Investigation of alternative catalyst and support materials and their effect on degradation in high-temperature polymer-electrolyte-membrane fuel cells

Von der Fakultät für Georessourcen und Materialtechnik
der Rheinisch-Westfälischen Technischen Hochschule Aachen

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vorgelegt von M. Sc.

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Diese Dissertation ist auf den Internetseiten der Hochschulbibliothek online verfügbar
„Nun, was wird an Stelle der Kohle als Treibstoff dienen?“ fragte Pencroff.

„...das in seine Elementarbestandteile zerlegte Wasser“, belehrte ihn Cyrus Smith,

„...das Wasser ist die Kohle der Zukunft."

(Jules Verne, „die geheimnisvolle Insel“, 1874) (S. 502/503)
Abstract

Climate change and scarcity of natural resources demand sustainable solutions to supply our worldwide growing need for electric energy. One possible contribution to satisfy this need is fuel cells, as they offer all qualifications required of a suitable replacement for currently applied energy sources: they are fed by easily accessible fuels like hydrogen or methanol, emit no climate-changing gases and the produced energy is retrieved on a demand based level. This PhD work contributes to this promising technology by studying high-temperature polymer-electrolyte-membrane fuel cells (HT-PEMFC) that can supply households with energy and heat.

The commonly used electrode material of HT-PEMFCs, high-surface-area carbon decorated with catalytic platinum (Pt) nanoparticles, suffers degradation during fuel cell operation. In this work, carbon is replaced by tungsten suboxide (WO$_{3-x}$) and Pt by a Pt/ruthenium (Pt/Ru) alloy. The individual components are studied by electron microscopy in the as-prepared state and partly after various HT-PEMFC operation times.

This study found that the growth behavior and distribution of Pt on WO$_{3-x}$ grains differ markedly from Pt on high-surface-area carbon. Instead of nanoparticles, the catalyst forms micrometer sized, highly porous, octahedral-shaped networks on the WO$_{3-x}$ support. These networks are developed during the applied 2-step synthesis route. Their growth mechanism was revealed by in-depth transmission electron microscopy (TEM) studies, including elemental distribution maps and electron tomography. The performance and degradation of the Pt/WO$_{3-x}$ system as a catalyst layer for the anode side of HT-PEMFCs was studied in detail in an earlier work.$^1$

The second investigated material system is a high-surface-area carbon supported Pt/Ru catalyst alloy that shows an improved carbon monoxide tolerance compared to Pt. Crystallographic analysis revealed that the Pt/Ru alloy forms a face centered cubic lattice (like Pt) rather than a hexagonal close packed lattice (like Ru) despite having locally high Ru contents exceeding the solubility limit. The degradation mechanisms during the dynamic fuel cell operation mode were investigated using cyclic voltammetry measurements combined with identical location scanning TEM (IL-STEM) analysis and electron tomography, where the same area was studied after several thousands of potential cycles. Dissolution was identified as the main degradation mechanism and the occurrence of agglomeration could also be demonstrated, while Ostwald ripening has minor effects.

Finally, the degradation mechanisms occurring in real HT-PEMFC stacks with the Pt/Ru loaded high-surface-area carbon as anode were studied. The long-term performance and the degradation behavior of this system were tested under constant current densities at an operation temperature of 160°C.
Detailed TEM analysis revealed an operation related redistribution of a small portion of both the anodic Pt/Ru and the cathodic Pt catalyst. Nanoparticles emerged in the whole membrane area after fuel cell operation, and they differed in size and elemental composition, depending on the distance to the electrodes. Additionally, a band of nanoparticles was present in the membrane close to the cathode side, whose position is related to the crossover rates of hydrogen and oxygen.

This thesis demonstrates that electron microscopy is a useful method to get insights in the microstructure and composition of new fuel cell materials and to discover micro- and nanometer changes and degradation mechanisms. Knowledge of these are prerequisite to continue with targeted optimization of fuel cell components.
Kurzzusammenfassung


Der zweite Teil der vorliegenden Dissertation handelt von Pt/Ru legierten Katalysator Nanopartikeln auf Ruß, mit dem Ziel, die CO-Toleranz von HT-PEM Brennstoffzellenanoden zu verbessern. Werden Pt und Ru im Verhältnis 1/1 eingesetzt, so besitzt die resultierende Legierung ein kubisch-flächenzentriertes Kristallgitter (wie Pt) und keine hexagonal dichteste Kugelpackung (wie Ru), obwohl der Ru-Gehalt lokal stark schwankt und zum Teil deutlich über der Löslichkeitsgrenze liegt. Das Degradationsverhalten der Pt/Ru Legierung bei verschiedenen Betriebsbedingungen und die
Preface

The following publications contributed to this thesis:

Paper I

**Growth of porous platinum catalyst structures on tungsten oxide support materials: A new design for electrodes**

Katharina Anna Hengge, Christoph Heinzl, Markus Perchthaler, Simon Geiger, Karl J. J. Mayrhofer, Christina Scheu

*Crystal Growth and Design* **2017**, *17*, 1661 – 1668

Paper II

**Accelerated fuel cell tests of anodic Pt/Ru catalyst via IL-TEM: New aspects of degradation behavior**

Katharina Anna Hengge, Thomas Gänsl, Enrico Pizzutilo, Christoph Heinzl, Michael Beetz, Karl J. J. Mayrhofer, Christina Scheu


Paper III

**Unraveling micro- and nanoscale degradation processes during operation of HT-PEMFCs**

Katharina Anna Hengge, Christoph Heinzl, Markus Perchthaler, Daniel Varley, Tim Lochner, Christina Scheu

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<th>Description</th>
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<tbody>
<tr>
<td>Å</td>
<td>Ångstrom ($10^{-10}$ m)</td>
</tr>
<tr>
<td>µm</td>
<td>Micrometer ($10^{-6}$ m)</td>
</tr>
<tr>
<td>ADF</td>
<td>Annular dark field</td>
</tr>
<tr>
<td>BF</td>
<td>Bright field</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered electrons</td>
</tr>
<tr>
<td>CL</td>
<td>Catalyst layer</td>
</tr>
<tr>
<td>CO</td>
<td>Carbon monoxide</td>
</tr>
<tr>
<td>C$_s$</td>
<td>Spherical aberration</td>
</tr>
<tr>
<td>CTEM</td>
<td>Conventional TEM</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>d</td>
<td>Lattice plane distance</td>
</tr>
<tr>
<td>ECSA</td>
<td>Electrochemical active surface area</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt</td>
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<tr>
<td>FC</td>
<td>Fuel cell</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
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<tr>
<td>GDL</td>
<td>Gas diffusion layer</td>
</tr>
<tr>
<td>h</td>
<td>hours</td>
</tr>
<tr>
<td>HAADF</td>
<td>High angle annular dark field</td>
</tr>
<tr>
<td>hkl</td>
<td>Miller indices</td>
</tr>
<tr>
<td>HOR</td>
<td>Hydrogen oxidation reaction</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution TEM</td>
</tr>
<tr>
<td>HSAC</td>
<td>High-surface-area carbon</td>
</tr>
<tr>
<td>HT-PEMFC</td>
<td>High-temperature polymer-electrolyte-membrane fuel cell</td>
</tr>
<tr>
<td>kV</td>
<td>Acceleration voltage in kilovolts</td>
</tr>
<tr>
<td>MEA</td>
<td>Membrane-electrode-assembly</td>
</tr>
<tr>
<td>min</td>
<td>Minutes</td>
</tr>
<tr>
<td>mm</td>
<td>Millimeter ($10^{-3}$ m)</td>
</tr>
<tr>
<td>MPL</td>
<td>Microporous layer</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer ($10^{-9}$ m)</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
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</tr>
<tr>
<td>OCV</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen reduction reaction</td>
</tr>
<tr>
<td>PBI</td>
<td>Polybenzimidazole</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Polymer-electrolyte-membrane fuel cell</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>Pt/Ru</td>
<td>Platinum/Ruthenium alloy</td>
</tr>
<tr>
<td>Ru</td>
<td>Ruthenium</td>
</tr>
<tr>
<td>s</td>
<td>Seconds</td>
</tr>
<tr>
<td>SAD</td>
<td>Selected area diffraction</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning TEM</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>V_{RHE}</td>
<td>Potential versus the reversible hydrogen electrode</td>
</tr>
<tr>
<td>WO_{3-x}</td>
<td>Tungsten suboxide</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Z</td>
<td>Atomic number</td>
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</table>
1 Introduction

Have you ever tried to count the number of electrical appliances you are using at home and at work? Starting from TV, audio or communication devices to kitchen appliances like electric cooker, fridge or dish washer, to all sorts of small equipment like shaver, hairdryer, charger and many more, we possess plenty of them. And their number is increasing steadily. To give an example, in 2003 only ca. 10.7% of all German households possessed a mobile PC like a laptop or netbook, 72.5% a mobile phone and 56.6% a dishwasher. Only 10 years later, in 2013, a mobile PC was present already in 65.2% of all German households, a mobile phone in 92.7% and a dishwasher in 67.3%. And concomitantly with these numbers, the need for electrical energy to sustain all these appliances is increasing.

Up until now, the major part of our energy supply depends on fossil fuels like oil, coal or natural gas. Although it is a commonly used phrase, energy cannot be generated. It can only be converted from one form of energy into another. Fossil fuels, for example, exhibit chemically bound energy which can be transformed into electrical energy. In most power plants, this conversion process is fulfilled by passing through several stages. The combustion of the fossil fuels produces heat, which is then transformed to mechanical energy by a thermomechanical process, and subsequently electromechanically converted into electrical energy. The net efficiency of this process lies in the range of 35 – 45%, which is higher than the energy conversion efficiency in cars, where only 20 – 25% of the fossil fuels´ energy is converted into kinetic energy. Moreover, energy conversion from fossil fuels has several drawbacks. Not only are we running out of natural resources within the next decades, an exorbitantly large amount of CO₂ is also emitted in the energy conversion process, which impacts the world´s climate. A lot of effort has been spent on the development of environmentally friendly, economic and sustainable energy sources. Solar, water and wind power are inexhaustible, and yet they depend on daytime or seasonal conditions and are therefore not retrieved on a demand-based level. Batteries and fuel cells (FCs), on the other hand, can provide energy independent on external influences and can be applied in stationary, mobile and portable applications. Therefore, they are considered promising alternatives to the energy sources used at present.

Generally, fuel cells exhibit some characteristics of both combustion engines and batteries. Like in combustion engines, fuel cells need to be fueled with reactants permanently. Similar to batteries, fuel cells directly convert the chemically bound energy of the reactants into electrical energy without intermediate combustion. Several types of FCs exist which can be classified by their operation
temperature in high-temperature, medium-temperature and low-temperature FCs. However, all of
them exhibit a similar architecture: the anodic and cathodic half cells are separated by an electrolyte
which is both permeable for ions and insulating for electrons. Also, the fuel supplies for anode and
cathode side are separated.

Molten carbonate FCs (MCFC) and solid oxide FCs (SOFC) belong to the group of high-temperature
FCs. Since their operation temperatures lie around ca. 600–800°C (MCFC) and 800–1000°C
(SOFC), their reaction kinetics are high enough to abstain from expensive, precious-metal catalysts.
However, starting up and ramping down of these fuel cells is effortful and time consuming.
Additionally, the high operation temperatures render only a limited number of materials suitable as
durable FC components. As electrolyte, in MCFCs usually different alkali carbonates are used while
in SOFCs, yttrium stabilized zirconia is standardly employed.

Among the low-temperature FCs, alkaline FCs (AFCs), low-temperature polymer-electrolyte-
membrane FCs (LT-PEMFCs) and direct methanol FCs (DMFCs) are counted. For AFCs, operation
temperatures in the range of 60–90°C are required. Their electrical efficiency is high, however the electrolyte, which is 30 wt% potassium chloride, is prone to CO₂ impurities. Consequently the gases need to be cleaned before entering the AFC, which adds up their operation costs. LT-PEMFCs are operated at 50–90°C and the perfluorinated ion exchange membrane
Nafion® is used as electrolyte. Its proton conductivity is guaranteed by humidification with water.
This requires an effortful water- and heat management of the whole FC. DMFCs, which are
operated between 80–150°C, derive from LT-PEMFCs. Here, instead of gaseous fuels, liquid methanol
is used and reformed inside the cell. Generally, the advantages of low operation temperatures are
the fast ramping up and down times of the fuel cells. However, the energy supplying reactions require
the use of a catalyst. Despite extensive research activities, the most active and durable catalytic
materials are precious-metals, which consequently are among the most expensive components of these
FCs. Additionally, CO poisoning of the catalyst is a big problem that needs to be overcome.

Medium temperature FCs are phosphoric acid FCs (PAFCs), operated at 160–220°C, and high-
temperature polymer-electrolyte-membrane FCs (HT-PEMFCs), operated at 160–200°C. These
fuel cells exhibit advantages of both high-temperature FCs and low-temperature FCs: an improved
carbon monoxide tolerance of the catalyst while the corrosion resistance of the fuel cell components
is high and the ramping up and down times are fast. In PAFCs, the electrolyte is concentrated
(100 wt%) phosphoric acid, implemented in a siliconcarbid matrix and the catalyst usually is platinum
(Pt). The electrolyte in HT-PEMFCs is the heat stable, organic polymer polybenzimidazole (PBI)
and proton conductivity is ensured by phosphoric acid doping. Standardly, the electrodes are
composed of a high-surface-area carbon (HSAC) material acting as support for the Pt or Pt-based
catalyst.

The present work focuses on HT-PEMFCs, which can be applied stationary as combined power and
heat supplier for households. According to Jannelli et al. HT-PEMFCs exhibit a net efficiency of up
to 40% considering only the output of electrical energy. When heat is taken into account additionally,
their net efficiency increases to values of up to 79%. Great advances were made in the recent decades
to further enhance the efficiency and long-term stability of fuel cells, and yet there is still room for improvement. In HT-PEMFCs, ongoing fuel cell operation as well as ramping up and down procedures, elevated operation temperatures and the overall present electrochemical environment cause degradation processes, most of which occur on the micro- and nanometer scale.\textsuperscript{33, 35-38} The energy conversion process, which is taking place on the molecular level in the form of two separated oxidation and reduction reactions in the electrodes, is catalyzed on the surface of nanometer-sized catalyst particles that are standardly located on a porous high-surface-area support material.\textsuperscript{39-40} The electrolyte, a polymer-based membrane that separates these two half-cells, needs to be permeable for protons and concomitantly insulating for electrons.\textsuperscript{41-42} The overall thickness of electrodes and membrane is in the range of several tens of micrometers. Different microscopy techniques are required to visualize the structure and the composition of the involved materials and their changes occurring during operation. Since the resolution of light microscopes is insufficient to study nanometer-sized features, electron microscopic techniques have to be applied. By the use of scanning electron microscopy (SEM) and focused ion beam (FIB) sectioning, the whole micrometer scale down to a resolution limit of ca. 10 nm is covered.\textsuperscript{43} For an in-depth analysis to visualize even the sub-nanometer changes, transmission electron microscopy (TEM) and related techniques can be used.\textsuperscript{44}

In literature a great number of SEM and TEM studies is available where HT-PEMFCs are concerned.\textsuperscript{25, 32-33, 45} The focus of these research works covers the whole range, from the analysis of the standardly used fuel cell material combinations and their degradation behavior during both continuous and dynamic FC operation modes,\textsuperscript{40, 46-52} to different materials and varying operation strategies and their effect on the resulting FC performance.\textsuperscript{39, 53-55} Nevertheless, the development of new components is on-going and as such these investigations are of great importance.

The electrodes of HT-PEMFCs are standardly composed of a high-surface-area carbon support material, decorated with dispersed Pt catalyst nanoparticles. However, oxidation of carbon and different, well defined catalyst degradation mechanisms are commonly reported to take place and as such diminish the overall performance of fuel cells and reduce their lifetime.\textsuperscript{46, 48, 56-59} The stability of the carbon support is reported to depend on its sub-structural characteristics (porosity, surface area, texture) and its pre-processing procedure.\textsuperscript{60} The operation related durability of different carbon materials like carbon nanotubes,\textsuperscript{61-63} mesoporous carbon\textsuperscript{64-65} or carbon nanofibers\textsuperscript{66} was in the focus of many research activities. Additionally, carbon was replaced by alternative, corrosion resistant materials like SiC\textsuperscript{67-68}, SiC\textsuperscript{69} or tungsten materials like WO\textsubscript{x}\textsuperscript{70} or WC\textsubscript{70-71}.

The performance, stability and degradation behavior of Pt on its support material during both real and simulated fuel cell operation, is another, widely studied research field.\textsuperscript{68, 72-73} In this context, the so called identical location TEM (IL-TEM) method was established. The alternation between simulated fuel cell operation and intermitted TEM analysis of always the same areas gives insight into the degradation mechanisms of single catalyst particles.\textsuperscript{58, 74-76}

Even though Pt is standardly used as electrocatalyst on both anode and cathode side, it is commonly intended to be, at least partially, replaced. Besides its high costs and its operation related stability issues, the reaction kinetics of the cathodic oxygen reduction reaction are insufficiently slow.
Additionally, Pt is prone to catalyst poisons like carbon monoxide, nitrous gases or sulfur dioxide, which can all be present in the anodic supplied fuel.\textsuperscript{77-80} To enhance the cathodic reaction kinetics and concomitantly reduce costs, a variety of mainly Pt-based bimetallic and ternary catalyst alloys are tested\textsuperscript{73, 81-87} among others are carbon supported Pt/cobalt (Pt/Co)\textsuperscript{88-92}, Pt/palladium (Pt/Pd)\textsuperscript{93} and Pt/nickel (Pt/Ni)\textsuperscript{94}. Likewise at the anode side, a better performance and CO tolerance could be achieved by the use of either bimetallic, carbon supported electrocatalysts,\textsuperscript{95-96} for example Pt/W\textsuperscript{97} and Pt/Ru,\textsuperscript{47, 98-99} or complex catalysts\textsuperscript{100}.

