that may persist during shutdown. As the humidity affects the carbon corrosion rate, the effect of its inhomogeneity during shutdown remains unclear. The carbon loss was therefore investigated locally for both uniform and nonuniform humidity profiles at the cathode. Figure 7.12 shows the relative carbon losses during shutdown at a nominal gas velocity of 0.15 m s\(^{-1}\) for a uniform relative humidity of 70% and for a linearly increasing relative humidity that ran from 35% to 80% (see Figure 7.12, right Y-axis). The nonuniform water profile was established by operating the cell at 0.25 A cm\(^{-2}\) and 35% inlet RH until fuel cell shutdown. No difference in the relative carbon loss was
7.2 Results and Discussion of Local Carbon Support Corrosion

Figure 7.12 Effect of an inhomogeneous water distribution on the local carbon loss at 80 °C, ambient pressure and a nominal gas velocity of 0.15 m s\(^{-1}\). Lines with cross symbols refer to the uniform water distribution along the channel, whereas lines with dot symbols refer to the inhomogeneous water distribution. The water partial pressure (gas RH) was also measured by mass spectrometry. Reproduced from Kreitmeier et al. [45] with permission from the Electrochemical Society.

Observed between the uniform and nonuniform water profile experiments. This may be understood by recalling the fact that for moderate or high RH, the humidity is no longer the rate limiting step for carbon corrosion during shutdown. Therefore, the applied humidity variation does not affect significantly the local carbon corrosion rate.

Both electrochemical reactions and the gas exchange rates (through diffusion coefficients) are temperature dependent, i.e. the temperature affects the pseudo-capacitive effect and the diffusive mass transport, thus influencing the local carbon corrosion rates. Figure 7.13 shows the carbon loss for different temperatures at standard conditions and a nominal gas velocity of 0.3 m s\(^{-1}\). Carbon corrosion increases with the temperature due to improved kinetics [46, 166]. The flattening at high temperatures can be explained by a change in the platinum oxidation behavior [46]. No significant difference in the trend for start-up and shutdown is detectable. Accordingly, carbon corrosion increases with the temperature in the inlet and outlet in the same way (Figure 7.13B), and the relative carbon loss does not change along the channel (Figure 7.13C). Even though a slight trend may seem to exist, it is not statistically significant, as the variations are within the uncertainty of the analysis.

All previous experiments were performed isothermally for start-up and shutdown. However, a fuel cell system is usually started at low temperatures (e.g. RT) and shut
Figure 7.13 Carbon losses per start/stop cycle for different cell temperatures at 70% RH, ambient pressure and a nominal gas velocity of 0.3 m s\(^{-1}\); A) total carbon losses; B) local absolute carbon losses; C) local relative carbon losses. Reproduced from Kreitmeier et al. [45] with permission from the Electrochemical Society.

down at high temperatures (e.g. 80 °C), which will affect the local carbon corrosion rates. Figure 7.14 shows the local losses for a start-up at 35 °C and a shutdown at 80 °C at a nominal gas velocity of 0.3 m s\(^{-1}\), ambient pressure and 70% RH. The carbon losses are similar at the inlet and outlet. Under the given conditions, the elevated temperature and absolute humidity increase the oxidation rate during shutdown, which dominates over the pseudo-capacitive effect.

Carbon corrosion during start-up and shutdown can be mitigated by increasing the

Figure 7.14 Combined carbon losses for a start-up at 35 °C and a shutdown at 80 °C at a nominal gas velocity of 0.3 m s\(^{-1}\), ambient pressure and 70% RH. Reproduced from Kreitmeier et al. [45] with permission from the Electrochemical Society.
purring gas velocity at the anode, since the cathode electrode is exposed to the detrimental potential for a shorter time [196, 197]. For this situation, modeling work predicts lower carbon corrosion rates for the inlet than for the outlet, since the pseudo-capacitive effect should be more pronounced at low corrosion rates, i.e. at a high gas velocity [201]. Figure 7.15 shows carbon corrosion for different purging gas velocities. With increasing gas velocity, the carbon loss decreases in the same manner for start-up and shutdown (Figure 7.15A), resulting in equivalent losses at the inlet and outlet, as depicted in Figure 7.15B. However, the relative losses increase at the inlet and outlet while decreasing in the center (Figure 7.15C). This observation is inconsistent with the model, but may be explained via the following argument. As the potential rises at the cathode due to the formation of the hydrogen/air front, it induces first platinum oxidation, followed by carbon and water oxidation at higher potentials. The higher the gas velocity, the further down the channel the hydrogen/air front propagates before the cathode potential increases to detrimental values. The onset of carbon oxidation is thus shifted towards the outlet during start-up, and then fades toward the inlet during shutdown. This means that the oxidation of platinum mitigates the carbon corrosion rates for both start-up and shutdown. The convolution of both phenomena results in slower corrosion rates, especially in the center. A shift in the onset of carbon corrosion may also be deduced from estimated local carbon losses as reported by Lamibrac et al. [202]. They calculated the carbon loss along the channel during start-up on the basis of local current density measurements.