To obtain better insight into the distribution of catalyst nanoparticles on their support and to study the morphology of single particles, 3D electron tomography was performed in some research works additionally to the SEM and TEM techniques mentioned above.\textsuperscript{57, 101-102}

Besides the electrodes, also the polymer based, heat stable membrane was in the focus of many research activities.\textsuperscript{103-104} Its long-term stability needs to be improved and a variety of solution approaches are presented in literature: one way is the induced cross-linkage of the polymer molecules\textsuperscript{105-107} or the regulation of their molecular weight distribution\textsuperscript{36}. Another possibility is based on the addition of inorganic nanoparticles into the polymer matrix like ceria (CeO\textsubscript{2})\textsuperscript{108}, titania (TiO\textsubscript{2})\textsuperscript{109}, zirconium phosphate (ZrP)\textsuperscript{109} or silica (SiO\textsubscript{2})\textsuperscript{35, 109-110}. Additionally, alternatives for the standardly used, polybenzimidazole based membrane are studied to improve the mechanical stability of the electrolyte.\textsuperscript{111-113} Still, a commonly reported degradation mechanism concerning the membrane comprises catalyst nanoparticles that accumulate at a certain position in the ionomer to form a band.\textsuperscript{114-117}

### 1.1 Aim of the thesis

This thesis is dedicated to the optimization of HT-PEMFC materials and components with the aim to increase their lifetime during operation. In this work, fuel cell operation is both conducted in real fuel cell stacks and simulated by cyclic voltammetry experiments. Alternative anode materials are examined that are less prone to degradation than the standardly used high-surface-area carbon support materials decorated with Pt nanoparticles in the size-range of a few nanometers. The strategy in this work is to replace always one component a time and study its distribution and its influence on the overall fuel cell performance. The aim is to discover the atomistic processes which occur during operation, leading to an altered and degraded structure. Detailed information on the crystal structure, local chemical composition as well as morphology of individual catalyst nanoparticles and support materials are obtained by TEM, including energy dispersive X-ray spectroscopy (EDX). FIB sectioning and SEM are used to analyze the overall changes of the layer thicknesses and homogeneity in the µm-scale range. Electrochemical analysis methods, for example cyclic voltammetry or CO stripping are performed to obtain information on the average extent of the accessible surface area of the catalyst, which is then compared to data obtained by electron tomography.
In the beginning of this PhD work, the HSAC support is replaced by tungsten suboxide (WO$_{3.\text{x}}$) grains and the Pt catalyst is deposited on top. The distribution and growth behavior of Pt on WO$_{3.\text{x}}$ are presented and analyzed in chapter Growth of porous platinum catalyst structures on tungsten oxide support materials: A new design for electrodes. The degradation mechanisms of this material combination applied as anode in real HT-PEMFCs had been studied recently.$^1$

In a second approach, the HSAC support is decorated with a Pt/ruthenium (Pt/Ru) alloy rather than pure Pt to improve the carbon monoxide tolerance of the anode. The morphology of the catalyst and its stability during simulated fuel cell ramping up conditions are analyzed in chapter 5. Additionally, the catalyst redistribution during real fuel cell operation is studied and presented in chapter 6.
2 Fundamentals

High-temperature polymer-electrolyte-membrane fuel cells are the object of interest in the present research work where their operation characteristics and accompanying degradation phenomena are studied for different catalyst and support materials. This chapter firstly addresses the basic assembly and the operation principle of HT-PEMFCs (chapter 2.1), then introduces operation related degradation mechanisms (chapter 2.2) and finally summarizes the structure and properties of different catalyst and support materials studied in the present work (chapter 2.3).

2.1 High-temperature polymer-electrolyte-membrane fuel cells

The correlation between the construction and the operation principle of HT-PEMFCs can best be illustrated by a multiscale transition from the macroscopic fuel cell stack, which is the centerpiece of a fuel cell (Figure 2.1a and Figure 2.1b), down to its micro- and nanoscale architecture, which is the focus of this research work (Figure 2.2). A photograph of a real FC stack is presented in Figure 2.1a and a schematic sketch illustrating its construction is shown in Figure 2.1b. The FC stack is composed of repetitive units of bipolar plates and membrane-electrode-assemblies (MEAs) which are located between two endplates. The total number of these repeat units determines the voltage supplied by the stack.

The bipolar plates not only support the mechanical stability of the whole FC stack, they also have channels to distribute different gases uniformly over the whole cell without mixing them up.
Furthermore, they are used for current collection and for the temperature control of the stack.\textsuperscript{121-123} The MEAs, on the other hand, are responsible for the conversion of the reactants’ chemical energy to electrical energy and heat. To accomplish this decisive process, they are subdivided into several functional layers as schematically displayed in Figure 2.2.\textsuperscript{52} The construction of MEAs is symmetrical, where the center is formed by the polymer based membrane and adjacent, the electrodes (anode and cathode) are located (Figure 2.2). Both anode and cathode are separated into a catalyst layer (CL, adjacent to the membrane), a microporous layer (MPL) and a gas diffusion layer (GDL).

The operation principle of HT-PEMFCs is based on a simple redox reaction. At the anode side, hydrogen (H\textsubscript{2}) is oxidized to form protons and electrons. The associated H\textsubscript{2} oxidation reaction (HOR) is presented in Equation 2.1. The electrons and protons are then transported to the cathode side via separate paths. The protons traverse the membrane while the electrons supply an end-consumer. At the cathode side, oxygen is reduced by the electrons, and in the presence of protons, water is formed (see oxygen reduction reaction (ORR) in Equation 2.2). The total redox reaction is given in Equation 2.3.

\[
\text{HOR:} \quad \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \quad \text{Eq. 2.1}
\]
\[
\text{ORR:} \quad \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad \text{Eq. 2.2}
\]
\[
\text{Total:} \quad 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \quad \text{Eq. 2.3}
\]

The total reaction enthalpy $\Delta H$ equals -241.82 kJ/mol.\textsuperscript{124} Thus, in addition to water, heat is released at the cathode side. The designed operation temperature of HT-PEMFCs is around 160°C, although the produced heat may cause a remarkable temperature increase. For this reason, the fuel cell stack
needs to be cooled during operation, and the derived thermal oversupply can be used by the end-consumer as well.

To prevent mixing of the anodic reactant $\text{H}_2$ and the cathodic reactant $\text{O}_2$, the two half cells of the anode and cathode side need to be separated. Therefore, organic polymer polybenzimidazole is incorporated as membrane in the center of each MEA (see orange area in Figure 2.2). However, the fuel cell can only be operative if the ionomer is permeable for protons and simultaneously an electron insulator. Since the PBI material itself is an insufficiently slow proton conductor, its proton conductivity is enhanced by phosphoric acid doping.

The anodic and cathodic catalyst layers are located adjacent to both sides of the ionomer (see Figure 2.2). There, the two half-cell reactions (HOR and ORR, described in Equation 2.1 – Equation 2.2) are catalyzed to ensure a continuous fuel cell operation. Nanoparticles composed of Pt or Pt-based alloys (for example, Pt/Ru) are usually used as catalysts, which are deposited on a specially designed support. To render a material suitable as catalyst support, it needs to fulfill several criteria: electron and proton conductivity, a large surface to maximize the number of catalyst-support contact areas, a strong interaction with the catalyst and an overall stability in the electrochemical environment of HT-PEMFCs.

It is essential to establish and preserve a three-phase boundary between reactants, the catalyst and the ionomer. The electrochemical reactions presented in the Equations 2.1 – 2.3 can only take place continuously, when all three components are connected to each other. MPL and GDL are therefore designed to distribute the reactants uniformly over the whole cell. This is done by the wide pore system of the GDL and the finer pores of the MPL. The optimum fuel cell performance is enabled by a smooth interaction among all the components described. However, there are several obstacles to consider in designing an HT-PEMFC, as will be discussed in the following chapter.

### 2.2 Fuel cell degradation mechanisms during operation

Operation related degradation is a key point to control in order to extend the life time of fuel cells. Several degradation mechanisms can occur on the micrometer and nanometer scales as will be summarized and discussed in this chapter. More information can be found in literature.

#### 2.2.1 Degradation of functional layers

Thinning of the functional layers, especially of membrane and catalyst layers, is occurring in the micrometer scale range. As was explained in chapter 2.1, the membrane in HT-PEMFCs is composed of the heat resistant, organic polymer PBI that needs to withstand harsh conditions: the elevated FC operation temperatures of 160°C, the oxidizing and reducing environment in the adjacent anode and cathode sides and the presence of phosphoric acid. Consequently, the impact of extended fuel cell
operation can be observed by a progressive thinning. As long as the polymer layer remains, the occurrence of the thinning is acceptable. Problems arise when holes are present. The reactants can pass through holes in the PBI layer to their counter electrode, where they directly react to form water. The result is an uncontrollable generation of heat and hence a failure of the affected single cell. Since all single cells are connected in series, the whole fuel cell stack would suffer progressive deterioration, eventually resulting in a complete failure.

The most commonly employed material for catalyst support is high-surface-area carbon. However, a progressive thinning of the anode and cathode catalyst layers due to carbon corrosion can be observed with ongoing fuel cell operation. The mechanism of carbon corrosion is schematically displayed in Figure 2.3.

Due to the different standard potentials on both sides (E°(Anode) = 0 V, E°(Cathode) = 1.23 V), the impact of carbon corrosion is more severe at the cathode side. Additionally, elevated operation temperatures of ca. 160°C further intensify this effect. Consequently, the catalyst nanoparticles located on the carbon support are found to detach or approach each other until contact, thus reducing the catalytically active surface of the catalyst and the overall extent of the three-phase boundary. Several approaches are established to overcome carbon corrosion, including different synthesis strategies, addition of stabilizing elements or a complete replacement of carbon.

### 2.2.2 Degradation of the catalyst

Reactions can only be catalyzed on accessible surface areas of a catalyst, while bulk atoms are inactive for catalysis. Therefore, the aim is to design catalyst structures with a surface/volume ratio as high as possible. For example, in spherical particles with a diameter of 2 nm, ca. 50% of the atoms are located on their surface. However, large surface areas are energetically not favorable, and thus nanoparticles tend to suffer degradation during fuel cell operation. On the nanometer scale, catalyst degradation mechanisms of single-element particles (e.g. Pt) can be assigned to four specific processes: dissolution, Ostwald ripening, agglomeration and particle detachment (Figure 2.4a – Figure 2.4d). For particles formed by at least two elements (e.g. Pt/Ru), dealloying can occur additionally. On the atomic scale, catalyst poisoning by surface adsorption of impurities like CO, S, NO₃ or Cl can reduce the catalytic activity. The following description focuses on the degradation behavior of pure Pt.
nanoparticles and Pt/Ru alloys as these are studied as catalyst species in the present research work to accomplish the ORR and HOR described in Equations 2.1 – 2.3.

Figure 2.4: Schematic drawing illustrating the mechanisms of a) dissolution, b) Ostwald ripening, c) agglomeration, d) particle detachment. The image is modified from Meier et al.37.

Dissolution and dealloying

Particle dissolution is among the main degradation mechanisms that occur during fuel cell operation (Figure 2.4a37). In general, the dissolution rate depends on factors including the pH value, the type of acid, the temperature, the maximum potential value and the potential dynamics38, 39, 145-149 In the case of pure Pt bulk material, the Pourbaix diagram150 predicts thermodynamic stability in a wide pH and potential range. However, Pt bulk material can also dissolve, as it is exposed to conditions typically present in HT-PEMFCs: pH values lower than 2 and potential values higher than 0.85 V_RHE. Additionally, the operation temperature of 160°C and the size of the Pt catalyst, which come in form of nanoparticles instead of a bulk phase, promote its dissolution. Furthermore, the roughness and the surface plane of Pt nanoparticles also influence the solubility. According to Komanicky et al.151, primary locations for dissolution are high-index surfaces as well as edge and corner sites of particles. Two main pathways can be found in literature that describe the atomic process of Pt dissolution during fuel cell operation: a direct oxidation of Pt to Pt^{2+} (Equation 2.4) or Pt oxidation with an intermediate surface oxide formation (Equation 2.5 and 2.6)146, 152-153

\[ \text{Pt} \rightarrow \text{Pt}^{2+} + 2e^- \]  
\[ \text{Pt} + \text{H}_2\text{O} \rightarrow \text{PtO} + 2\text{H}^+ + 2e^- \]  
\[ \text{PtO} + 2\text{H}^+ \rightarrow \text{Pt}^{2+} + \text{H}_2\text{O} \]

Upon dissolution, Pt ions are not bound to one specific site and they can start to migrate. Generally there are three different locations reported, where the catalyst can be found:
i) Pt can be present in the water stream that exits the fuel cell. This is the worst possible case since these catalyst species are lost for catalysis.

ii) Pt nanoparticles were found to be present in the ionomer after fuel cell operation.\textsuperscript{115-116, 144, 148, 154-158} Disagreement prevails in literature whether Pt dissolution only takes place at the cathode side or both electrodes are affected. Yet there is a scientific consensus that the catalyst particles present in the ionomer were formed by periodically repeated ion deposition and particle dissolution with intermitted ion diffusion rather than migration of whole nanoparticles. A detailed analysis of this phenomenon has been performed in this work for the case of HT-PEMFCs (chapter 6).

iii) The third possibility for previously dissolved Pt ions to redeposit is the surface of other catalyst nanoparticles. This process is known as Ostwald ripening and causes particle growth.\textsuperscript{159-161}

**Ostwald ripening**

Ostwald ripening is one of two mechanisms that explains particle growth during fuel cell operation. Upon dissolution, a part of the dissolved platinum redepsoits on the surface of bigger particles which further grow in size (Figure 2.4b\textsuperscript{37}). Simultaneously, the surface/volume ratio and surface energy of these particles decrease.\textsuperscript{159-161} The occurrence of Ostwald ripening during fuel cell operation in a real MEA can be demonstrated by plotting the catalyst particle size distribution over the operation time. A progressively forming tail towards smaller particles sizes is reported to be indicative for the occurrence of Ostwald ripening.\textsuperscript{38}

**Agglomeration and coalescence**

The second degradation mechanism that explains particle growth is agglomeration with subsequent coalescence.\textsuperscript{52, 162} This mechanism defines a process during which at least two separate particles merge to one bigger sized sphere with a decreased surface/volume ratio (Figure 2.4c\textsuperscript{37}). The most decisive requirement to enable agglomeration is particle contact. Generally, one can distinguish between three different types of agglomeration.\textsuperscript{57-58, 76, 143, 163} If two particles are in contact, surface diffusion can take place at elevated temperatures and as a result, the two particles merge to one bigger particle. In the other two cases, contact between particles needs to be established first. This can either occur due to migration of whole particles on the surface of their support or due to corrosion of the support that brings the particles closer together. Corrosion of HSAC support materials has been reported (Figure 2.4).\textsuperscript{37}

**Particle detachment**

Carbon corrosion can give rise to the detachment of whole particles from their support (Figure 2.4d\textsuperscript{37}). As a result, the electric contact between the catalyst and its support is lost and catalysis cannot proceed in this state.\textsuperscript{49, 56-57, 162}
**Catalyst poisoning**

The most efficient and frequently employed electrocatalyst in fuel cells has been and is still Pt. However, Pt catalyst poisoning occurs with ongoing fuel cell operation. Especially at the anode side of HT-PEMFCs, where the voltages present typically do not exceed 0.5 V, catalyst poisons like Cl, CO, NOx, or SO2 are known to adsorb on the surface of Pt and are hardly removed.\(^78\)\(^-\)\(^80\) As a result, the accessible surface area of Pt diminishes with ongoing fuel cell operation. In the case of HT-PEMFCs, which are fueled at the anode side by previously reformed natural gas, CO is present to a small extent (roughly 1.2 Vol-%). Due to the constant supply of freshly formed and slightly contaminated H2, the amount is sufficient to progressively reduce the catalyst’s performance at the anode side. Additionally, due to the low abundance and high cost of Pt, replacement of the noble metal has been suggested.\(^84,\)\(^164\)\(^-\)\(^165\) Several research groups studied Pt-based alloys with different alloying elements like Ce\(^166\), Co\(^166\), Fe\(^166\)\(^-\)\(^167\), Ni\(^166\), Mo\(^166\), Os\(^166\)\(^-\)\(^168\), Pb\(^166\), Pd\(^169\), Rh\(^166,\)\(^168\), Ru\(^99,\)\(^166\)\(^-\)\(^167,\)\(^169\)\(^-\)\(^170\)\(^-\)\(^177\), Sn\(^166,\)\(^168\) and W\(^166,\)\(^168\). Pt-free electrocatalysts have also been employed.\(^178\)\(^-\)\(^183\) In the present work, pure Pt is replaced by a Pt/Ru alloy. Two mechanisms are proposed in literature to reduce the CO poisoning effect of this system, depending on the overpotential present at the anode. At low overpotentials, Ru has an electronic effect on the 5d-band structure of Pt,\(^176,\)\(^184\)\(^-\)\(^187\) while at high overpotentials, water splitting and subsequent CO oxidation take place on Ru sites.\(^172,\)\(^176\) Both cases promote desorption of CO from the surface of Pt. However, it is also known and frequently reported that Ru has a slightly lower stability compared to Pt in the electrochemical environment of a fuel cell.\(^188\)\(^-\)\(^189\) Therefore, dealloying and also Ru diffusion into the membrane as a result of dissolution is proposed to be the main degradation mechanism of Pt/Ru alloys.\(^189\)\(^-\)\(^190\)

### 2.3 Investigated materials

Operation performance and degradation behavior of HT-PEMFCs depend on the choice of material used as electrodes, membrane and catalyst. To guarantee an extended fuel cell life-time of more than 40000 working hours, a good stability at an elevated operation temperature of 160°C in an electrochemical environment is crucial. The most important structural and thermodynamic properties of the materials used in the present work are summarized in the following. The investigated HT-PEMFCs were studied in cooperation with the company ELCORE GmbH. Fuel cells were prepared and electrochemically characterized by ELCORE GmbH, and the most promising and interesting samples were studied in-depth at the MPIE using different electron microscopic techniques.

#### 2.3.1 Electrodes

**Catalyst material**

As catalyst materials, pure Pt and a Pt/Ru based alloy are used. Pt is known to adopt the face centered cubic (fcc) lattice; all relevant structural details are given in Table 2.1.\(^191\) In the present work, two
different morphologies of Pt were designed: nanoparticles and porous networks. In both cases, the catalyst exhibits a high surface/volume ratio, which is crucial for an efficient fuel cell performance. Ru, on the other hand, has the hexagonal close packed (hcp) structure with the crystallographic details presented in Table 2.1.\textsuperscript{191} According to the phase diagram, a miscibility gap exists between Pt and Ru.\textsuperscript{192} However the Pt/Ru threshold ratio for the phase transformation depend on whether the system is in its equilibrium state or not.

<table>
<thead>
<tr>
<th></th>
<th>Pt</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>cubic</td>
<td>hexagonal</td>
</tr>
<tr>
<td>Lattice constants [Å]</td>
<td>a = 3.9231</td>
<td>a = 2.7039</td>
</tr>
<tr>
<td></td>
<td>c = 4.2817</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>Fm3m</td>
<td>P6\textsubscript{3}/mmc</td>
</tr>
</tbody>
</table>

**Catalyst support material**

High-surface-area carbon materials are widely used as support for catalyst nanoparticles in HT-PEMFCs. They exhibit several advantages: electron conductivity, a high surface area to guarantee a widespread distribution of the catalyst nanoparticles and a good anchoring for them. In the present work, amorphous carbon is employed at the cathode side and tungsten suboxide (WO\textsubscript{3-x}, chapter 4) or turbostratic carbon (chapter 5 and chapter 6) at the anode side. Carbon corrosion in the electrochemical environment of fuel cells is reported in literature.\textsuperscript{52, 57, 138-139} WO\textsubscript{3-x} is an alternative candidate for the anode side as replacement for HSAC.\textsuperscript{70} It is an n-type semiconductor exhibiting a band gap in the range of 2.6 – 2.8 eV.\textsuperscript{130} Proton conductivity is ensured by hydrogen spill over and the subsequent formation of tungsten bronzes.\textsuperscript{195-197} Moreover, its high corrosion resistance, stability in an electrochemical environment, high melting temperature (1700°C) and good CO tolerance render it a suitable and durable replacement for carbon.\textsuperscript{130, 197-199}

### 2.3.2 Membrane

As membrane material, cross-linked, phosphoric acid doped polybenzimidazole is used (Figure 2.5). It is a heterocyclic, organic thermostable that is heat stable in the HT-PEMFC operation temperature range of 160°C. The PBI material itself exhibits neither electron nor proton conductivity. And while it is vital for an efficient fuel cell operation to maintain the membrane insulating for electrons, on the other hand permeability for protons is important. Proton conductivity is implemented by doping the PBI with phosphoric acid.\textsuperscript{35-36, 107, 110}
Figure 2.5: Drawing of the chemical structure of polybenzimidazole used as membrane for HT-PEMFCs.
3 Characterization methods

This chapter introduces characterization methods that were applied while studying different components of the MEAs of HT-PEMFCs. The main focus lies on electron microscopy based techniques and in addition, electrochemical analysis methods were applied. A brief description of the different methods is given below. More details can be found in textbooks.13-44, 200-204

3.1 Electron microscopy

Electron microscopy is an imaging and analytical method that gives insight into the micrometer, nanometer and even sub-nanometer scale range of a region of interest.44 There exist different design strategies to build a variety of microscopes that cover the whole magnification range from the micrometer scale down to the atomic level, yet all of them are based on the same fundamental principle: electron-matter-interactions are intendedly induced and depending on the nature of the resulting signals, different characteristics of the sample can be studied. Therefore, a variety of detectors are needed and applied to an electron microscope in designated positions. Figure 3.1 summarizes the different types of signals that are generated when an electron beam interacts with the atoms of a specimen.

![Figure 3.1: Schematic drawing of possible interactions between an electron beam and a sample.](image)

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In a first instance one can differentiate between elastically and inelastically scattered electrons. Elastically scattered electrons, to which also backscattered electrons belong, are deflected by the atoms of the sample while they conserve their overall energy. As opposed to this, inelastically scattered electrons transfer a part of their energy to the electrons of the specimen. As a result, additional electrons (secondary electrons or Auger electrons) or photons (X-radiation or bremsstrahlung) are emitted. Secondary electrons are generated when an electron from the incident beam knocks out an electron from one of the outermost shells of an atom of the sample. During this process, the primary electron transfers a part of its energy to the secondary electron. The amount of transferred energy is unspecific and no conclusions can be drawn regarding the origin of the electron. The case is different for Auger electrons and X-rays. Both signals carry information of their origin atom, however their evolution is based on a competitive process. In both cases, a primary electron knocks out an electron from an inner shell of an atom of the sample. The resulting, energetically favorable hole is filled by another electron located in an orbital farther away from the core of the same atom. This process generates excess energy which needs to be released. Thus, the atom can either emit an X-ray or another electron from the outermost shell. In either case, the energy of the released signal is element specific and can be used for elemental analysis. Light elements have higher probabilities to emit Auger electrons, while heavier elements preferably generate X-rays. Bremsstrahlung on the other hand, is a non-specific radiation and originates when an electron is decelerated in the Coulomb field of an atom. In an SEM, bulk materials usually are studied, thus the only detectable signal is the one that exits the sample through the surface. Hence detectors in the SEM are mounted above the sample. In contrast, TEM samples need specialized preparation techniques to have a thickness of 100 nm and less. In this case, electrons transmit the sample and signals are detected above and below.

3.1.1 Scanning electron microscopy

In an SEM, a focused electron beam is scanned over a region of interest and the subsequently emitted secondary electrons, backscattered electrons or X-rays are detected. Thus, SEM is the method of choice in order to characterize micro- and nanometer scale features on the surface of a specimen, to determine the distribution of different materials or to analyze the thickness of layers. In the present work, two machines were used to perform SEM analysis: a JEOL JSM 6490 and an AURIGA ZEISS SEM.

Overview micrographs of cross-sectional samples were obtained in the JEOL SEM operated at 15 kV using the backscattered electron (BSE) detector. As mentioned in chapter 2, different Pt catalyst loadings are usually applied in the anode and cathode catalyst layers, and the lighter element Ru was used additionally in the anode. Since the amount of detectable backscattered electrons depends on the beam current and the atomic number of the atoms in the specimen, the utilization of the latter named effect is a reliable method to distinguish the different functional layers of an MEA to study their quality and mean width over wide areas (chapter 6).
High-resolution SEM micrographs were obtained using the in-lens secondary electron detector of the ZEISS machine and an acceleration voltage of 3 kV – 5 kV. This was essential for the investigation of porous Pt networks exhibiting an overall size of a few micrometers and fine features in the nanometer scale (chapter 4). However, single nanoparticles with a mean diameter of a few nanometers were not resolved by this machine. EDX measurements were performed in both JEOL and ZEISS SEM machines at an acceleration voltage of 15 kV using the attached standard EDAX detectors.

SEM sample preparation was performed in two ways, depending on the area of interest. Fuel cell catalyst layers and the GDL were prepared as SEM top view samples. Therefore, small pieces were cut off the electrode or the MEA and glued onto an aluminum SEM sample holder with the layer of interest facing up. On the other hand, cross-sectional samples of whole MEAs were prepared by cutting rectangular pieces off the MEA with the help of a scalpel and fixing them in an aluminum clamp, mounted with the cross-section facing up.

### 3.1.2 Transmission electron microscopy

In-depth characterization of differently shaped and compounded catalyst particles on their support material was performed with the help of TEM. Two machines were used: a JEOL JEM-2200FS operated at 200 kV and an FEI 60 – 300 Titan Themis operated at 60 kV and 300 kV.

The JEOL TEM is equipped with a charge-coupled device (CCD) camera from Gatan exhibiting a pixel size of 2048 x 2048, an EM-24630UHADF STEM detector from JEOL and an EDX detector from JEOL exhibiting a 30 mm² detection area. Annular dark field (ADF) and high-angle annular dark field (HAADF) STEM measurements were carried out using a camera length of 40 mm. Hence the ADF detection scattering semi-angle was in the range of 10 mrad and ~170 mrad and in the case of HAADF measurements the inner scattering angle was larger to cut off contributions from Bragg contrast.

The Titan Themis is equipped with a Cs corrector for the condenser system and a monochromator. STEM imaging can be performed by use of the attached HAADF detector from Fischione Instruments (model number M3000). At a camera length of 100 mm the HAADF detection scattering semi angle was 73 mrad – 352 mrad, at a camera length of 77 mm it was in the range of 96 mrad – 450 mrad and at 60 mm camera length, electrons in the scattering range of 123 mrad – 552 mrad were detected. A 70 µm condenser aperture was used in STEM mode, the convergence angle was standardly set to 23.8 mrad and a spot size around 1.5 Å (Spot 6) was employed. Quantitative EDX analysis was performed by use of the attached Super X-EDX detector from Bruker. It consists of four silicon drift detectors (SDD) with a total active area of 120 mm² and a solid angle of collection of 0.9 srad. Diffraction analysis was performed using a selected area diffraction aperture exhibiting a diameter of ca. 200 nm and the attached BM Ceta camera from FEI with a pixel size of 4096 x 4096.

The basic setup of the two TEM machines that were used in the present work is displayed in Figure 3.2 and the most important components and devices are highlighted.
Characterization methods

TEM mode and STEM mode are based on two contrary imaging techniques and the resulting micrographs help to interpret different aspects of the investigated samples.

In TEM mode the specimen is illuminated by an ideally parallel electron beam and only non-deflected or elastically scattered electrons are used for imaging. Light elements and amorphous areas appear bright in TEM mode while heavy elements or crystalline parts appear dark when only the central beam is used. Generally the TEM measurement mode can further be sub-divided into conventional TEM (CTEM) and high resolution TEM (HRTEM). In CTEM, due to the use of an objective aperture, wide-angle diffracted electrons are cut off and the obtained images are based on an amplitude contrast. In HRTEM on the other hand, no aperture is used and both amplitude- and phase-contrast of Bragg deflected electrons contribute to the imaging. Additionally, for thin samples the assumption is made that the amplitude of the electron wave stays constant and only its phase changes (weak-phase object). As a consequence it is not possible any more to directly correlate the actual positions of the atoms in the sample with their locations in the obtained HRTEM micrographs. The only chance to do so would be the simulation of the obtained micrographs e. g. by use of the commercially available program JEMS.

In the present work, with the help of CTEM, large overview areas were depicted to study the distribution of both support material and catalyst particles over a wide range. HRTEM on the other hand was used to investigate the crystallinity of individual nanoparticles. This can be done either by
measuring the average distance between single lattice planes or by calculating the Fourier transform of crystalline areas and measure the d-values in the reciprocal space.

Additionally, electron diffraction analysis was carried out in TEM mode. With the help of a selected area diffraction (SAD) aperture, areas of interest were chosen and electron diffraction patterns were obtained from them. This way, the crystallinity of overview areas was studied without allocating lattice planes to single particles.

In STEM mode the electron beam is focused to one spot and systematically scanned over an area of interest. Thus, similar to an SEM, interactions of the incident electrons with the atoms of the sample are recorded for each spot and the resulting micrographs are created progressively. The benefit of this acquisition technique is that electron energy loss spectroscopy (EELS) and EDX can be performed simultaneously at high resolution. The detector system in STEM mode is based on annular bright field and dark field detectors and the detection semi-angle defines the nature of electrons that contribute to the acquired micrograph. For the DF detectors, the intensity in the obtained micrographs is related to the average atomic number of the elements (I ~ Z^2 in HAADF STEM micrographs) or the orientation of crystals in the specimen (in ADF STEM micrographs). In the work in hand the ADF and HAADF detectors were mainly used. ADF STEM was the method of choice to obtain micrographs of the high-surface-area Pt networks on WO_3_x in the JEOL TEM (chapter 4). HAADF STEM micrographs were obtained in the FEI Titan TEM to study the degradation behavior of the Pt/Ru catalyst on its carbon support (chapter 5 and chapter 6). Especially in the latter named example, HAADF STEM offers an easy way to distinguish between the heavy metal particles and the light carbon support. Additionally it would be even possible to distinguish between Pt and Ru solely by their contrast in HAADF detection. However, this was not feasible in the samples presented here. The two elements formed alloys rather than separated element-pure particles or core-shell structures.

EDX measurements were as well performed in STEM mode. This way it was possible to obtain elemental distribution maps of previously defined areas and locally quantify the elemental composition of particles.

Additionally tilt series at defined tilt angles were obtained in STEM mode in both JEOL and FEI TEM. A detailed explanation of requirements and acquisition methods is described in the following chapter which is based on electron tomography (chapter 3.1.3).

### 3.1.3 Electron tomography

Electron tomography was performed to obtain information on the three-dimensional volume and surface expansion of different catalyst particles on their support material. A thoroughly measured tilt series is the basis of a successful reconstruction of an area of interest. Both TEM machines described in chapter 3.1.2 were used: The JEOL TEM and a single tilt holder from JEOL were used to acquire a tilt series of a catalyst network (see chapter 4). The image acquisition was performed in STEM mode by use of the attached ADF detector. Tilt angles were chosen according to the schema of Saxton et al.\textsuperscript{208}: small tilt increments at high tilt angles and larger tilt increments around the 0–projection. This
method is useful to minimize the missing wedge effect since due to device specific restrictions of TEM and holder, tilt angles not larger than 80° can be adjusted. For the acquisition of the tilt series, a previously fabricated FIB lamella was used. In the end, undesired overlap and sample thickness at higher tilt angles caused a reduced tilt range of +28.0° – 44.1° that was used for the final reconstruction.

The degradation behavior of Pt/Ru catalyst alloys was studied by acquiring high resolution HAADF STEM micrographs at defined tilt angles in the FEI Titan Themis TEM by use of a single tilt holder from FEI. Scratch samples were prepared and drop casted on carbon-coated Au finder grids. The maximum adjustable tilt range was +/- 60°; higher tilt angles caused an overlap of the investigated catalyst structure with the Au net of the grid. Tilt increments were chosen to be 10° and the acquisition was performed in two intervals of 20° steps each. An acquisition protocol, starting with a first, rough tilt series (60°, 40°, 20°, 0°, -20°, -40°, -60°) followed by the refining, intermediate angle steps (-50°, -30°, -10°, 10°, 30°, 50°) allows to register changes of the catalyst particle when the first and last micrographs are compared. This is crucial for a successful and reliable reconstruction.

The full reconstruction procedure, starting from the obtained tilt series and ranging to the final 3D volume, was performed according to a protocol of A. Wisnet and will be described briefly in the following. Generally, the quality of the final reconstruction is strongly dependent on the initially performed image processing routine of the obtained tilt series. The freeware called ImageJ is used for this. First, with the help of the plugin Tomof, the translational motion of the series is roughly aligned and further refined by the landmarks based alignment where a 3D correction of the tilt axis is performed. Sometimes this last step needs manual support in case the automatic mode fails to generate landmarks. A further important step in the image processing routine is the background subtraction to exclude its influence on the final reconstruction. After all required steps have been performed successfully, the files of the aligned tilt series are converted to .em-files for a further processing by the TOM software toolbox in the commercially available software package MATLAB (Matlab R2013a, The MathWorks Inc., Natick, MA). Here, a mask is generated in a first step to define a rough volume inside which the particle is located. Afterwards the simultaneous iterative reconstruction technique (SIRT) is used to calculate the intensity of each voxel within this predefined volume. This is done in 15 – 20 iterations with the help of the previously aligned tilt series.

The intensity distribution of the calculated voxels is used to define material values for the final discrete algebraic reconstruction technique (DART). The distribution of up to five different materials can be reconstructed in this step. However, their previously calculated intensity values, which are extracted from TEM or HAADF STEM micrographs, must differ significantly; otherwise it is not possible to distinguish between them. This problem occurred in the present work when the distribution of Pt and Ru within Pt/Ru catalyst particles was planned to be featured. Since the two elements formed differently composed alloys instead of separate particles, the resulting intensity in the HAADF STEM micrographs barely altered. Nevertheless it was possible to reconstruct the volume of the Pt/Ru catalyst alloys and thus obtain all required 3D information like interconnection of chains and the overall accessible surface area (chapter 5).
3.1.1 TEM sample preparation

Several approaches can be applied to obtain electron transparent samples of less than 100 nm thickness, which is a crucial requirement to perform in-depth TEM investigation. Firstly, the preparation of scratch samples can be performed. Additionally, there is the possibility to manually prepare conventional cross-sections by grinding, dimpling and ion milling the sample as described by Strecker et al.\textsuperscript{219}, or by using a tripod.\textsuperscript{220-221} Another way is the utilization of a focused ion beam in an SEM to prepare site specific TEM samples. Generally the method of choice depends on the type of sample and the information one is aiming for. In the present work, only FIB samples and scratch samples were prepared, and the two methods will be described in the following subsections.

**Scratch samples**

The preparation of scratch samples is a fast and cheap method to obtain electron transparent samples for TEM investigations. Using a scalpel, a small fraction of the surface of a sample is scratched off and ultra-sonicated in 2-propanol/water (1:1) for 10 min. Subsequently, one droplet of the obtained suspension is dripped onto a TEM grid and dried for several hours in air. The choice of grid depends on the measurement that is planned. In the present work, carbon-coated gold (Au) finder grids were used. They have letters at defined intervals on junctions of the Au net, so that the TEM user can find previously measured areas again. The finder grids have been purchased from Plano.\textsuperscript{222} Unfortunately, the TEM scratch sample preparation procedure is not suitable for all types of samples. In the present work, it was used for catalyst nanoparticles that are deposited on different high-surface-area carbon support materials. However, the method is neither suitable for the PBI based membrane of an HT-PEMFC nor for µm-sized networks of Pt. In both cases, site specific sample preparation needs to be performed as it is enabled by using a FIB microscope.

**Focused ion beam sectioning**

Two machines were used to accomplish FIB sample preparation: a ZeissNVision 40 FIB microscope and an FEI Helios NanoLab600, both integrated in an SEM. A view of the chamber of the FEI machine with the SEM and FIB guns exhibiting an angle of 52° between them is displayed in Figure 3.3a. Starting from a bulk specimen, the conventional lift-out technique was performed to obtain thin samples with a thickness of less than 100 nm.\textsuperscript{223} The sequence of steps is the same in both machines and also the applied acceleration voltages are similar. However, specific values regarding the beam current differ in the ZEISS and the FEI microscopes. For this reason, the parameters named in the following description are only valid for the FEI Helios NanoLab600 machine. The images shown in Figure 3.3 illustrate the basic steps that need to be performed during the preparation of a TEM lamella; the secondary electron micrographs are taken from different samples and during different preparation procedures.
Firstly, the gas injection system (GIS) is used to cover the surface of the specimen by a Pt or C deposition layer of ca. 10 µm length and 1 µm width (Figure 3.3b): the bottom layer is electron beam deposited with a height of 0.3 µm (5 kV and 1.4 nA in the SEM) and the top layer is deposited by gallium (Ga) ions with a thickness of ca. 3 µm (30 kV and 48 pA in the FIB). The first layer is applied to protect the surface of the sample in the beginning of the process, and the second one is used to obtain a sufficiently thick protection layer for the subsequent preparation steps without spending too much time on it. Afterwards, the surrounding material is removed with the help of the Ga beam at an acceleration voltage of 30 kV and a beam current of 6.5 nA (Figure 3.3c). The tilt angle of the stage is 52° in this step. The height of the resulting lamella is chosen depending on the region of interest in the sample. If only surface structures will be studied in TEM, ca. 3 µm thickness is sufficient. If the interface region between the membrane and the electrode is of interest, which is perpendicular to the deposition layer on the surface, the lamellae are prepared to have at least 6 µm in height. In the next step, the lamella is cut free from the surrounding sample material at a tilt angle of 0°, and then the lift-out is performed with the help of a manipulator from Kleindiek (Figure 3.3d – Figure 3.3f). After that, the lamella is transferred to a copper grid and attached to it with the help of a manipulator.
Characterization methods

of the GIS (Figure 3.3g). Subsequently, the stage is tilted to angles in the range of 50° – 54° and the region of interest in the lamella is thinned to electron transparency (<100 nm, Figure 3.3h – Figure 3.3i). In the beginning, the acceleration voltage of the FIB is set to 30 kV while the beam current is progressively reduced from 0.45 nA down to 47 pA until the lamella has a thickness of ca. 100 nm. Afterwards, 5 kV acceleration voltage and 15 pA beam current are used for a final polishing step.