To summarize, the total carbon corrosion decreases with increasing gas velocity, but this leads to a more inhomogeneous degradation rate along the channel, i.e. higher relative rates at the inlet and outlet.

**Figure 7.15** Carbon losses per start/stop cycle for different purging gas velocities at 80 °C, 70% RH and ambient pressure; A) total carbon losses; B) local absolute carbon losses; C) local relative carbon losses. Reproduced from Kreitmeier et al. [45] with permission from the Electrochemical Society.
7 Local Catalyst Support Degradation

7.3 Conclusions

Online mass spectrometry was employed to investigate local CO₂ production during fuel cell start-up and shutdown in order to provide a fundamental understanding of the relevant carbon corrosion processes. During start-up, the rate of carbon corrosion increases along the channel, while it decreases during shutdown. The carbon losses vary by a factor of up to 4 along the channel. Typically, the corrosion rate is highest at the outlet due to enhanced corrosion associated with the start process, followed by the inlet (shutdown-related corrosion) and lowest in the center. This pattern is in line with SEM measurements of the catalyst layer thickness and local limiting current measurements.

The differences in the local corrosion rates, which also reflect the global differences in carbon loss between start and stop, are the result of two opposite effects: the diffusive mass transport in the GDE and the pseudo-capacitive effect of the platinum catalyst. The gas exchange by diffusive transport is slower during shutdown (oxygen replaces hydrogen) than during start-up (hydrogen replaces oxygen). This increases carbon corrosion during shutdown as compared to start-up. In contrast, the pseudo-capacitive effect mitigates the carbon corrosion for both processes. However, the attenuation is more effective during shutdown. The combination of the two effects, i.e. addition of their relative magnitude, sets the corrosion ratio between start-up and shutdown.

The differences between start-up and shutdown, and thus between inlet and outlet, are also affected by operating conditions. Most prominent is the effect of the gas velocity and humidity. Increasing the gas velocity decreases the carbon corrosion rates in total, but amplifies the relative carbon loss at the inlet and the outlet. Furthermore, the pseudo-capacitive effect is alleviated at low humidities, leading to higher corrosion rates in the inlet, while increasing humidity favors carbon corrosion in the outlet. Finally, the catalyst degradation status itself affects local corrosion rates, with the rates being the least uniform for pristine MEAs.
8 Conclusions & Outlook

8.1 Conclusions

Degradation processes are nonuniform and locally defined in technical sized cells because the operating conditions are nonuniform across the cell and material properties are inhomogeneous. Localized degradation processes are undesirable because they can lead to nonuniform cell performance. This makes it difficult to find operating conditions that are optimized for high electrical efficiencies or power densities. In addition, if only a single cell fails due to local degradation processes, the entire stack must be shut down because cells are connected in series. Therefore, nonuniform and localized degradation processes have been investigated in this work to improve the existing degradation mechanisms by incorporating nonuniform degradation phenomena. Membrane degradation and catalyst support corrosion during fuel cell start-up and shutdown were investigated. The following conclusions were made:

Membrane Degradation  The loss of the gas separation capability of polymer electrolyte membranes was investigated locally and online by analyzing the gas crossover. Adequate stress tests accelerated membrane degradation during fuel cell operation. Unlike for non-stabilized perfluorosulfonic acid membranes, chemical membrane thinning was not observed and did not contribute to the increase of the gas crossover in Nafion NR 211 membranes. The main degradation process is rather the mechanical formation of membrane defects induced by humidity fluctuations and imperfections of the GDE. In the early stages, the gas crossover through these defects (about 10 µm in diameter) does not affect the cell performance significantly, but it does accelerate local membrane degradation. Chemical, mechanical and also thermal degradation processes were identified and investigated locally at membrane defects. Polymer decomposes partially up to 1–2 pinhole diameters away from the defect, the catalyst and carbon material from the MPL degrade and are lost at defects and the temperature increases locally above 140 °C due to the catalytic combustion of hydrogen. The combination of degradation processes, which are side-selective, causes a synergetic effect which accelerates the degradation exponentially, thus leading to significant increases in the gas crossover. From these results, a comprehensive degradation
mechanism at membrane defects was deduced.