3.2 Fuel cell characterization methods

3.2.1 Cyclic voltammetry

In this research work, cyclic voltammetry experiments have been performed both ex-situ on isolated catalyst particles on their support and in-situ on single MEAs of HT-PEMFC stacks.

For the ex-situ measurements, a potentiostat from Gamry instruments (reference 600) was employed and operated using an in-house-developed LabVIEW based software that as well controlled the gas system. As electrolyte, 0.1 M perchloric acid (HClO₄), diluted from concentrated HClO₄ (Merck, Suprapur), was used. The measurements were carried out by Enrico Pizzutilo. The in-situ measurements were performed by the project partners at ELCORE GmbH with an electrochemical workstation from Zahner Elektrik (Zahner PP241 and Zahner IM6ex).

A cyclic voltammogram as typically obtained is displayed in Figure 3.4. It can be divided into two half cycles which are determined by the sign of the measured current: Surface oxidation processes like hydrogen desorption and Pt oxidation occur at the anodic half cycle in the direction of positive current values. At negative current values (the cathodic half cycle), surface reduction processes like Pt-O reduction and hydrogen adsorption take place.

![Cyclic voltammogram](image)

Figure 3.4: Cyclic voltammogram of Pt nanoparticles located on a HSAC support. The characteristic peaks can be attributed to H desorption, Pt oxidation, Pt-O reduction and H adsorption.
The area under the hydrogen desorption peak in the cyclic voltammogram is proportional to the electrochemically active surface area (ECSA) of Pt and used for its calculation.\textsuperscript{19,121} Generally, the shape of the cyclic voltammogram is dependent on the type of electrode used, the ECSA of Pt and contaminants adsorbed to it.

\textit{Ex-situ} measurements were performed to simulate accelerated fuel cell operation, through which the influence of different accelerated degradation protocols on the degradation behavior of the catalyst was studied. For cyclic voltammetry experiments, a non compact three-electrode teflon electrochemical cell was used.\textsuperscript{38} The investigated catalyst was connected to a glassy carbon disc embedded in a teflon rotating disk electrode that can be mounted on a commercial rotating shaft. This construction was used as the working electrode. A graphite rod was employed as the counter electrode and a Ag/AgCl electrode was the reference electrode. All three electrodes were housed in separate compartments. To prevent chloride (Cl$^-$) contamination, a Nafion membrane was applied to separate the reference electrode from the working electrode and the counter electrode. 0.1 M HClO$_4$, saturated with H$_2$, was used as the electrolyte. TEM analysis was performed after designed intervals of potential cycling to visualize the influence of the cyclic voltammetry experiments on the same areas of interest. The execution of alternating cyclic voltammetry measurements and TEM analysis is referred to as identical location (IL) TEM.\textsuperscript{75-76}

\textit{In-situ} measurements were performed to quantify the ECSA of cathodic Pt catalyst nanoparticles in an MEA. The measurements provide insight into the influence of the operation time and varying operation conditions on the degradation of the catalyst. Operation-related changes of the Pt ECSA can be observed. For the measurements, the cathode, which serves as the working electrode, was nitrogen-purged to render it inert. The anode was used as a pseudo-reference electrode and the counter electrode. It was purged with dry hydrogen and the resulting potential was 0 V. To determine the ECSA of the cathodic Pt catalyst, a triangular voltage was applied at the cathode and the resulting current was measured.\textsuperscript{224} In this research work, carbon supported Pt nanoparticles were applied as the cathode catalyst layer and the potential was cycled between 0.095 V and 1.0 V.

### 3.2.2 CO stripping

To analyze the ECSA of the Pt catalyst and investigate the influence of Ru on its CO tolerance, the CO-stripping method was employed and combined with cyclic voltammetry experiments using the following strategy: before and after previously defined numbers of potential cycles, a monolayer of CO was adsorbed to the surface of the catalyst. From the charge it took to oxidize and thereafter desorb CO again, both the electrochemically active surface area and the mass activity of the catalyst were obtained. For the calculation of the ECSA, a charge density of 195 $\mu$C/cm$^2$ was assumed.\textsuperscript{225} The measurements have been performed by Enrico Pizzutilo.
3.2.3 Long term fuel cell test in continuous operation condition

Long term fuel cell degradation tests were performed under real fuel cell operation conditions in stacks consisting of 20 single cells and exhibiting a total active surface area of 153 cm$^2$. The time-dependent change of the potential of each single cell was monitored under a constant load of 0.2 A/cm$^2$ and an operation temperature of 160°C. Air was used as fuel at the cathode side and the anode was fed with reformed methanol exhibiting 1.2 Vol-% CO, 22.8 Vol-% CO$_2$ and 76 Vol-% H$_2$. Typically the cell voltages measured are plotted against operation time and the resulting slope in the diagram indicates the degradation of the stack. The experiments have been performed by the project partners at ELCORE GMBH.

3.2.4 Long term fuel cell test in start-stop cycles

Accelerated fuel cell degradation tests were performed in a cyclic operation mode by use of single cells exhibiting an active surface area of 50 cm$^2$. During the measurement, the single cell was started up until its standard operating status was reached and after that, it was ramped down again. This process usually takes several hours and it can be repeated periodically. During the alternating heating to 160°C and cooling down to room temperature and the periodical load change, the material is electrochemically and mechanically stressed. The operation protocol of start-stop cycles was performed to study the degradation stability of the material used and investigate the reliability of the fuel cell system in case of regularly executed start-ups and shut-downs. One start-stop cycle comprises the following steps which are executed one by one:

- heat single cell to 80°C
- purge cathode with dry air for 5 min
- heat the cell to 120°C
- purge anode with nitrogen and switch on H$_2$ and O$_2$
- heat the cell to 160°C and concomitantly drain power at 0.25 A/cm$^2$
- at 160°C: drain power at 0.5 A/cm$^2$
- hold for 4 h
- cool the cell down to 120°C and concomitantly drain power at 0.25 A/cm$^2$
- at 120°C: switch off the current
- purge anode with nitrogen while the cell is cooled down to room temperature for 4 h

The strategies for this accelerated degradation protocol were developed by Reiser et al. and the measurements were executed by the project partners at ELCORE GMBH.
4 Growth of porous platinum catalyst structures on tungsten oxide support materials: A new design for electrodes

In this chapter, the growth of porous Pt catalyst structures on a tungsten suboxide (WO$_{3-x}$) support material is reported. It is based on publication$^{227}$. An in-depth TEM study of the distribution and growth behavior of Pt on WO$_{3-x}$, including elemental distribution maps and electron tomography is presented in the following.

4.1 Literature overview

Catalysts are used in a wide variety of applications. Their purpose is to decrease the activation energy of a chemical reaction without taking part in the reaction itself. In polymer-electrolyte-membrane fuel cells (PEMFCs), catalysts promote the oxidation of hydrogen to protons and electrons at the anode and the reduction of oxygen at the cathode side. The overall exothermic formation of water during fuel cell operation efficiently provides power for the operation of electric motors, but also releases heat that can be used by end consumers.$^{128}$ The corresponding reverse reaction of water electrolysis in turn requires catalysts that reduce the energy, required for the endothermic splitting of water, to form oxygen and hydrogen.$^{228}$ To maintain a maximum amount of catalytic activity throughout a long time period, the used material not only needs to be active but also stable in the environment of its field of application. This involves mainly chemical and mechanical stability but also a high tolerance against catalyst contaminants like CO, NO$_x$, or SO$_2$.$^{78-80}$ The most commonly used catalyst materials in PEMFCs currently are either highly dispersed Pt nanoparticles or Pt alloys. The research focus at the moment is set on reducing the amount of noble Pt required, or even replacing it completely with more abundant materials.$^{88,229-233}$ Ideally, since the catalyst material is not consumed, it would be sufficient to use only a relatively small amount of catalyst material per surface area of the support material.$^{234}$ The catalyst loading varies in different fields of application and depends on the activity of the catalyst material toward its catalyzed reaction. At the anode side of PEMFCs the Pt loading can be reduced to as low as 0.05 mgPt/cm$^2$ without any significant performance loss. In contrast, the kinetics of the oxygen reduction reaction on Pt at the cathode side are about 6 orders of magnitude slower, so that higher Pt loadings of up to 0.4 mgPt/cm$^2$ are necessary.$^{235-236}$ Catalyzed
reactions only take place in areas accessible to the reactants, which mostly are the surfaces of the catalyst material. For this reason, a decisive factor in catalysis is the surface to volume ratio. In many applications catalysts can be found in the form of dispersed nanoparticles exhibiting a diameter in the range of several nanometers, but porous materials are also under investigation. In the latter case, templates are usually required to obtain nanoporous morphologies. The support material on which the catalyst is deposited plays a major role in the performance of the whole system. High-surface-area carbon materials are widely used as support for Pt nanoparticles in PEMFCs. However, long-term and dynamic operation modes show constantly recurring phenomena: Pt nanoparticle detachment, diffusion, dissolution, agglomeration and Ostwald ripening. Moreover, oxidation of the carbon material occurs in the oxidizing environment at the cathode of a fuel cell. To reduce these impacts, the carbon support material can be replaced for instance by a polycrystalline tungsten suboxide (WO$_{3-x}$) support. WO$_{3-x}$ is a semiconductor that forms tungsten bronzes in the presence of H$^+$. We found that depositing Pt on WO$_{3-x}$ support material leads to a self-organized, highly porous, octahedral shaped Pt catalyst network. The Pt network loaded on WO$_{3-x}$ support has been successfully applied previously as an anode in high-temperature PEMFCs (HT-PEMFCs), which were operated for up to 2000 h in accelerated and continuous fuel cell tests. Electron microscopy and electrochemical analysis of the ready-to-use and operated fuel cells of the Pt loaded WO$_{3-x}$ system (Pt/WO$_{3-x}$) have been performed and compared to a standard Pt loaded high-surface-area carbon system (Pt/C). The slightly lower cell voltages of Pt/WO$_{3-x}$ compared to Pt/C are balanced out by the lower degradation rate of Pt/WO$_{3-x}$ during fuel cell operation. As such, the HT-PEMFCs using Pt/WO$_{3-x}$ are expected to outperform fuel cells using Pt/C with ongoing operation time. The excellent long-term stability and reduced degradation behavior of the Pt loaded WO$_{3-x}$ based anodes were demonstrated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis.

While the performance of Pt on WO$_{3-x}$ has been thoroughly studied, the synthesis process is not well understood so far. The question, how the catalyst morphologies form, remained open. Therefore, in the present work we analyze the growth of the porous Pt morphologies in depth. We modify the deposition time of Pt and investigate the architecture and the meso- and microscopic growth procedure of the three-dimensional (3D) Pt networks. In addition, the important extent of the active surface area of the formed catalyst structures is studied in the present work by electron tomography and compared to electrochemical evaluation. This work focuses on the growth behavior of a self-organized, nanoporous 3D Pt network as a durable, long-term stable, and active catalyst, which will aid in optimizing the structures for an effective use in fuel cells in the future.
4.2 Experimental details

4.2.1 Synthesis

WO$_{3-x}$ was synthesized according to the procedure described in the literature. As a starting product, commercially available tungsten carbide raw powder (WC CRC 010u, Wolfram Bergbau und Hütten AG) with a BET surface area of 2.71 ± 0.08 m$^2$/g and a grain size of 0.47 ± 0.01 µm was used. Oxidation of WC was performed by dispersing 3 g of the raw powder in a 50 mL mixture (3:2) of HNO$_3$ (65 wt %, BDH Prolabo, AnalR Normapur) and H$_2$SO$_4$ (98 wt %, MERCK KGAA, EMSURE) before heating the dispersion for 6 h under reflux. This treatment results in a green powder, with an average grain size of 0.26 ± 0.04 µm. The WO$_{3-x}$ powder needs to be washed with deionized water until a neutral pH is achieved. The catalyst support slurry consists of polytetrafluoroethylene (PTFE) dispersion (Dyneon, TF 5035 PTFE), used as a hydrophobic reagent and binder, deionized water and isopropanol (gradient grade, Merck). The applied slurry is dried at 170°C. Then the Pt catalyst is deposited on the catalyst support layer via an electroless deposition method with subsequent thermal reduction, following the procedure described by Ossiander et al. The redox reaction presented in Eq. 4.1 describes this process:

$$ \text{H}_2\text{PtCl}_6 \cdot n\text{H}_2\text{O} \xrightarrow{\text{reducing agent, } \Delta T} \text{Pt} + 6 \text{HCl} + m\text{H}_2\text{O} $$  \hspace{1cm} (Eq. 4.1)

Three different time intervals ($\Delta T$) were chosen to accomplish the reduction process of the Pt precursor on WO$_{3-x}$. In sample S1 the catalyst precursor was reduced for 4 min, in S2 for 20 min, and in S3 the formation time was increased to 60 min (Table 4.1).

Table 4.1: List of the three investigated Samples S1, S2 and S3. The formation time corresponds to the time period of the thermal reduction.

<table>
<thead>
<tr>
<th>Formation time of Pt on WO$_{3-x}$</th>
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<tbody>
<tr>
<td>S 1</td>
</tr>
<tr>
<td>S 2</td>
</tr>
<tr>
<td>S 3</td>
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</table>

These specific time intervals were chosen deliberately. S1 provides insight into the initial stages of the porous Pt network formation, where Cl is still present. S3 reveals the final network where the transformation from the bulk is completed. S2 is representative for the transition state and has been used and investigated as anode in HT-PEMFCs as well. To gain better insight into the initial stages of the network formation process, the Pt loading in S1 is twice the loading in S2 and S3. When doubling the amount of the precursor material, the size of the resulting octahedrons is more or less...
doubled too. This way we were able to monitor more easily the formation process of the high-surface-area Pt network starting from the Pt precursor bulk material as will be presented below. The described samples S1, S2, and S3 are listed in Table 4.1.

4.2.2 Characterization methods

SEM
SEM was performed to investigate the morphology of the Pt loaded WO$_{3-x}$ based samples. SEM top view samples were prepared by cutting small pieces off the electrode and gluing them onto an SEM sample holder. An AURIGA ZEISS SEM operated at 3-5 kV was used. Secondary electron (SE) micrographs were obtained by use of an in-lens detector from Zeiss. Quantitative energy dispersive X-ray (EDX) analysis was performed with the help of a standard EDAX detector and an electron acceleration voltage of 15 kV.

FIB
Cross-sectional TEM samples were prepared by focused ion beam (FIB) sectioning. Site-specific TEM lamellae were made by use of two machines: a ZeissNVision40 FIB microscope and an FEI Helios NanoLab600, both with integrated SEM. All samples were prepared by the conventional lift-out technique.$^{223}$ Lamellae of 10 µm length, 1 µm width, and 3 µm depth were fabricated by removing the surrounding material using gallium (Ga) ions with an acceleration voltage of 30 kV and a beam current of 6.5 nA. After the lift-out was performed and the cut-free lamella was glued to a Cu support grid, the region of interest inside the transferred lamella was thinned to electron transparency (<100 nm). Further, the Ga beam current was reduced step by step to 47 pA. Final polishing was performed by reducing the Ga acceleration voltage to 5 kV and the beam current to 15 pA.

TEM
TEM investigations were carried out on a JEOL JEM-2200FS and an FEI 60-300 Titan Themis. The JEOL TEM was operated at 200 kV and was equipped with a JEOL EDX detector. Annular dark field (ADF) scanning TEM (STEM) imaging was carried out with the attached EM-24630UHADF detector from JEOL using a collection angle of 10–170 mrad. For electron tomography, large tilt angles of $\pm$80° are required, and a special holder from JEOL was used for this. The FEI Titan Themis is equipped with a C$_c$-corrector for the condenser system. The machine was operated at 300 kV. EDX measurements were carried out using the attached Super X-EDX detector from Bruker. EDX quantification was based on the Cliff Lorimer equation and performed using the Bruker software Esprit 1.9.4.3348. STEM imaging was achieved by use of the attached high angle annular dark field (HAADF), ADF and bright field (BF) detectors simultaneously. The convergence angle was 23.8 mrad, and the spot size was around 1.5 Å.
4.2.3 Electrochemical characterization

A scanning flow cell (SFC) was used to investigate the electrochemical surface area (ECSA). In short, the material of 1 cm² of the Pt/WO₃₋ₓ electrode was removed from the gas diffusion layer and suspended in 3 mL ultrapure water via ultrasonic treatment. After the addition of 20 µL of Nafion solution (5 wt %, Sigma-Aldrich), 0.3 µL of the suspension were dropcasted on a glassy carbon plate and measured with the SFC.

4.3 Results

4.3.1 Structural analysis

In Figure 4.1, representative areas of the sample S1 that have been reduced for 4 min, are displayed. Note that the Pt loading in this case is twice the loading of S2 and S3 to grow bigger Pt morphologies and get better insight into the initial growth stages of the catalyst 3D morphologies on WO₃₋ₓ. An exemplary SEM image of catalyst 3D networks on the WO₃₋ₓ support is shown in Figure 4.1a. The Pt catalyst morphologies which develop during this rather short reduction period exhibit the shape of octahedrons as well as truncated octahedrons. Their overall size distribution is in the range of 2.7 ± 1.3 µm. SEM overview micrographs show dark parts and holes on the surface of the 3D catalyst (Figure 4.1a). EDX measurements performed in the SEM and averaged over large areas of different Pt catalyst morphologies show a comparatively high amount of Cl, which are confirmed by TEM measurements. Figure 4.1b displays a cross-section of a catalyst 3D network on WO₃₋ₓ grains acquired in STEM mode. The black areas in the image are vacuum; the sample in these areas was removed by the Ga ion beam while thinning the lamella down to electron transparency. To protect the Pt 3D network from being damaged during FIB sectioning, first a thin gold/palladium and then a thicker Pt protection layer were deposited on the surface of the catalyst structure. Focusing on the Pt network located on the WO₃₋ₓ support, a few observations become apparent. The cross-section displayed in Figure 4.1b clearly exhibits a crystalline outer area formed by interconnected Pt rods (Figure 4.1d). HRTEM measurements clearly show that these nanorods are Pt single crystals which are elongated in one direction. They are grown together, thus forming the polycrystalline 3D Pt network. The width of these nanorods is in the range of 6.7 ± 1.4 nm, the distance between two junctions of Pt rods is about 23.7 ± 4.5 nm. In contrast, the interior of the 3D catalyst as presented in Figure 4.1b is bulk material. Magnifying this area, we found crystalline Pt nanoparticles with a mean diameter of 3.0 ± 0.6 nm embedded in an amorphous, solid matrix (Figure 4.1c), which is confirmed by electron diffraction experiments. The insets on the left sides of Figure 4.1c and Figure 4.1d show the electron diffraction patterns from the respective areas of the two different regions. In either case, the investigated sample areas contain many monocrystalline Pt particles with different orientations. The diffraction patterns obtained consist of spots forming circular rings. In the case of the solid interior of the Pt catalyst, the experiments clearly show an additional amorphous component; this can be
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identified by the diffuse rings in the diffraction pattern and the decreasing intensity gradient with increasing distance from its central point.

Figure 4.1: Pt 3D network on $\text{WO}_3^{-x}$ after a formation time of 4 min: a) SEM image of the Pt network on $\text{WO}_3^{-x}$; b) STEM overview image of a cross-section of a Pt catalyst 3D network; c), d) HRSTEM images of the interior (c) and the shell (d) of the Pt catalyst on $\text{WO}_3^{-x}$. The insets show electron diffraction patterns of the respective areas, the indicated values belong to the corresponding lattice planes (in Å).

For further analysis, EDX measurements in STEM mode were carried out by scanning over an area of interest and measuring the elemental distribution in a defined raster. Figure 4.2 shows EDX maps from the left side of the Pt catalyst morphology displayed in Figure 4.1b. The HAADF STEM image in Figure 4.2a shows the area of the Pt 3D catalyst cross-section investigated by EDX. The distribution of the elements Pt, Cl, and W is illustrated by the red (Pt), blue (Cl), and green (W) coloring in Figure 4.2b. $\text{WO}_3^{-x}$ grains as the catalyst support are located only in the lower part of the image. The distribution of Pt and Cl are additionally displayed separately in Figure 4.2c and Figure 4.2d. Clearly, the outer area of the 3D catalyst is mainly built from pure Pt nanorods, while its core is composed of Pt as well as Cl. The inhomogeneous signal of Cl-Kα in the 3D catalyst core is due to an uneven TEM lamella thickness of this area and not related to gradients in the chemical composition. In Figure 4.2e, a magnified section of a representative core region is displayed (yellow marked square in Figure 4.2b). The results of the EDX analysis confirm the aforementioned conclusion from electron diffraction experiments and HRSTEM measurements: Crystalline Pt nanoparticles are embedded in a matrix of a Pt-Cl-compound. This compound presumably is a reduced form of the precursor $\text{H}_2\text{PtCl}_6$. The transition from the core to the outer area of the 3D catalyst is displayed in Figure 4.2f (dashed, white square in Figure 4.2b). The interface region clearly contains Pt and Cl. Quantitative EDX analysis in this region compared to both the outer area and the core of the 3D catalyst was
performed to obtain insight into the progress of the redox reaction that transforms H$_2$PtCl$_6$ into metallic Pt and side products.

![Figure 4.2: EDX STEM maps from a cross-section of a Pt 3D catalyst on WO$_3$ support: a) STEM image of the left side of the catalyst displayed in Figure 4.1b; b) overlay of the Pt (red) and Cl (blue) distribution within the catalyst structure measured by EDX; c, d) distribution of Cl and Pt; e) magnified area of the yellow marked square in b); f) magnified area of the dashed, white square in b).](image)

The Pt–Lα (9.441 keV) and Cl–Kα (2.621 keV) lines have been used for the quantification, and average values were obtained by analyzing several rectangular areas in the obtained EDX maps. The results are listed in Table 4.2. The outer area of the 3D catalyst is formed by Pt nanorods; it is therefore mainly composed of pure, metallic Pt. The interface region and the core of the 3D catalyst contain Pt and Cl in different concentrations. At the interface between core and outer area, the Pt/Cl ratio was calculated to be roughly 6:1. The core exhibits a ratio of 3:1, while in the starting compound Pt/Cl is 0.17:1. First of all, this result shows that even after a reduction time of only 4 min the redox reaction has progressed to a large extent. Second, these measurements prove that the redox reaction starts from the outside of the bulk precursor structure and advances to the inside with ongoing reaction time.
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Table 4.2: Results of the averaged quantitative EDX analysis from the outer area, the interface and the core of the 3D catalyst displayed in Figure 4.2.

<table>
<thead>
<tr>
<th></th>
<th>Outer area</th>
<th>Interface</th>
<th>Core</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt L [atom%]</td>
<td>98.6 ± 1.2</td>
<td>85.2 ± 5.2</td>
<td>73.3 ± 6.2</td>
</tr>
<tr>
<td>Cl K [atom%]</td>
<td>1.4 ± 1.2</td>
<td>14.8 ± 5.2</td>
<td>26.7 ± 6.2</td>
</tr>
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</table>

To obtain an overview of the connectivity and pore size distribution of the Pt 3D network, a 100 nm × 100 nm area of the porous catalyst was reconstructed in 3D. A movie showing the reconstructed network portion in 3D is available in mpg format online. Because of device-specific restrictions of both the TEM and the sample holder, it is only possible to achieve tilt angles less than (±) 80°. This leads to a missing wedge giving anisotropic resolution that has to be overcome during 3D reconstruction. Choosing tilt angles according to Saxton et al. reduces the effect of anisotropy. Their scheme is based on small tilt increments at high tilt angles, which is an effective method to maximize data information near the missing wedge. For the reconstruction performed here, tilt angles of up to (±) 80° gave undesired overlapping, so a reduced tilt range of -28° to -44.1° was used. Altogether, ADF STEM images were taken at nine predefined tilt angles. The 3D reconstruction of the 2D STEM images was performed using the simultaneous iterative reconstruction technique (SIRT) followed by the discrete algebraic reconstruction technique (DART). Figure 4.3 shows the ADF STEM image of the reconstructed region at a tilt angle of 0° (Figure 4.3a) and two perspectives of the final DART reconstruction of the Pt network which is formed by crystalline nanorods (Figure 4.3b and Figure 4.3c). The size of the pores of the Pt based network is irregular. This can be ascribed to the fact that neither capping agents nor templates were used; the network formation is self-organized. The volume-specific surface area determined from the 3D reconstruction was found to be 0.7 × 10³ m²/cm³. The specific surface area in terms of mass is 32.5 m²/g. This calculated value will be compared to the results from cyclic voltammetry experiments in the section below.

Figure 4.3: 3D reconstruction of the porous Pt network: a) 2D STEM image of the reconstructed area at 0° tilt angle; b) and c) different perspectives of the reconstructed Pt 3D network (see also movie in mpg-format online).
Figure 4.4 presents a collection of SEM and TEM images of the Pt 3D catalyst on WO$_{3-x}$ after a precursor reduction time of 20 min. The two SEM overview images in Figure 4.4a and Figure 4.4b show representative areas of the investigated sample. Analogous to S1, octahedral shaped 3D Pt morphologies on the WO$_{3-x}$ substrate are present. Since the amount of Pt in S2 is half of the one used in S1, the average size of the catalyst morphologies is smaller (1.1 ± 0.3 µm, see Table 4.3). Also the porous Pt network is clearly visible. A FIB prepared cross-section of a Pt 3D morphology reveals the interior as displayed in the STEM image in Figure 4.4c. The Pt catalyst is completely formed by a network of Pt rods exhibiting a mean width of 7.3 ± 1.5 nm and a distance of 36.0 ± 9.2 nm between the network’s junctions (Table 4.3). In some areas this Pt network is less dense than in others. Furthermore, there are three holes in the Pt network which could be ascribed to the FIB sectioning. These holes are predominately adjacent to solid particles inside the catalyst structure. Electron diffraction and EDX measurements confirm that these particles are composed of pure Pt. Figure 4.4d shows a magnified TEM image of the interior of a Pt 3D catalyst, with denser sections in the upper and sparser ones in the lower part. The Pt nanorods that form the 3D catalyst are monocry stalline but randomly aligned to each other, analogous to S1, as confirmed by HRTEM (Figure 4.4e) and electron diffraction experiments (Figure 4.4f).

Figure 4.4: Pt crystals on WO$_{3-x}$ after a formation time of 20 min: a), b) SEM images of Pt on WO$_{3-x}$; c) STEM overview image of a Pt catalyst network; d) TEM image of a magnified area of the Pt 3D network; e) HRTEM image of a crystalline Pt nanorod; f) electron diffraction pattern of the Pt catalyst network displayed in c.

To obtain an overview of the highly porous 3D Pt network on WO$_{3-x}$ after a formation time of 60 min, SEM images of various catalyst morphologies were taken (Figure 4.5a). Analogous to the samples S1 and S2, the shapes of the Pt catalyst (as shown here exemplarily) are either complete or truncated
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octahedrons. The average size of these structures is in the range of $1.1 \pm 0.6 \mu m$ (Table 4.3). A similar size distribution was obtained in S2, where the amount of Pt is the same as in S3.

Figure 4.5: Pt catalyst 3D network on $WO_{3-x}$ after a formation time of 60 min: a) SEM image of Pt catalyst with different sizes and morphologies; b) STEM overview image of a cross-section of one Pt catalyst 3D network on $WO_{3-x}$ grains; c) magnified STEM image of the Pt network forming the Pt 3D morphology; d) HRTEM image of an intersection of Pt nanorods; e) electron diffraction patterns of the Pt network can be attributed to randomly oriented, single Pt crystals. The schematic drawing illustrates the Wulff shape of the Pt catalyst material.

Figure 4.5b displays an overview STEM image of the investigated FIB sample, representing a cross-section of a 3D Pt catalyst network located on $WO_{3-x}$ grains. In comparison with sample S2, the density of the Pt network after 60 min of deposition time is more homogeneous. Figure 4.5c shows a STEM image of a magnified area from the interior of the investigated octahedral shaped 3D catalyst. Interconnected Pt rods with a mean width of $6.5 \pm 1.5$ nm and a distance of $34.8 \pm 9.1$ nm between their junctions (Table 4.3) are clearly visible. The 3D network formed by the Pt rods is quite dense; nevertheless it still reveals a high internal surface area. HRTEM images of single Pt nanorods as exemplarily shown in Figure 4.5d confirm their crystallinity. The Pt rods are randomly oriented and do not seem to follow specific crystallographic directions. Electron diffraction experiments on the Pt network were carried out to gain information on the crystallinity of the Pt catalyst (Figure 4.5e). The formation of spotty ring patterns can clearly be attributed to randomly oriented Pt single crystals.
4.3.2 Electrochemical characterization

The extent of the accessible surface area of the Pt catalyst morphologies on the WO$_{3-x}$ support was measured by cyclic voltammetry (Figure 4.6). According to the electrochemical measurements, sample S1 exhibits the highest surface area, while S2 and S3 were found to have a lower surface area. These results are expected since the catalyst loading in S1 is twice the loading of S2 and S3. This circumstance makes a direct comparison of the accessible surface area of S1 with S2 and S3 imprecise. On the other hand, sample S1 was designed to exhibit bigger Pt morphologies to monitor the formation process of the Pt network out of the Pt precursor bulk material which was successfully achieved. Clearly, because of the high amount of remaining Cl in the catalyst morphology, sample S1 is not applicable as a catalyst in its actual state. Nevertheless, normalization to Pt mass was performed for sample S1, and the result is shown in the inset of Figure 4.6. The ECSA of Pt in S3 was calculated to be $10.4 \pm 1.2 \, \text{m}^2/\text{g}$, which is higher than in S2 ($7.5 \pm 1.0 \, \text{m}^2/\text{g}$) and S1 ($8.5 \pm 0.7 \, \text{m}^2/\text{g}$).

Figure 4.6: Cyclic voltammetry measured with 200 mV/s in 0.1 M H$_2$SO$_4$ purged with argon. Hydrogen underpotential deposition ($H_{\text{UPD}}$) is used to estimate the surface area as indicated by the filled area. The Pt loading in S1 is twice the loading in S2 and S3. Inset: electrochemical surface area (ECSA) normalized by mass of Pt obtained from EDX analysis.

Table 4.3 summarizes data of the 3D Pt catalyst morphologies in the three investigated samples S1, S2, and S3. The average sizes of the octahedral shaped Pt morphologies on the WO$_{3-x}$ support were obtained by SEM. The mean width of the catalyst nanorods in the 3D networks and the average distance between two of their junctions were determined by TEM. The estimation of the overall accessible surface of the Pt 3D networks in each sample was performed by cyclic voltammetry. The surface extent obtained by electron tomography of a 100 nm $\times$ 100 nm portion of a catalyst morphology in S1 was calculated to be 32.5 m$^2$/g and is about three times higher than the results from the electrochemical analysis. Possible reasons to explain this difference are discussed later.
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Table 4.3: Summary of the size of the 3D catalyst morphologies determined via SEM, the average width of the Pt nanorods and the distance between their junctions determined via TEM and the surface area of the 3D network as measured by cyclic voltammetry.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average size of the octahedral shaped Pt morphologies on WO$_3$-$x$ [µm]</th>
<th>Average width of Pt nanorods determined via TEM [nm]</th>
<th>Average distance between junctions of Pt nanorods determined via TEM [nm]</th>
<th>Surface estimation via cyclic voltammetry [m$^2$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>2.7 ± 1.3</td>
<td>6.7 ± 1.4</td>
<td>23.7 ± 4.5</td>
<td>8.5 ± 0.7</td>
</tr>
<tr>
<td>S2</td>
<td>1.1 ± 0.3</td>
<td>7.3 ± 1.5</td>
<td>36.0 ± 9.2</td>
<td>7.5 ± 1.0</td>
</tr>
<tr>
<td>S3</td>
<td>1.1 ± 0.6</td>
<td>6.5 ± 1.5</td>
<td>34.8 ± 9.1</td>
<td>10.4 ± 1.2</td>
</tr>
</tbody>
</table>

4.4 Discussion

The WO$_3$-$x$ support material shows hydrophobic behavior during wetting with the aqueous Pt precursor solution. The subsequent dehumidifying step at elevated temperatures in air, results in the crystallization of octahedral shaped Pt-Cl$_x$ bulk crystals rather than the formation of homogeneously distributed Pt nanoparticles, as is the case with high-surface-area carbon. The average sizes of these bulk crystals in the three investigated samples are listed in Table 4.3. They depend on the different amounts of Pt precursor used during the preparation procedure. The average size of the catalyst 3D structures in S1 is in the range of 2.7 ± 1.3 µm, while S2 and S3 exhibit structures of about 1.1 ± 0.3 µm and 1.1 ± 0.6 µm in size, which is in good agreement with the lower precursor amount. Octahedrons are mostly defined by eight close packed $\{111\}$ facets. Since octahedral shaped crystals exhibit a high surface to volume ratio they are energetically disfavored, especially at large crystal sizes. To minimize their surface energy, the vertices of octahedra can be cut, resulting in six additional, square $\{100\}$ facets (see inset in Figure 4.5). The optimum equilibrium shape of these truncated octahedra (TO) can be calculated by the Wulff construction developed in 1901 and, among others, confirmed and enhanced by Gibbs (1906), Liebmann (1914), and von Laue (1943). Its concept is the minimization of the surface energy of a macroscopic crystal at a fixed volume. In fcc crystals it is known that surface energies of specific crystallographic planes follow the rule: $\{110\} > \{100\} > \{111\}$. Additionally it is known that $\{111\}$ facets are catalytically more active than $\{110\}$ and $\{100\}$. In our case we observe octahedral as well as TO shaped Pt morphologies in the µm-scale similar as reported by Baletto and co-workers, who found that TO shapes are preferred for large crystals. The porosity of our catalyst structures on the WO$_3$-$x$ support is related to the thermal reduction process in the second step of the preparation procedure. The presence of a reducing agent is assumed to promote the redox reaction shown in section 4.2.1 in Equation 4.1. Pt$^{4+}$ is reduced to metallic Pt while protons (H$^+$) and chloride anions (Cl$^-$) form hydrogen chloride (HCl), which is
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released together with product water. As a consequence, metallic Pt remains on the WO$_{3-x}$ support in the shape of the previously formed octahedrons and truncated octahedrons. For this reason, a highly porous 3D network of Pt nanorods is formed while preserving the initial growth morphology. A 3D reconstruction of a 100 nm × 100 nm portion of the Pt network of S1 clearly shows that the Pt nanorods are connected to each other. Pores are formed as a result, exhibiting an uneven size distribution after a formation time of up to 20 min. Increasing the formation time to 60 min leads to smaller pores with a more uniform size distribution. A comparison of the average width of several hundred individually measured Pt nanorods and the distance between their junctions is presented in Table 4.3. A formation time of 4 min results in Pt nanorods with an average width of 6.7 ± 1.4 nm and a junction distance of 23.7 ± 4.5 nm. With ongoing reduction time two contrary trends are observed. A reduction time of 20 min leads to an increased width (7.3 ± 1.5 nm) of the network forming rods and the distance of their junctions (36.0 ± 9.2 nm). After continued reduction period up to 60 min, the distance between the junctions of the Pt rods remained constant within the error range (34.8 ± 9.1 nm), but the width of the nanorods slightly decreased in size (6.5 ± 1.5 nm). Electron tomography experiments at a 100 nm × 100 nm portion of the crystalline outer shell of a Pt morphology in S1 reveal a mass-specific surface area of 32.5 m$^2$/g, whereas electrochemical analysis indicates an overall accessible surface area in all three samples in the range of 8–10 m$^2$/g. TEM, in contrast to cyclic voltammetry, is a very local analysis method which allows a detailed analysis of a comparatively small area of interest. For this reason the result obtained by electron tomography cannot be expected to be representative for the whole sample. Nevertheless, the Pt surface areas obtained by electrochemical analysis and electron tomography range in the same order of magnitude. This result strongly indicates that both methods are valid. The overall surface extent of the obtained catalyst structures after the three different reduction times was measured by H$_{UPD}$. The obtained results can be correlated with the findings from TEM investigations, but are by approximately a factor of 3 smaller. This might be due to two reasons: When inserting the samples into sulfuric acid (H$_2$SO$_4$), the remaining Pt precursor will dissolve and expose the preformed Pt nanoparticles in the cores of the 3D catalyst morphologies. While these are principally expected to increase the active surface area, they might also lack connection to the electron conducting backbone and/or even detach from the surface during dissolution of the matrix. Moreover, an influence of chlorine on the electrochemical measurements cannot be completely excluded. Another explanation for the lower Pt surface extent measured in comparison to the TEM results could be the small porous architecture of the catalyst morphologies in combination with the hydrophobic support properties. In the case that the inner part of the catalyst structures could not be wetted by the sulfuric acid used as electrolyte in the SFC, only the outer area would be taken into account for the estimation of the accessible surface area of the catalyst. Nevertheless, when the samples are compared, the surface extent of Pt in S3 was calculated to be 10.4 ± 1.2 m$^2$/g, which is slightly higher than in S2 (7.5 ± 1.0 m$^2$/g). This result goes along with the reduced width of the Pt nanorods after the full formation time of 60 min compared to the 20 min sample. In the case of sample S1 (reduction time of 4 min), TEM measurements clearly show that the inner part of the 3D catalyst structures is still bulk partially precursor material,
consisting of Pt nanoparticles embedded in an amorphous Pt/Cl compound. The size of the Pt morphologies in S1 was designed to be larger than in S2 and S3, nevertheless in cyclic voltammetry experiments, when normalizing to Pt mass, a similar Pt surface area to S2 was obtained \((8.5 \pm 0.7 \text{ m}^2/\text{g})\), which can be again explained by the reasoning above.