The formation and evolution of membrane defects is nonuniform across the cell for several reasons. Humidity fluctuations are the main reason for the inhomogeneous formation rate of membrane defects. The fluctuations are nonuniform along the flow field channels because the gas diffusion layer acts as storage media, buffering fluctuations along the channel. Nonuniform absolute humidity has a similar effect that results from the electrochemical production of water. Finally, surface properties of the gas diffusion electrode are inhomogeneous on the micro-scale; cracks, carbon fibers and carbon agglomerates affect both the formation and evolution of membrane defects. The main reason for an inhomogeneous degradation rate at membrane defects across the cell is the presence of both a local pressure gradient across the MEA as well as liquid water. The liquid water can seal membrane defects and block further degradation. This leads to inhomogeneous degradation, as liquid water is nonuniformly distributed across the cell area depending on the flow configuration, current density and relative inlet humidities of the gases. Furthermore, the pressure gradient between anode and cathode controls the gas crossover through membrane defects and thus chemical polymer decomposition. The magnitude (and in counterflow configuration also the direction) of the pressure gradient differs between the gas inlet and outlet, and thus the intensity of chemical polymer decomposition is different as well. The combination of all these effects controls the local degradation rate. This is the reason why defects form and grow at different rates. Some of them do not grow at all, which in principle offers the prospect to develop mitigation strategies for improving the service life of the membranes even in the presence of defects.

The gas crossover is often used as an indicator for the membrane’s health. However, certain restrictions arise for degraded membranes with larger defects (≥ 15–30 µm). In these cases, the GDE is the main gas transport resistance rather than the membrane, so the sensitivity to changes in the gas transport resistance of the membrane will be weak. In addition, the GDE gas permeability can change due to degradation processes, which could mask or simulate a change in the membrane’s health. Moreover, the electrochemical analysis of the hydrogen crossover may underestimate the real gas crossover through membranes with defects, since hydrogen is not oxidized quantitatively at defects. A significant amount of the hydrogen crossover permeates further through the gas diffusion layer and is not detected by electrochemical techniques because the catalyst layer is lost at membrane defects. This is also the mechanism by which hydrogen accumulates in the cathode channel, which may require an emergency stop of the fuel cell system when approaching the lower explosion limit of hydrogen.
Carbon Support Degradation  Carbon support corrosion was investigated in a fuel cell of technical size during start-up and shutdown. Start/stop cycles were simulated by purging the anode alternately with hydrogen and air, and carbon corrosion was analyzed locally by measuring the CO₂ concentration along the cathode channel with mass spectrometry. Carbon support corrosion is nonuniform across the active area during fuel cell start-up and shutdown. The local corrosion rates across the cell display differences in magnitude up to factors of 4–5. The corrosion rate is highest at the outlet during start-up, while it is highest at the inlet during shutdown. The combination of both leads to the overall degradation pattern of a start/stop procedure. The ratio of the carbon corrosion rate between start-up and shutdown is controlled by the operating conditions and by two opposing mechanisms: the pseudo-capacitive effect of the platinum electrode and diffusive mass transport limitations in the gas diffusion electrode. The pseudo-capacitance dampens carbon corrosion, while mass transport limitations increase carbon corrosion. Both effects are most pronounced during shutdown and thus are more significant at the inlet. Depending on the operating conditions (relative humidity and gas purging speed), the cell design and the material properties of the gas diffusion electrode, the effect of both mechanisms is different, thus yielding a specific, nonuniform degradation pattern, which is associated with a spatially inhomogeneous loss in cell performance.

Because carbon support corrosion is different in magnitude and in position for start-up and shutdown, mitigation strategies should not only be optimized to reduce the degradation rate, but also to obtain the most uniform degradation. The set of parameters investigated in this work are a basis to evaluate and predict local carbon support corrosion rates during fuel cell start-up and shutdown for different operating conditions. Furthermore, the analysis method is capable of studying the effect of specific mitigation strategies on the local corrosion rate.