### 4.5 Conclusion

In this paper the growth behavior of high surface area Pt 3D networks on \(\text{WO}_3\) synthesized in a template-free process is investigated. The synthesis route is based on a two-step procedure, where in a first step the liquid \(\text{H}_2\text{PtCl}_6\) precursor is deposited on the \(\text{WO}_3\) support and dried at elevated temperatures. In a second step the Pt precursor salt is thermally reduced to form metallic Pt. It was found that the precursor reduction starts at the outside of the Pt–Cl bulk crystals formed during step one and penetrates through the cuboctahedrons with ongoing reaction time. In an early reduction phase the bulk interior of the Pt catalyst contains Pt nanocrystals embedded in an amorphous Pt–Cl matrix with a reduced Pt/Cl ratio compared to the precursor used. A formation time of 20 min turned out to be sufficient for completely removing Cl from the sample and forming a Pt network with an irregular pore size distribution. Thermal treatment of the precursor for 1 h leads to a dense network of Pt nanorods which exhibits the highest surface area of the three discussed samples. Overall, the electrochemical surface area of the Pt catalyst network increases with increasing reduction time of the precursor on the \(\text{WO}_3\) support. Moreover, the aspect ratio of the Pt nanorods as well as the pore size distribution can be slightly modified with the treatment. This can be utilized in the future to eventually design and tailor active catalyst structures in PEMFC electrodes for an effective distribution of gas channels and ion conducting channels. Moreover, the controlled formation of pores in catalysts can be beneficial for separating gaseous components or even adjusting selectivity in more complex heterogeneous reactions.

### 4.6 Performance

The performance and degradation behavior of a Pt loaded \(\text{WO}_3\) catalyst layer at the anode side of HT-PEMFCs during fuel cell operation were analyzed and compared to the standard Pt/HSAC system in a previous publication.\(^1\)\(^,\)\(^2\)\(^,\)\(^2\)\(^,\)\(^4\) This work was performed at the LMU of Munich with main contributions from Christoph Heinzl. FIB preparation and parts of the SEM measurements and the data analysis were done by Katharina Hengge.

A comparison with an identically constructed, as-prepared MEA reveals a good stability of the Pt networks on \(\text{WO}_3\) both during continuous and dynamic fuel cell operation. Even though the networks become denser with operation time, their porosity and consequently their high internal surface area remained. In addition, an MEA containing a Pt/\(\text{WO}_3\) based anode was compared to a standard Pt/HSAC based MEA during a 2000 h lasting \textit{in-situ} long-term fuel cell operation test. The
results show that in the beginning, the cell voltage of the standard Pt/C containing MEA is ca. 10 mV higher, however, the degradation rate of the Pt/WO$_3$-x containing MEA is lower with ongoing fuel cell operation time. This confirms the applicability of WO$_3$-x to use as replacement for HSAC support materials at the anode side.
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New aspects of degradation behavior

In this chapter, accelerated fuel cell tests of an anodic, carbon supported Pt/Ru catalyst are performed via identical location TEM. It is based on publication. The in-depth STEM study reveals elemental composition and crystal structure of a HSAC supported Pt/Ru catalyst alloy exhibiting a nominal atomic ratio of 1/1. The influence of degradation on single Pt/Ru catalyst particles is studied using IL-TEM. Electron tomography reveals the morphology of single Pt/Ru catalyst clusters before and after operation, and their surface and volume evolution are calculated.

5.1 Literature overview

Catalyst design is an important aspect in the continuously growing field of fuel cell application. Long-term stability and activity of the nanoparticles are considered to be among the key challenges to guarantee performance continuity over an extended lifetime. The most prevalent catalyst system for polymer-electrolyte-membrane fuel cells is based on platinum nanoparticles dispersed on a carbon support (Pt/C). When applied as catalyst for a fuel cell anode, where the hydrogen oxidation reaction (HOR) occurs, different degradation mechanisms take place. In the case of the catalyst support, carbon corrosion is frequently reported to occur. A collapse of the basic framework of the carbon support results in a reduced porosity and hence mass transport limitations for the reactants. Macroscopically this can be seen in a diminishing fuel cell performance. To circumvent corrosion, other support materials like metal oxides have been tested. Not only the support material but also the highly dispersed catalyst nanoparticles are subject to diverse degradation mechanisms. The most frequently reported phenomena are particle dissolution, agglomeration, Ostwald ripening and particle detachment. Particle dissolution is one of the main degradation mechanisms taking place during fuel cell operation. On the atomic level, only atoms in the outermost surface shell can dissolve and their specific dissolution rate was found to be more or less independent of the particles’ diameter. However, since already in a 2 nm sized particle about 50% of the atoms are located in the outermost surface layer, smaller particles generally vanish faster than bigger ones. The dissolved catalyst species can either leave the fuel cell in the water stream or
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redeposit at different locations of the fuel cell’s electrode or membrane. Several studies report the presence of catalyst nanoparticles in the ionomer after fuel cell operation. These particles were redeposited by cross-leaking hydrogen. Also, when the dissolved atoms redeposit on neighboring particles, Ostwald ripening is taking place. Small, energetically disfavored particles decrease in size while bigger particles grow further. The driving force of this process is the reduction of the surface energy since the fraction of atoms on the surface decreases with increasing particle size. The overall increase in particle size during fuel cell operation can be also described by agglomeration. In this process, minimum two nanoparticles coalesce to form one bigger sized particle. The mechanism depends on the particles’ distance and support properties. Hence, either previously separated particles actively move together or a shrinkage of the carbon support as a result of corrosion is taking place to meet this requirement. A further degradation mechanism, particle detachment, involves particles that detach from the carbon support as a whole. This can occur as a consequence of carbon corrosion. By use of a bimetallic catalyst, dealloying can take place additionally. It is defined as selective dissolution of the less noble component when a certain potential threshold value is exceeded. Surface atoms dissolve first and as such expose underlying atoms of the second component. The result is an enrichment of the more noble metal on the surface of the particle. This can be either beneficial or harmful, depending on whether the metal composition on the particle’s surface is important for the designated purpose of the catalyst. Meier et al. reported that the degradation mechanisms depend on the metal-support interaction and the composition of the support but concluded that the weighting of these phenomena is not possible.

To prove the occurrence of different particle degradation mechanisms and track changes of single particles, identical location transmission electron microscopy (IL-TEM) was employed. TEM investigations and electrochemical tests are performed on the same location by using a TEM finder grid. The particles are studied in the as-prepared state and after an accelerated degradation protocol (ADP). The ADP typically consists of accelerated cyclic voltammetry (high scan rates) to simulate fuel cell start-stop operation in a standard three-compartment electrochemical cell. Sequential TEM investigations of the previously measured, electrochemically altered catalyst reveal particle-specific degradation mechanisms.

The work in hand focusses on a high-surface-area carbon (HSAC) supported Pt/Ru based catalyst alloy which is applied as anode in high-temperature polymer-electrolyte-membrane fuel cells (HT-PEMFCs). The Pt/Ru system is the most frequently used alloy to enhance the carbon monoxide (CO) tolerance of Pt. Depending on the overpotential applied, two mechanisms are proposed: At higher potentials water activation on Ru sites on the surface of the Pt/Ru based particle is taking place. A maximum activity was found when the Pt/Ru ratio was set to 1, as this is frequently reported to be the most active composition due to the maximum achievable number of Pt-Ru pairs on the particles’ surface. However other studies reveal a Pt/Ru ratio of 3/1 to exhibit the best CO tolerance. At lower potentials Ru is reported to induce electronic changes on Pt. The reduced electron density in the Pt 5d band weakens the Pt-CO interaction (ligand effect). While pure Pt is known to adopt the face centered cubic (fcc) lattice, Ru crystallizes in the hexagonal close packed
The crystal structure of the alloy is depending on the ratio of Pt/Ru used. According to Yamada et al., an alloy exhibiting a Pt/Ru ratio of 1/1 will adopt the Pt fcc lattice, where half of the Pt sites in the crystal lattice are occupied by Ru atoms. When the Pt/Ru ratio is decreased to 1/2, the solubility limit of Ru in the Pt fcc phase is exceeded and concomitantly, both a Pt-Ru fcc phase and a Ru(-Pt) hcp phase are formed. This explanation conforms to the Pt-Ru bulk phase diagram where a miscibility gap is present at higher Ru contents. Besides Pt/Ru alloyed catalyst species, also Ru-core Pt-shell particles were in the focus of several research activities.

During regular fuel cell operation, the anode potential typically ranges from 0.0 V_RHE to a maximum of ca. 0.5 V_RHE. However, prior to operation, air can diffuse into the anode compartment resulting in a rise of the initial potential to an air open circuit voltage of ca. 1.0 V_RHE. These conditions are applied in the present work to investigate the occurring degradation mechanisms during ramping up of the fuel cell, starting from room temperature. Moreover, during start-stop cycling, cell reversal can occur when a fuel cell stack is loaded but the anode is not supplied with enough fuel. In this case, the amount of current drawn from the fuel cell exceeds the amount that can be produced. As a result the anode potential increases up to values which are even more positive than the cathode potential and subsequently the cell voltage reverses. According to Taniguchi et al., several minutes in the cell reversal condition are sufficient to cause severe damage on the anode catalyst. Thereby, depending on the hydrogen stoichiometry supplied, the anode potential can vary in a wide range. Liang et al. presented a study where they progressively decrease the hydrogen stoichiometry from 1.09 to 0.55 and the resulting anode potential increased from 0.955 V to 2.058 V. In the present work 1.2 V_RHE is set as upper anode potential to study the influence of higher potentials on the Pt/Ru catalyst degradation.

The results presented are representative for the start-stop fuel cell operation procedure. The weighting for the different degradation mechanisms observed varies compared to continuous fuel cell operation where constant current densities and high temperatures are present. Still the obtained results can help to proceed with the targeted optimization of the Pt/Ru catalyst alloy and the development of a long-term stable catalyst to use in fuel cells.

5.2 Experimental details

5.2.1 Material

A layered carbon based support, consisting of a gas diffusion layer (GDL) at the bottom, a microporous layer (MPL) in the middle and a high surface area carbon on top (provided by elcomax GmbH) was impregnated with a mixture of the Pt and Ru precursors via an electroless deposition technique and subsequently thermally reduced. The so obtained catalyst layer (CL) on top was investigated in depth in the present work. The nominal Pt/Ru ratio was chosen to be close to 1. To conduct TEM and electrochemical analyses, the Pt/Ru loaded HSAC support was scratched off from
the microporous layer and the gas diffusion layer with the help of a scalpel and ultrasonicated in 2-propanol/water (1:1) for 10 min.

## 5.2.2 Characterization methods

### XRD

The crystal structure and lattice constants of the Pt/Ru catalyst were determined by X-ray diffraction. The measurement was performed with a Philips PW1830 diffractometer, equipped with a proportional counter detector, type PW 1711, and a cobalt X-ray source (λ = 1.79 Å). The 2θ detection range was set between 10° and 130°. The XRD data were acquired in a continuous mode by using a step size of 2θ = 0.02° and a count time of 25 s per step. A power setup of 40 kV/30 mA and a rotation speed of 1 loop/s were used.

### TEM

Transmission electron microscopy and related techniques were performed to study the structural degradation behavior of the Pt/Ru catalyst on the sub-nanometer scale. For TEM sample preparation the previously prepared suspension (see section 5.2.1) was diluted and dropcasted onto a lacey carbon film coated gold finder grid (NH7 from Plano). The finder grids used exhibit small letters with defined distances between them, thus enabling the TEM user to find pre-investigated areas again. TEM measurements were done on an FEI 60–300 Titan Themis which was operated at 300 kV, a JEOL JEM-2200FS and a Phillips CM20 both operated at 200 kV. The Titan Themis is equipped with a Cc-corrector for the condenser system. For STEM imaging the attached high-angle annular dark-field (HAADF), ADF and bright-field (BF) detectors were used. The convergence angle was 23.8 mrad, the collection angle 73–352 mrad (HAADF) and the spot size was about 1.5 Å. Quantitative EDX analysis was performed using the attached Super X-EDX detector from Bruker and the Bruker software Esprit 1.9.4.3348. Electron diffraction experiments were carried out on the JEOL TEM and the CM20.

### Electron tomography

The 3D spatial arrangement of the Pt/Ru catalyst and their volume as well as surface area were analyzed via electron tomography. Tilt series were acquired in the Titan Themis using a dedicated single-tilt tomography holder from FEI. Tilt angles were chosen in the range of +/-60° with tilt increments of 10°. The reconstruction of the 3D volume was performed by use of the simultaneous iterative reconstruction technique (SIRT) refined by the discrete algebraic reconstruction technique (DART).

### Cyclic voltammetry

A non compact three-electrode teflon electrochemical cell is used to perform the electrochemical measurements. The counter electrode and reference electrode, a graphite rod and a commercial Ag/AgCl electrode (Metrohm) are housed in separate compartments. Furthermore, the reference electrode is separated by a Nafion membrane (Tschurl modification) to prevent any chloride
contamination of the electrolyte. The working electrode is a glassy carbon disk embedded in a teflon rotating disk electrode tip that can be mounted on a commercial rotating shaft (Radiometer Analytical, France). For the IL-TEM measurement the prepared TEM finder grid is placed on top of the glassy carbon rotating disk electrode tip. Two different accelerated degradation protocols (ADPs) were used in this study:

ADP-1.0: cyclic voltammetry \([0–1.0] \text{ V}_\text{RHE}\), \(200 \text{ mV/s}\), \(\text{H}_2\) saturated \(\text{HClO}_4\), room temperature, no rotation;
ADP-1.2: cyclic voltammetry \([0–1.2] \text{ V}_\text{RHE}\), \(200 \text{ mV/s}\), \(\text{H}_2\) saturated \(\text{HClO}_4\), room temperature, no rotation;

The ADPs were stopped after regular intervals of cycles (ADP-1.0 after 5000, 15000 and 25000 cycles, whereas ADP-1.2 after 2000 and 7000 cycles) to perform IL-TEM analysis at different degradation stages. In the case of ADP-1.0 a separate measurement was added in order to monitor the evolution of the electrochemical surface area. In this case the catalyst ink was directly dropcasted \((20 \mu\text{L})\) onto the glassy carbon electrode; after drying the homogeneity of the film was verified. The electrochemical surface area (ECSA) was then evaluated with the CO-stripping method (after 1, 100, 200, 500, 1000, 5000, 15000, 25000 of ADP-1.0) and the charge underlying the CO-stripping peak was calculated. A charge density of \(195 \mu\text{C/cm}^2\) was assumed for evaluating the Pt surface area. Further information about the CO-stripping method can be found in literature.\(^{225}\) All electrochemical parameter, as well the potentiostat (Gamry reference 600), the gas system and the rotator were controlled through an in-house-developed LabVIEW based software. The electrolyte was \(0.1 \text{ M HClO}_4\) prepared from concentrated \(\text{HClO}_4\) (Merck, Suprapur) and ultrapure water (UPW, 18 M\(\Omega\), Millipore).

5.3 Results and discussion

5.3.1 Structure and composition of an as-prepared Pt/Ru catalyst

An overview TEM micrograph of a representative sample area is displayed in Figure 5.1a. The spherical particles are the HSAC support material with a diameter in the range of 50–100 nm. Each particle exhibits the characteristic structure of turbostratic carbon as visible in the high resolution (HR) TEM micrograph (Figure 5.1b) with nearly parallel \((0001)\) planes possessing a distance of \(4.90 \pm 0.08 \text{ Å}\). On the surface of the carbon support, the Pt/Ru catalyst is located. It can be recognized by its dark contrast in the bright field TEM images which is mainly due to diffraction and the high atomic mass of Pt and Ru. Electron diffraction analysis reveals circular diffraction patterns consisting of many individual spots, thus indicating the presence of several Pt/Ru catalyst nanoparticles (Figure 5.1). Distinct features are visible: diffuse rings due to the turbostratic carbon support and diffraction spots lying on rings. A detailed discussion of the results of the diffraction analysis, including crystal structure and lattice distortion, is presented below.
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Figure 5.1: TEM and STEM micrographs of Pt/Ru catalyst nanoparticles on their HSAC support in the anode catalyst layer: a) TEM overview micrograph reveals several spheres of the catalyst loaded HSAC support; b) HRTEM image exhibits characteristic structure of turbostratic carbon and the dark features are the catalyst particles; c) HAADF STEM overview micrograph where the bright areas are the Pt/Ru catalyst; d) polycrystalline chain of grown-together catalyst nanoparticles.

To take advantage of the difference in the atomic weight of Pt and Ru compared to the carbon based support material, HAADF STEM images were taken where the intensity is roughly proportional to the square of the atomic number of the elements. In Figure 5.1c an overview HAADF STEM micrograph is presented, showing bright appearing catalyst nanoparticles on the dark appearing HSAC support. The black regions are vacuum. Generally two different shapes of the Pt/Ru catalyst can be found: spherical catalyst nanoparticles and bigger sized morphologies of polycrystalline chains which are formed by interconnected catalyst nanoparticles. The size of the individual, spherical NPs is in the range of 1.21 ± 0.36 nm. Several interconnected, monocrystalline nanoparticles, forming a
bigger sized chain, are displayed in Figure 5.1d. The chains reveal on average a width of 2.1 ± 0.4 nm, the overall length is varying in a broad range from ca. 10–30 nm.

EDX measurements were performed in STEM mode on a variety of individual Pt/Ru catalyst nanoparticles, bigger sized chains and large areas exhibiting a size of 100 nm x 100 nm and more. Although a Pt/Ru precursor ratio of 1 was used, the actual composition of the catalyst was found to vary in a broad range. When all EDX measurements are taken together, the lowest amount of Ru in a single particle was found to be 14.8 atom% while the largest amount was 87.9 atom%. The amount of Pt is vice versa. Figure 5.2 displays two representative EDX maps exhibiting the elemental distribution of Pt and Ru in single nanoparticles (Figure 5.2a) and in a bigger sized catalyst morphology (Figure 5.2b). The numbers give the Pt/Ru ratio of the different regions. The data show that it is not possible to predict the elemental composition of single particles solely by visual interpretation of the HAADF STEM micrographs.

![Figure 5.2](image)

**Figure 5.2:** EDX maps reveal the elemental distribution of Pt (red) and Ru (blue) in a) single nanoparticles; b) bigger sized network of chains of interconnected nanoparticles.

The crystal structure of the nanoparticles was determined by three complementary methods: Electron diffraction experiments were carried out by use of a selected area diffraction aperture (size ca. 200 nm) to obtain information on the crystallinity of several Pt/Ru catalyst nanoparticles. Additionally, high-resolution (HR) TEM measurements were performed to investigate the crystal structure of single Pt/Ru alloyed NPs by calculating their Fourier transform. The crystallinity of a millimeter sized sample area was analyzed by XRD measurements.

An exemplary electron diffraction pattern of several Pt/Ru catalyst NPs exhibiting different shapes and elemental composition is displayed in the inset in Figure 5.1. It reveals the presence of an fcc lattice even though the d-spacings measured are on average 1%–2% smaller than literature values of Pt. This can be explained by the smaller atomic radius of Ru which, in the alloy, substitutes some of the Pt atoms in the fcc lattice. Analysis of HRTEM micrographs also reveals solely the presence of
the fcc lattice. Single particles were investigated by measuring the distance and the angle between their lattice planes in the Fourier transform.

Figure 5.3 presents the XRD pattern of the Pt/Ru electrocatalyst in the as-prepared anode of a high-temperature polymer-electrolyte-membrane fuel cell (HT PEMFC). The diffraction peak at 20.9° corresponds to the turbostratic HSAC material \( (d = 4.90 \pm 0.08 \text{ Å}) \) used as catalyst support and the one at 29.3° is stemming from the carbon fibrous web \( (d = 3.54 \pm 2.47 \text{ Å}) \) which is the gas diffusion layer. Apart from these two, the other diffraction peaks originate from the Pt/Ru electrocatalyst. The grey and blue lines correspond to the positions of the peaks of pure Pt in fcc modification \( (a = 3.9231 \text{ Å}^{391}, \text{marked with } \ast) \) and Ru in hcp modification \( (a = 2.7039 \text{ Å}, c = 4.2817 \text{ Å}^{391}, \text{marked with } o) \). The Pt/Ru diffractogram resembles all the reflections from the Pt fcc lattice. However, analogous to the electron diffraction analysis, there is a clear shift toward higher angles observed. This can be explained by the substitution of the smaller Ru atoms on the Pt fcc lattice sites and the subsequent formation of a Pt/Ru fcc alloy. The lattice parameter of this alloy was calculated to be \( 3.91 \pm 0.01 \text{ Å} \). Hence the lattice distortion in the investigated Pt/Ru electrocatalyst compared to the pure Pt fcc lattice is about 0.31%. The average crystallite size in the millimeter sized area measured was calculated to be 2.11 nm.

Figure 5.3: Result of the XRD measurement of the investigated Pt/Ru catalyst (purple) in comparison to literature values of polycrystalline Pt (\( \ast \)) and Ru (\( o \)).\(^{391}\) The shift of the diffraction peaks measured toward higher angles indicates the formation of an fcc Pt/Ru alloy with smaller lattice constants than fcc Pt.
Additional peaks, indicating the presence of the Ru hcp phase, are not visible in the Pt/Ru diffractogram. Even though this is no proof for the absence of a Ru hcp phase in the sample, the amount would be below the detection limit.

To summarize, EDX measurements revealed local Ru contents of up to 87.9 atom% where the Pt/Ru bulk phase diagram would predict the hcp lattice. However, electron diffraction patterns, HRTEM investigations and XRD measurements reveal that the investigated Pt/Ru catalyst particles solely adopt the fcc lattice but exhibit a slightly smaller lattice constant than the pure Pt fcc lattice. These results conform to the work of Yamada et al. The authors studied Pt/Ru catalysts exhibiting a 1/1 ratio and solely found the presence of the fcc lattice. However when they decreased the atomic ratio to 1/2, the solubility limit of Ru in the Pt fcc phase was exceeded and a small amount of the Ru hcp phase was present in their sample.

To obtain information whether different chains of catalyst nanoparticles are connected and to address the accessibility of the surface in the bigger Pt/Ru catalyst networks for the gaseous H₂, electron tomography experiments were performed (see below). Even though in the final reconstruction it is not possible any more to distinguish between single nanoparticles due to limited resolution, the chains that are formed by them can be studied. From the 3D reconstructed catalyst morphologies, the surface area and volume can be calculated and thereby the influence of the potential cycling can be quantified. In none of the reconstructed 3D volumes of Pt/Ru catalyst networks it is possible to distinguish between Pt and Ru. However pure Pt and pure Ru should in principle be distinguishable solely by their contrast in the HAADF STEM micrographs. Therefore the result indicates that the two elements formed Pt/Ru alloys in accordance to the EDX analysis.

### 5.3.2 Degradation under HOR at the ramp-up procedure

#### Structural changes

During ramping up of the fuel cell, air can be present in the anode leading to an initial open circuit voltage of ca. 1.0 V_RHE. The influence of these high potentials on the anode catalyst is studied in the following. Similar to fuel cell ramping up conditions, the measurements were carried out at room temperature. To track small changes and intermediate steps of catalyst degradation, electrochemical cycling experiments were performed in the potential range between [0–1.0] V_RHE. Two characteristic sample areas were studied in detail: single Pt/Ru agglomerates formed by chains of catalyst nanoparticles and overview areas exhibiting both single, spherical nanoparticles and bigger morphologies. A HAADF STEM micrograph of an as-prepared larger sample region is displayed in Figure 5.4a while Figure 5.4b – Figure 5.4d are taken after 5000, 15000 and 25000 cycles in the potential range [0–1.0] V_RHE. A single Pt/Ru electrocatalyst network on its carbon support is displayed before simulating fuel cell operation (Figure 5.4e) as well as after 5000 (Figure 5.4f), 15000 (Figure 5.4g) and 25000 (Figure 5.4h) cycles. Clearly, after each series of cyclic voltammetry, the Pt/Ru catalyst has altered.
Accelerated fuel cell tests of anodic Pt/Ru catalyst via IL-TEM:

New aspects of degradation behavior

Figure 5.4: HAADF STEM micrographs of an overview area (a–d) and a bigger sized Pt/Ru catalyst morphology (e–h); a), e) The images show the as-prepared state; b), f) after 5000 cycles; c), g) after 15000 cycles; d), h) after 25000 cycles in the potential range [0–1.0] V_RHE; i)–l) display the reconstructed volume obtained by electron tomography.

The as-prepared anode (Figure 5.4a) exhibits a variety of small and bigger particles which are more or less equally distributed on their support. Additionally bigger agglomerates are present. After each series of potential cycling, the structure of the investigated area changed. The overall degradation effect is strongest after the first 5000 cycles and the smaller particles are more prone to degradation than the bigger ones. Two explanations are likely to be the reason for this observation: initial degradation due to severe dissolution of the smallest nanoparticles and coalescence of particles which are in close vicinity. Both mechanisms are thermodynamically driven in order to reduce the surface/volume ratio of the catalyst. Five characteristic areas highlighting different degradation mechanisms that occur during the electrochemical cycling are marked in Figure 5.4a – Figure 5.4d. The green circle (1) emphasizes a particle that gradually dissolves during the electrochemical treatment. The shrinkage in diameter can nicely be seen in the first 15000 cycles and after an overall number of 25000 cycles the particle dissolved almost completely. The blue circle (2) highlights a bigger catalyst particle which is surrounded by small nanoparticles in the as-prepared state. All of these small particles vanished after the first interval of potential cycling and either dissolved and redeposited or migrated on the surface of the carbon support to the bigger particle close by. The
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elongated, bigger sized particle changes its shape during the electrochemical treatment to become almost spherical after 25000 cycles. This reshaping process is thermodynamically driven as well. The third example is marked by 3 (yellow circle). Here two particles are located on the carbon support exhibiting a distance of ca. 3 nm between them. Potential cycling causes these nanoparticles to migrate in direction of each other, to form a bridge after 15000 cycles and finally, after 25000 cycles, to agglomerate. The circle numbered 4 (pink circle) presents an area where several degradation mechanisms are taking place in sequence. In the first 5000 cycles, four distinct nanoparticles exhibiting a similar diameter were formed out of differently shaped particles from the as-prepared state. After 15000 potential cycles, the upper two particles agglomerated, thus forming one bigger spherical particle. With ongoing potential cycling, the nanoparticle in the middle decreases in size due to dissolution. Supposedly further cycling would cause this particle to dissolve completely. The fifth and last example highlights a collection of 11 differently sized particles on the carbon support (labelled with 5). Electrochemical cycling causes distinct changes: coalescence of the uppermost three particles and dissolution of the five smallest particles while the three bigger sized particles on the lower right side stay visually unchanged.

These five different examples show that there are always several degradation mechanisms taking place simultaneously during the potential cycling experiment. However, assigning certain changes to a specific degradation mechanism can be ambiguous. For example, when a nanoparticle is missing after previously performed potential cycling, it could have either dissolved, moved to another particle close by or detached. However, when taking the particle’s environment into account, the possibility for one or another degradation mechanism changes. For this reason the mechanisms described above are the most likely ones to occur. Also the intensity of the degradation processes can vary. Dissolution is the obvious example: while the greatest part of the catalyst particles dissolved after the first 5000 cycles there are still some areas left where gradual dissolution can be observed (see circle marked with 1 in Figure 5.4a – Figure 5.4d). A variety of parameters are conceivable to affect the severity of the resulting degradation mechanisms on single particles: major roles play, apart from composition, also the metal-carbon interaction, the constitution of the carbon support, the wetting of the catalyst’s surface with the hypochloric acid used as electrolyte and the conductivity between the catalyst morphology and the electrodes of the electrochemical cell. Unfortunately these parameters are not quantifiable.

The particle size distribution diagram in Figure 5.5 visualizes changes of the catalyst nanoparticles’ dimensions in the area displayed in Figure 5.4a – Figure 5.4d. In the as-prepared sample the diameter of the catalyst particles is on average 1.21 ± 0.36 nm. After 5000 potential cycles, the mean particle size was found to increase (1.57 ± 0.68 nm) and also the size distribution range of the catalyst particles broadened. Additionally a tail towards bigger particle sizes becomes apparent in the log-normal particle size distribution. Both trends, particle growth and an increasing spread in the particle size distribution, intensify with ongoing potential cycling. After 15000 cycles, the mean size of the particles was found to be in the range of 1.64 ± 0.71 nm and increasing to 1.73 ± 0.61 nm after 25000 cycles. A tail towards bigger particle sizes in a log-normal particle size distribution diagram is an indication
of agglomeration taking place. A tail towards smaller particle sizes would be a hint for Ostwald ripening.

![Particle size distribution](image)

Figure 5.5: Particle size distribution in the overview area presented in Figure 5.4a–Figure 5.4d. With increasing potential cycling time, a tail towards bigger particle sizes becomes apparent.

After 5000 cycles, the greatest part of the particles dissolved or agglomerated and simultaneously the average distance between particles increased. In this state agglomeration becomes less likely and dissolution remains as the main and most likely degradation mechanism. However, after each potential cycling interval there are still small NPs in the nanometer scale range left on the HSAC support. Interestingly the greatest part of these particles stays on their location and does neither dissolve nor grow in size. A possible reason could either be that these NPs are sheltered by surrounding carbon material (and would no longer be electrochemically active) or that the metal-carbon interaction in these areas is big enough to keep the particles in place.

EDX measurements were performed to study the chemical composition of the nanoparticles before and after the electrochemical cycling. The change of the ratio of Ru and Pt is measured. From previous studies and literature research it is known that during FC operation Ru is more prone to dissolution than Pt. This is as well the case in the investigated sample. The observed dealloying effect is caused by a faster dissolution of the less noble metal, which is Ru. In the case of the bimetallic Pt/Cu system, the formation of a core-shell structure is reported. However, this is not the case for the investigated Pt/Ru catalyst. Rather an irregular distribution of the two components within single catalyst morphologies is observed. The average chemical composition in the initial state is designed to be 1/1. This has been proven by EDX measurements on other overview areas but not specifically on the location presented in Figure 5.4a. In the case of the as-prepared state, the data given in Table 5.1 are nominal values. After each series of electrochemical cycling, the Pt/Ru ratio increased, thus indicating that Ru slowly is leaching out of the alloy. After 5000 cycles the Pt/Ru ratio is 1.22,
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After 15000 cycles 1.28 and after 25000 cycles 1.82 (Table 5.1). These results stem from overview EDX measurements of the continuously altering area as displayed in Figure 5.4a–Figure 5.4d. After 25000 cycles the Ru content in different particles ranges between 30 and 50 atom%.

Table 5.1: Elemental composition of the overview area presented in Figure 5.4a–Figure 5.4d. Please note that the initial composition of the as-prepared state is designed to be 1 and was not specifically measured at this location.

<table>
<thead>
<tr>
<th></th>
<th>as prepared</th>
<th>5000 cycles</th>
<th>15000 cycles</th>
<th>25000 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru [atom%]</td>
<td>50</td>
<td>45.1</td>
<td>43.8</td>
<td>35.6</td>
</tr>
<tr>
<td>Pt [atom%]</td>
<td>50</td>
<td>54.9</td>
<td>56.2</td>
<td>64.4</td>
</tr>
<tr>
<td>Pt/Ru</td>
<td>1</td>
<td>1.22</td>
<td>1.28</td>
<td>1.82</td>
</tr>
</tbody>
</table>

Additional to overview areas, individual, bigger sized Pt/Ru catalyst networks exhibiting a high Ru content were analyzed at higher magnification before and after potential cycling between [0–1.0] V_RHE. A representative example is displayed in Figure 5.4e–Figure 5.4h. The results of the corresponding electron tomography are shown in Figure 5.4i–Figure 5.4l before and after 5000, 15000 and 25000 cycles. Additionally a movie in gif-format, where the reconstructed particles are rotated, is provided online. Here, but also in the other Pt/Ru catalyst structures, particle growth was found to be the main degradation mechanism. This could be either due to agglomeration of particles or due to Ostwald ripening as discussed above. Since the individual particles are in close vicinity and/or connected to each other, thus forming the bigger sized network, the catalyst material is supposed to diffuse and grow together during potential cycling. Concomitant with this reshaping process is the minimization of the surface area of the morphology. This process is thermodynamically driven. Additionally there are also individual nanoparticles located in the vicinity of the catalyst morphology as displayed in Figure 5.4e and highlighted by an arrow. These nanoparticles vanished after the first 5000 cycles. Presumably they either moved towards the bigger catalyst morphology close by and grew together or dissolved and redeposited on it.

Of the 3D reconstructed Pt/Ru catalyst particle, the change of volume and corresponding accessible surface area was calculated and summarized in Table 5.2. The as-prepared catalyst morphology exhibits a volume of 577 nm³ with an accessible surface area of 917 nm², resulting in a surface/volume ratio of 1.6 nm²/nm³. After 5000 cycles, the volume of the investigated Pt/Ru catalyst network stayed more or less constant (V = 567 nm³), however the surface area decreased (A = 725 nm²) and so did the surface/volume ratio (1.3 nm²/nm³). The rapid decay of the extent of the accessible surface area can be explained by the collapse of the lower part of the network and the concomitant formation of a compact particle. This degradation process can mainly be attributed to agglomeration. After 15000 cycles, the volume of the investigated particle was found to increase (V = 655 nm³) while the accessible surface area further decreased to 663 nm². Compared to the state after 5000 cycles the related surface/volume ratio further decreased to 1.0 nm²/nm³. An explanation for this could be that during the second potential cycling interval, Ostwald ripening was taking place preferably. The additional atoms stemming from the surrounding increased the particle’s volume while they scarcely influence
the extent of the particle’s surface. However, simultaneously occurring agglomeration results in a lower surface area. After 25000 cycles both volume and surface area of the catalyst further decreased due to dissolution taking place preferably ($V = 602 \, \text{nm}^3$ and $A = 621 \, \text{nm}^2$). The surface/volume ratio stayed constant and the whole particle was becoming more compact. Supposedly when the potential cycling experiment would be continued, the investigated catalyst particle would adopt a spherical shape which is thermodynamically preferred.

Figure 5.6: Presentation of the main steps of the tomography experiment performed for the particle displayed in Figure 5.4e: the first column shows every second image of the HAADF STEM tilt series obtained in the tilt range of $+/-60^\circ$ with $10^\circ$ tilt increments; the second column presents the results of the DART reconstruction; in the third column the 3D reconstructed volumes from the according perspectives are displayed.
To get an idea of the fineness of the reconstruction that was performed, every second micrograph of the tilt series in the tilt range of ±60° obtained from the particle presented in Figure 5.4e is given in Figure 5.6. The images are compared to the DART reconstruction and the resulting 3D volume. The intensity distribution obtained from the DART reconstruction is very similar to the HAADF STEM micrographs for all tilt angles indicating a good reliability of the data extracted from the reconstruction.

EDX measurements were carried out in STEM mode and elemental distribution maps were obtained from the network displayed in Figure 5.4e–Figure 5.4h. Quantification of Pt and Ru revealed an increasing Pt/Ru ratio with an increasing number of potential cycles (Table 5.2). Starting with a Pt/Ru ratio of 0.34 in the as-prepared sample, the ratio increased to 0.54 after 5000 cycles, 0.63 after 15000 cycles and 0.75 after 25000 cycles. The distribution of both elements is non-uniform within the catalyst network. Locally changing Ru contents between 55.8 atom% in the chain on the left side, up to 83.4 atom% on the right side are present in the as-prepared morphology. After 25000 potential cycles, the left side of the catalyst is composed of 38.1 atom% Ru while its right side contains up to 65.5 atom% Ru.

<table>
<thead>
<tr>
<th></th>
<th>as-prepared</th>
<th>5000 cycles</th>
<th>15000 cycles</th>
<th>25000 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume [nm³]</td>
<td>577</td>
<td>568</td>
<td>655</td>
<td>602</td>
</tr>
<tr>
<td>Surface area [nm²]</td>
<td>917</td>
<td>725</td>
<td>663</td>
<td>621</td>
</tr>
<tr>
<td>Surface/Volume [nm²/nm³]</td>
<td>1.6</td>
<td>1.3</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Ru [atom%]</td>
<td>74.7</td>
<td>64.8</td>
<td>61.3</td>
<td>57.1</td>
</tr>
<tr>
<td>Pt [atom%]</td>
<td>25.3</td>
<td>35.2</td>
<td>38.7</td>
<td>42.9</td>
</tr>
<tr>
<td>Pt/Ru</td>
<td>0.34</td>
<td>0.54</td>
<td>0.63</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Electrochemical surface area evolution

The evolution of the electrochemical surface area is monitored with the CO-stripping technique under ADP-1.0. Cyclic voltammetry in the potential range of [0–1.0] V_RHE at 200 mV/s in 0.1 M perchloric acid is interrupted to perform CO stripping experiments after deliberately chosen intervals of 1, 100, 200, 500, 1000, 5000, 15000 and 25000 cycles (Figure 5.7). Additionally, the accessible surface area of Pt in the investigated Pt/Ru alloy was calculated from the CO-stripping voltammogram (see inset in Figure 5.7).
Figure 5.7: CO-stripping voltammogram evolution at different stages of the ADP-1.0 ([0–1.0] V_RHE). From the integrated peak the percentage evolution of the accessible surface of Pt is calculated (inset).

In the as-prepared initial state, the adsorbed monolayer of CO is removed from the Pt active sites at a potential of ~0.65 V_RHE. This value is in the order of 0.2 V_RHE lower compared to pure Pt/C nanoparticles with a mean diameter of ca. 3 nm (~0.83 V_RHE, see Figure 5.8).