Experimental Methods  Within this work, the following experimental techniques were developed: i) local and online gas phase analysis was further extended to a differentially operated small fuel cell. This allows for complementary gas phase analysis at the technical and the laboratory scale. ii) Synchrotron based FTIR spectro-microscopy and X-ray tomographic microscopy were optimized for local analysis of membrane defects at the Swiss Light Source. iii) A novel temperature analysis technique based on thermochromic pigments was developed to measure temperature at membrane defects during operation for the first time. iv) Focused ion beam milling and electron beam lithography were applied to implement small defects artificially in membranes (artificial pinholes).
8 Conclusions & Outlook

8.2 Outlook

Membrane Degradation  The formation and evolution of membrane defects was investigated in detail, and a complex degradation mechanism at membrane defects was elaborated in this work. Interestingly, not all membrane defects undergo degradation. A better understanding of this phenomenon may help to develop mitigation strategies for a longer service lifetime of polymer electrolyte membranes. The local gas crossover affects membrane degradation at defects. However, it is not the total amount of hydrogen and oxygen permeated through the defect, but the amount of gas reacted to radicals which controls the degradation rate. A fundamental understanding of how much hydrogen and oxygen react to radicals may provide a better understanding of the degradation mechanism at defects. Online mass spectrometry can be used to determine the conversion rate of permeated hydrogen and oxygen at different operating conditions and levels of catalyst layer degradation. EPR spectroscopy with a combined spin trapping method may be used to analyze the radical concentration at membrane defects.

Strong indications for thermal polymer decomposition are given by XTM and local temperature analysis using thermochromic pigments. However, conclusive evidence is still missing. Local hotspots were observed at membrane defects, but the measured temperature was below the decomposition temperature of Nafion. As this result may be due to limitation in the analysis method, alternative methods should be developed to measure the local temperature at membrane defects, such as the use of micro-thermocouples. This would allow for the online investigation of the local temperature and the identification of conditions that lead to thermal polymer decomposition. The implementation and exact positioning of the micro-thermocouple at the membrane defect is, however, a challenge, as are heat dissipation by the thermocouple and the limited spatial resolution.

In addition to thermal processes, mechanical stress significantly affects the degradation rate at defects. In this work, accelerated stress tests were applied with humidity fluctuations of a fixed amplitude, yet the amplitude will affect the strength of mechanical stress. Investigating the evolution of the gas crossover at different humidity fluctuations would allow for a correlation between the strength of mechanical stress and the overall degradation rate. In this way, the significance of mechanical stress on the degradation rate at membrane defects can be further elaborated. Local degradation at defects may be also investigated for reinforced membranes, as they are currently the most advanced products, which show the best resistance to mechanical stress. Reinforced membranes are known to delay the formation of defects, but the extent to which reinforcement can also decrease the degradation rate at defects is unclear.
This work provides a fundamental understanding of parameters that affect the degradation rate at membrane defects. From these findings, a semi-empirical model may be developed to predict local degradation rates across the cell area in a PEFC stack. This would allow for the prediction of the earliest membrane failure, thus defining the ultimate service life of a stack. Strategies may be deduced to mitigate membrane degradation specifically at susceptible locations in a stack. Likewise, the model would be able to predict the susceptibility of different automotive drive cycles to membrane failures.

**Carbon Support Degradation**  In the present work, carbon support corrosion was investigated locally during start-up and shutdown, and a degradation mechanism incorporating the pseudo-capacitive effect and diffusive mass transport limitations was developed. The impact of these two degradation pathways changes with not only the operating conditions, but also with the fuel cell hardware, e.g. flow field design and GDE material. Modifying the rib width of the flow field, the GDE gas permeability and the flow field geometry (i.e. parallel, serpentine, etc.) will permit the investigation of the effect of the diffusive mass transport limitations in more detail, while changing the platinum loading allows for the investigation of the effect of the electrode’s pseudo-capacitance. With these findings, a model may be developed that incorporates both the pseudo-capacitive effect and diffusive mass transport limitations. This will enable predictions of local carbon corrosion rates for specific start/stop strategies and cell designs.

Water oxidation is a parallel reaction to carbon oxidation and mitigates the catalyst support degradation during start-up and shutdown. However, the mitigation effect under fuel cell operation is unclear. With online gas phase analysis, the concentration of both products oxygen and carbon dioxide can be measured simultaneously during start-up and shutdown. Investigating the oxygen evolution and carbon corrosion as a function of both operating conditions (relative humidity, temperature and degradation period) and catalyst materials (graphitized carbon and catalyst alloys) will improve the understanding of the carbon support degradation mechanism. From these results, mitigation strategies may be deduced to increase water oxidation and decrease carbon oxidation during start-up and shutdown. In addition, these experiments will allow for the differentiation of the water oxidation, carbon oxidation and capacitive electrical currents from the measured electrical current of the reverse current mechanism.

In this study, degradation processes at membrane defects resulting from the hydrogen and oxygen crossover were investigated in detail. When air permeates through the defect to the anode, nitrogen may accumulate and displace hydrogen in the vicinity of the defect. In this case, the cell suffers from local fuel starvation, which will initiate a further degrada-
tion mechanism: carbon support corrosion at the cathode according to the reverse current mechanism. To improve the understanding and evaluate the relevance of this mechanism at membrane defects, carbon corrosion should be investigated at the cathode when air permeates to the anode. With these results, modeling work on local carbon corrosion at membrane defects from Prof. Wolfgang Bessler (Deutsches Zentrum für Luft- und Raumfahrt) and Jan Ohs (Robert Bosch GmbH) can be validated. As carbon emissions will be low due to the small defect area, the sensitivity of the gas analysis hardware for carbon dioxide must be improved. In addition, oxygen luminescent dye films may be used at the anode [27, 28] in order to study the lateral dimension of the fuel starvation area.

Finally, the local gas phase analysis may be extended to the stack level in order to investigate global fuel starvation. In a PEFC stack, a temporally or locally insufficient hydrogen supply can cause fuel starvation in individual cells. The anode electrode potential will rise in these cells until carbon or water is oxidized to sustain the electrical current of the stack. This phenomenon is called global fuel starvation and it can seriously damage the anode catalyst layer within minutes. It may occur during fast load transients, low hydrogen stoichiometry or flooding of the cell. Knowledge of the local hydrogen, water and carbon dioxide partial pressures is important information for understanding the kinetics of carbon corrosion under these conditions. The gas analysis hardware is, therefore, most suitable to study this degradation process in more detail. The effect of hydrogen supply, water partial pressure, cell design and load transients on global fuel starvation may be evaluated in order to find mitigation strategies in process control. The existing fuel cell hardware can be equipped with a power supply to simulate global fuel starvation in a stack. In a following step, the gas phase analysis hardware may be applied to a stack, with gas extraction ports for the inlet and outlet of each cell.
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# Nomenclature

## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AST</td>
<td>Accelerated stress test</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller (surface area)</td>
</tr>
<tr>
<td>BOL</td>
<td>Beginning of life</td>
</tr>
<tr>
<td>CCM</td>
<td>Catalyst coated membrane</td>
</tr>
<tr>
<td>CL</td>
<td>Catalyst layer</td>
</tr>
<tr>
<td>DOE</td>
<td>US Department of Energy</td>
</tr>
<tr>
<td>EBL</td>
<td>Electron beam lithography</td>
</tr>
<tr>
<td>EOL</td>
<td>End of life</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron paramagnetic resonance (spectroscopy)</td>
</tr>
<tr>
<td>ESB</td>
<td>Backscattered electron (detector)</td>
</tr>
<tr>
<td>EW</td>
<td>Equivalent weight</td>
</tr>
<tr>
<td>FER</td>
<td>Fluoride emission rate</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>GDE</td>
<td>Gas diffusion electrode</td>
</tr>
<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>ID</td>
<td>Inner diameter</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane electrode assembly</td>
</tr>
<tr>
<td>MPL</td>
<td>Microporous layer</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>MS</td>
<td>Mass spectrometer</td>
</tr>
<tr>
<td>NL</td>
<td>Norm liter at 25 °C and 101.3 kPa</td>
</tr>
<tr>
<td>NSTF</td>
<td>Nano-structured thin film</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>PEFC</td>
<td>Polymer electrolyte fuel cell</td>
</tr>
<tr>
<td>PFSA</td>
<td>Perfluorosulfonic acid</td>
</tr>
<tr>
<td>ppb</td>
<td>Parts per billion</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>sccm</td>
<td>Standard cubic centimeter per minute</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electron (detector)</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>SMSI</td>
<td>Strong metal-support interaction</td>
</tr>
<tr>
<td>XTM</td>
<td>X-ray tomographic microscopy</td>
</tr>
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### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>a</td>
<td>Chemical activity</td>
</tr>
<tr>
<td>B</td>
<td>Gas permeability</td>
</tr>
<tr>
<td>d</td>
<td>Pinhole diameter</td>
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<tr>
<td>E</td>
<td>Electrode potential</td>
</tr>
<tr>
<td>$E^\circ$</td>
<td>Standard electrode potential</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Free Gibbs energy</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>Standard formation enthalpy</td>
</tr>
<tr>
<td>i</td>
<td>Current</td>
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<td>j</td>
<td>Current density</td>
</tr>
<tr>
<td>$j_0$</td>
<td>Exchange current density</td>
</tr>
<tr>
<td>$k'$</td>
<td>Preexponential rate constant</td>
</tr>
<tr>
<td>m</td>
<td>Time decay exponent</td>
</tr>
<tr>
<td>n</td>
<td>Mole</td>
</tr>
<tr>
<td>$\dot{n}$</td>
<td>Molar flux</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>Pressure gradient</td>
</tr>
<tr>
<td>$P_c$</td>
<td>Capillary pressure</td>
</tr>
<tr>
<td>$P_w$</td>
<td>Partial water pressure</td>
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<td>Q</td>
<td>Charge</td>
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<tr>
<td>r</td>
<td>Radius</td>
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<tr>
<td>R</td>
<td>Ideal gas constant</td>
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<tr>
<td>$\Delta S$</td>
<td>Entropy</td>
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<tr>
<td>t</td>
<td>Time</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>$U_{cell}$</td>
<td>Cell voltage</td>
</tr>
<tr>
<td>$\dot{V}$</td>
<td>Volume flux</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<td>-----------------------------------------------------</td>
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<tr>
<td>$W_{el}$</td>
<td>Electrical energy</td>
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<td>$z$</td>
<td>Charge number</td>
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<tr>
<td>$\alpha_a$</td>
<td>Anodic transfer coefficient</td>
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<tr>
<td>$\alpha_c$</td>
<td>Cathodic transfer coefficient</td>
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<td>$\delta$</td>
<td>Membrane thickness</td>
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<tr>
<td>$\eta$</td>
<td>Dynamic viscosity</td>
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<td>$\eta_{conc}$</td>
<td>Concentration voltage loss</td>
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<tr>
<td>$\eta_{ohm}$</td>
<td>Ohmic voltage loss</td>
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<tr>
<td>$\eta_{CT}$</td>
<td>Charge transfer voltage loss</td>
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<tr>
<td>$\eta_{ocv}$</td>
<td>Open circuit voltage loss</td>
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<tr>
<td>$\gamma$</td>
<td>Order dependence of the reactant</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Gas density</td>
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<td>$\sigma$</td>
<td>Surface tension</td>
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<td>$\theta$</td>
<td>Contact angle</td>
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<td>$\varphi$</td>
<td>Potential</td>
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<tr>
<td>$\xi$</td>
<td>Empirical kinetic coefficient</td>
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Bibliography


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[181] M. K. Debe, Novel catalysts, catalysts support and catalysts coated membrane methods, in: W. Vielstich, H. Gasteiger, A. Lamm, H. Yokokawa (Eds.), Handbook of
Bibliography


Publications & Presentations

Peer Reviewed Papers


Other Papers


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<tr>
<td><strong>Talk:</strong> 222nd ECS meeting - The Electrochemical Society of Japan - 2012 Fall Meeting, Honolulu (USA), October 7-12, 2012.</td>
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<tr>
<td><strong>Talk:</strong> 9th Symposium on Fuel Cell and Battery Modeling and Experimental Validation, Sursee (Switzerland), April 08-09, 2012.</td>
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<tr>
<td><strong>Invited Talk:</strong> Laboratory seminar at the Max Planck Institut für Eisenforschung, Düsseldorf (Germany), 2012.</td>
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<tr>
<td><strong>Talk:</strong> 2nd International Workshop on Degradation Issues of Fuel Cells, Thessaloniki (Greece), September 21-23, 2011.</td>
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<td><strong>Talk:</strong> 8th Symposium on Fuel Cell Modeling and Experimental Validation, Bonn (Germany), March 08-09, 2011.</td>
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<td><strong>Talk:</strong> 3rd Autostack Stakeholder Workshop, Grenoble (France), February 07-08, 2011.</td>
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<tr>
<td><strong>Talk:</strong> 2nd Autostack Stakeholder Workshop, Ulm (Germany), November 16-17, 2010.</td>
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<tr>
<td><strong>Poster contribution:</strong> 12th Ulm ElectroChemical Talks, Neu-Ulm (Germany), June 15-17, 2010.</td>
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<tr>
<td><strong>Poster contribution:</strong> 7th Symposium on Fuel Cell Modeling and Experimental Validation, Morges (Switzerland), March 23-24, 2010.</td>
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