Figure 5.8: CO stripping voltammogram of Pt nanoparticles exhibiting a mean diameter in the range of 3 nm. The CO-monolayer on the Pt surface is removed at 0.83 V_RHE.
As mentioned before, Ru was added to enhance the CO tolerance of the Pt catalyst. This purpose was achieved: in the presence of Ru, CO oxidized from the surface of Pt more easily which explains the observed shift of the stripping towards lower potential (Figure 5.7). Similar observations illustrating the improved CO tolerance of a Pt/Ru catalyst alloy compared to pure Pt were reported by Gasteiger et al. In the present work, the CO-stripping voltammograms at different stages of the degradation experiment, display the following two trends (Figure 5.7): i) a shift in the first peak position towards lower potential values down to 0.58 V\textsubscript{RHE} and ii) after 500 cycles the gradual formation of a second peak at higher potentials in the range of 0.77–0.8 V\textsubscript{RHE}. The exact values after each potential cycling interval are listed in Table 5.3. As mentioned above, the observed shift of the first peak towards lower potentials indicates a more efficient removal of CO from the Pt surface in the Pt/Ru catalyst system. However, the appearance of the second peak implies that there is another contribution which removes the beneficial effect of Ru. Additionally the contribution of the first peak is decreasing with the catalyst degradation until it vanishes after 25000 cycles. Supposedly this is related to the change in surface composition as Ru is dissolving at a faster rate than Pt (this implies that there could be a threshold value of Ru to enhance the CO tolerance of Pt) and to the contribution of smaller particle being formed as a consequence of dissolution. However, a detailed interpretation is difficult as these changes are due to the superposition of several degradation mechanisms occurring in parallel.

Table 5.3: Results of the CO stripping experiment: shown are the surface evolution of the Pt/Ru nanoparticles and the positions of the CO desorption peaks with ongoing potential cycling.

<table>
<thead>
<tr>
<th>Pt area [cm\textsuperscript{2}]</th>
<th>peak position 1 [V\textsubscript{RHE}]</th>
<th>peak position 2 [V\textsubscript{RHE}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.37</td>
<td>0.65</td>
</tr>
<tr>
<td>100</td>
<td>0.41</td>
<td>0.63</td>
</tr>
<tr>
<td>200</td>
<td>0.41</td>
<td>0.62</td>
</tr>
<tr>
<td>500</td>
<td>0.51</td>
<td>0.59</td>
</tr>
<tr>
<td>1000</td>
<td>0.55</td>
<td>0.59</td>
</tr>
<tr>
<td>5000</td>
<td>0.49</td>
<td>0.57</td>
</tr>
<tr>
<td>15000</td>
<td>0.44</td>
<td>0.58</td>
</tr>
<tr>
<td>25000</td>
<td>0.14</td>
<td>/</td>
</tr>
</tbody>
</table>

The percentage evolution of the surface area of Pt (from the initial 0.37 cm\textsuperscript{2}) under ADP-1.0 was calculated from the CO-stripping charge, assuming a charge density of 195 µC/cm\textsuperscript{2} and is summarized in Table 5.3. Interestingly, during the initial cycles, a large increase of ca. 50% of the accessible surface area of Pt (up to 0.55 cm\textsuperscript{2} after 1000 cycles compared to the as-prepared state) is observed. Afterwards the surface area is decreasing gradually down to 0.14 cm\textsuperscript{2} after 25000 cycles. An
increasing surface area can be explained either by a decreasing particle size or by an increase of the available Pt surface area. Baldizzone et al.\textsuperscript{271} observed a similar increase of the ECSA of their Pt/Ni catalyst when starting their potential cycling experiment. The authors found that dealloying led to the formation of a porous catalyst structure, thus increasing the accessible surface area. However, in the work in hand no formation of porous structures was observed. Rather it is supposed that excess Ru is initially blocking catalytically active sites of Pt on the surface of the alloyed particles. Also the presence of a small amount of Ru-oxides and hydroxides on the Pt/Ru alloy is reported in literature to lower the performance.\textsuperscript{184,185,262,272} It is also known, that Ru oxides and hydroxides are less stable than fcc Pt/Ru solid solutions.\textsuperscript{186,273} Generally, since Ru is dissolved preferably (dealloyed), especially in the first 1000 cycles subjacent Pt is exposed and can be detected with CO-stripping. Thus, dealloying of surface Ru explains the increase in the accessible surface area of Pt as was also observed for a dealloyed Pt/Ni catalyst.\textsuperscript{256} Similar observations were made in the fuel cell stack where the full performance of the cell is only achieved after a certain conditioning phase.\textsuperscript{255}

As mentioned above, the described CO stripping measurements were performed in the potential range of \([0–1.0] \text{V}_{\text{RHE}}\). For comparison, the overview area and the individual Pt/Ru catalyst particle network displayed in Figure 5.4 were investigated after 5000, 15000 and 25000 cycles in the same potential interval. In the cyclic voltammetry experiment, the overall ECSA of the catalyst increases in the first 1000 cycles by ca. 50\% and decreases after 5000 cycles gradually while the most significant drop is recorded after 25000 cycles. However up until 15000 cycles, the extent of the accessible surface area of Pt measured is higher than in the as-prepared, initial state. This seems to contradict STEM observations. In the overview area in Figure 5.4a—Figure 5.4d dissolution and particle growth are taking place from the start. Both mechanisms result in a constantly decreasing accessible surface area of the catalyst. To explain the difference, a simple model can be used. Assuming an entirely alloyed Pt/Ru catalyst particle, both elements would be distributed homogeneously in the entire volume. That would as well imply that the surface of the particle would be composed of 50\% Pt atoms and 50\% Ru atoms. Consequently, since CO adsorbs to Pt atoms, the measurable surface area of Pt would correspond to half of the total surface area present. With ongoing potential cycling a preferred dissolution of the less noble Ru is recorded. Since the surface atoms dissolve first, the underlying Pt atoms are exposed thus increasing the measurable surface area of Pt. This effect is dominating in the first 1000 potential cycles and thus the available surface area of Pt is increasing. With ongoing potential cycling, other degradation mechanisms like agglomeration and particle coarsening gain influence and the Pt surface area is decreasing. Additionally, with ongoing dissolution of Ru, the CO tolerance of Pt is decreasing. The water activation and electronic effect of Ru on Pt are only present when both Ru and Pt are in close vicinity.\textsuperscript{99,182,261,272} The loss of this feature is the reason for the appearance of the second peak that forms during the CO stripping experiment at higher potential values. In fact, the overall amount of Ru after 25000 cycles is still considerably high: 36 atom\% of previously 50 atom\% are preserved. However, if the greatest part of the element is only present in the bulk of the particles and not on the surface, the measurable electrochemical behavior of the Pt/Ru alloy differs markedly. Cyclic voltammetry and CO stripping as well as catalysis are surface sensitive
mechanisms. EDX measurements on the other hand reveal the elemental composition of the overall 3D volume of particles. However, in case dissolution of Ru atoms at the surface of the catalyst particles is taking place, the resulting Pt-rich outer shell is either not continuous or so small in thickness that it was not detected by EDX measurements in STEM mode. Still the simple estimation allows combining all observations made from STEM and electrochemical analysis and completing the picture of nanometer and subnanometer scale degradation processes that are responsible for changing CO tolerance mechanisms during the electrochemical treatment: A depletion of Ru on the surface of Pt/Ru catalyst particles and subsequently a reduced CO tolerance of the overall system.

5.3.3 Degradation under cell reversal conditions

To study the influence of the Pt/Ru catalyst degradation behavior on the upper potential during start-stop cycling, a second cyclic voltammetry experiment was carried out in the interval range of \([0–1.2] \, V_{\text{RHE}}\) (Figure 5.9). Volume and accessible surface area of the investigated particle in the as-prepared state and after 2000 and 7000 cycles were calculated from the electron tomography data and are summarized in Table 5.4. A video in gif-format showing the reconstructed 3D volumes of the investigated particle is presented online.\(^{249}\)

![Figure 5.9: HAADF STEM micrographs of a bigger sized Pt/Ru catalyst morphology formed by polycrystalline chains of interconnected nanoparticles a) in the as prepared state; b) after 2000 cycles and c) after 7000 cycles in the potential range \([0–1.2] \, V_{\text{RHE}}\); d), e), f) are the corresponding electron tomography reconstructions. The scale bar is the same in all images.](image-url)
In the reconstruction, the as-prepared catalyst was found to exhibit a volume of 3770 nm$^3$ and a surface area of 5247 nm$^2$. In the first interval of the electrochemical cycling experiment (2000 CVs), the morphology of the Pt/Ru catalyst particles altered only in the nanometer scale range and volume and accessible surface area slightly decreased ($V = 3706$ nm$^3$ and $A = 4427$ nm$^2$). This is due to agglomeration or Ostwald ripening that balance dissolution. However, the shape of the overall morphology of the Pt/Ru catalyst is preserved. This is not the case after the second interval of the cyclic voltammetry experiment of 7000 cycles. The greatest part of the Pt/Ru particle has dissolved and only five larger nanoparticles are observed. The volume of these particles was calculated to be 204 nm$^3$ and their surface area is 312 nm$^2$. EDX measurements were performed after 7000 cycles and the amount of Pt and Ru was quantified. On average $33 \pm 3$ atom% Ru and $67 \pm 3$ atom% Pt are detected. Even though not specifically measured on the Pt/Ru catalyst morphology displayed in Figure 5.9a, similar Pt/Ru catalyst agglomerates were found to be composed of ca. 65–75 atom% Ru and 25–35 atom% Pt in the as-prepared state.

This experiment demonstrates that the Pt/Ru catalyst is stable in the simulated FC operation in the first 2000 cycles although the voltage used is larger than the ones which are typically applied in a real fuel cell stack (<0.5 V$_{RHE}$). A possible reason is, that the catalyst material is stabilized in the form of the agglomerate. Also Yamada et al. found the stability of the Pt/Ru alloy improved with a higher amount of Ru inserted. However with ongoing FC operation simulation, a severe dissolution is observed and the amount of Ru decreases from ca. 75 atom% (Pt/Ru ratio of 0.33) to 33 atom% (Pt/Ru ratio of ca. 2) with ongoing simulated operation time (Figure 5.9c). This is in accordance to literature where the long-term stability of Pt/Ru is reported to be low and a preferential dissolution of Ru occurred.

Table 5.4: Volume and accessible surface area of the catalyst network presented in Figure 5.9 in the as-prepared state and after 2000 and 7000 potential cycles in the range of [0–1.2]V$_{RHE}$.

<table>
<thead>
<tr>
<th></th>
<th>as-prepared</th>
<th>2000 cycles</th>
<th>7000 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume [nm$^3$]</td>
<td>3770</td>
<td>3706</td>
<td>204</td>
</tr>
<tr>
<td>Surface area [nm$^2$]</td>
<td>5248</td>
<td>4428</td>
<td>312</td>
</tr>
</tbody>
</table>

5.4 Summary

The operation related stability of the catalyst material is counted among the key factors to guarantee a reliable and long-term stable fuel cell performance. Indications of the weakest points of the catalyst NPs during starting up, long-term operation and ramping down of the fuel cell help to continue with targeted fuel cell optimization. The focus of the present work lies on the catalyst performance and degradation dependency during start-stop cycling, when high voltages are present at the anode. An in-depth analysis via TEM and STEM reveal that the Pt/Ru catalyst in the as-prepared sample exhibits different shapes: spherical nm-sized particles and bigger sized networks which are interconnected.
chains of nanoparticles. The particles possess a slightly distorted fcc lattice although locally changing Ru contents in the range of 14.8 atom% up to 87.9 atom% are present. The catalyst’s stability is investigated by combining IL-TEM and cyclic voltammetry measurements with a focus on the effect of the maximum potential value in the CV experiment. The Pt/Ru catalyst alloys show an intensified degradation behavior when the maximum potential value is set to 1.2 V_RHE. In the extreme case, the major part of the catalyst dissolved. When the potential cycling range is decreased to [0–1.0] V_RHE, the stability of the catalyst improved significantly. This could be observed in overview areas and on single Pt/Ru catalyst morphologies. Changes of the catalyst were investigated up to 25000 potential cycles. Despite the high stability observed in the STEM micrographs, cyclic voltammograms revealed a change in the CO-stripping behavior that is attributed to the change in surface composition as the dissolution of Ru is favored over the dissolution of Pt. Indeed, the formation of a second peak at higher potentials and the vanishing peak at lower potentials indicates a loss of Ru in accordance to EDX measurements. Dissolution/dealloying is found to be the main degradation mechanism and especially in the beginning of the electrochemical treatment also agglomeration and Ostwald ripening are taking place. Particle detachment is only occasionally observed. Generally, Ru proves to be less stable during the electrochemical treatment. However, its presence in the Pt/Ru catalyst alloy accounts for an easier removal of CO from the surface of Pt as demonstrated by a lower CO stripping voltage. While this study was focusing on the stability of Pt/Ru-C under start-stop conditions, we intend to investigate also the stability during regular operation (constant current density in the standard operation range and elevated temperatures) in a follow-up work to unravel the weighting of the degradation mechanisms that differ in continuous und dynamic fuel cell operation modes.
6 Unraveling micro- and nanoscale degradation processes during operation of high-temperature polymer-electrolyte-membrane fuel cells

This chapter reveals micro- and nanoscale degradation processes taking place during continuous operation of real HT-PEMFCs. It is based on publication\textsuperscript{255}. A HSAC supported Pt/Ru catalyst alloy is employed as anode in a real HT-PEMFC system to study its stability and long-term performance. Operation related redistribution of a small portion of both the anodic Pt/Ru and cathodic Pt catalyst is demonstrated. The formation of a band composed of star-like shaped catalyst nanoparticles in the membrane close to the cathode side is observed and investigated.

6.1 Literature overview

Long-term stability and performance continuity as well as affordable costs are key factors to give fuel cells their final breakthrough in our daily life. Extensive research and development have a visible impact, yet there is room for improvement. In polymer-electrolyte-membrane fuel cells (PEMFCs), the catalyst performance and stability in the electrochemical environment during operation has been and is still among the most frequently addressed issues in terms of fuel cell optimization. Catalyst diffusion, agglomeration, dissolution and Ostwald ripening are the most commonly known phenomena of catalyst degradation, but also CO tolerance of the anode catalyst of PEMFCs has been the focus of many research activities. Several CO poisoning mechanisms on the surface of Pt have been reported and reviewed by Lopes et al.\textsuperscript{176} Two types of free Pt site adsorption mechanisms are proposed: a linear and a bridge-type adsorption. Both mechanisms result in a positive shift of the reversible potential so the desorption process of CO from the surface of the Pt nanoparticles becomes difficult. The poisoning effect of CO can be overcome by either reducing the CO adsorption or enhancing the CO oxidation or reduction. To accomplish these requirements, several binary, ternary or even quaternary electrocatalysts are under investigation. A selection of elements used in combination with Pt are: Ce,\textsuperscript{166} Co,\textsuperscript{166} Fe,\textsuperscript{166,167} Ni,\textsuperscript{166} Mo,\textsuperscript{166} Os,\textsuperscript{166,168} Pb,\textsuperscript{166} Rh,\textsuperscript{166} Ru,\textsuperscript{166,167} Sn\textsuperscript{166,168} and W\textsuperscript{166,168}. Ternary or quaternary alloys are usually made by combining Pt with two or three of the aforementioned metals. Russel et al.\textsuperscript{172} compared the CO and CO\textsubscript{2} tolerance of the Pt-Mo/C system with the Pt-Ru/C system. The authors claim two different mechanisms to be responsible
for the decreased CO poisoning effect of the alloys compared to pure, metallic Pt: in the Pt-Mo/C system, the Mo-species, located on the surface of the alloyed NPs, promote the CO tolerance by a turn-over of the Mo(IV/VI) couple while in the Pt-Ru/C system, water activation at Ru sites is responsible for the enhanced CO tolerance. However, according to Lopes et al., this is the case only for high overpotentials at the anode whereas at low overpotentials, an electronic effect of Ru on the Pt 5d-band structure decreases the CO poisoning effect of the system. Even though in terms of CO tolerance the Pt-Mo/C turns out to exceed Pt-Ru/C, the stability of the Mo-containing system during operation is lower.

Another fuel cell degradation mechanism involves catalyst nanoparticle dissolution, migration and precipitation in the membrane with ongoing fuel cell operation time. These nanoparticles were quite often found to form a band in the membrane adjacent to the cathode catalyst layer. This phenomenon is well documented in literature for low temperature PEMFCs. High potentials at the cathode side are mostly stated to be the reason for Pt dissolution and migration into the membrane, where crossover hydrogen from the anode is supposed to reduce these ions to metallic Pt. Pt dissolution at the anode side was first reported by Xie et al. and further investigated by Kim et al. The authors claim hydrogen shortage at the anode side to be responsible for Pt oxidation and subsequent migration into the membrane. Pt oxidation due to fuel cell operation conditions is unlikely since the anode potential is considerably lower than the Pt redox potential. Rau et al. are, according to their own statement, the first ones to address operation related catalyst migration in HT-PEMFCs. The authors observed a Pt band in the PBI membrane adjacent to the cathode catalyst layer in secondary electron and backscattered electron images taken in the scanning electron microscope (SEM). A detailed analysis of the catalyst distribution on the nanometer scale was not provided.

In the present work, the bimetallic Pt-Ru/C system was used as anode catalyst and deposited on a high surface area (HSAC) carbon support to realize the hydrogen oxidation reaction. For the cathode catalyst layer, Pt nanoparticles were deposited on HSAC to perform the oxygen reduction reaction. Stability issues and degradation behavior of the two catalyst types in the course of continuous HT-PEMFC operation are addressed by use of electron microscopy and electrochemical analysis.

The HT-PEMFCs investigated in this work have been operated in real fuel cell systems and are designed to last for more than 40000 h. To gain insight into the processes that take place on the nanoscale during operation, we stopped the fuel cells prematurely after deliberately chosen time intervals and analyzed the individual components with scanning TEM (STEM). For this reason, the work in hand does not show any catastrophic failure of the investigated HT-PEMFCs. Rather, the MEAs presented are still operational and show intermediate states of the MEAs in the course of ongoing fuel cell operation time.
6.2 Experimental details

6.2.1 Synthesis

The fuel cell fabrication procedure starts with the production of the catalyst layers for anode and cathode side. Therefore, Pt and Ru catalyst precursors are deposited onto the carbon based support layers (provided by elcomax GmbH) via an electroless deposition method. The HT-PEM membrane electrode assemblies (MEAs) are manufactured by doping the electrodes, including the catalyst layers, with phosphoric acid and hot pressing them with a cross-linked polybenzimidazole (BPI) based membrane. The membrane was fabricated by stirring meta-PBI powder and N,N-dimethylacetamide (Merck) for 3 h at 200°C under pressure. After adding a solution of bisphenol A diglycidyl ether in DMAc (Sigma Aldrich), the membranes were casted on a carrier foil and dried at 70 – 100°C. More details are given by Ossiander et al.107

The architecture of the so prepared MEAs is based on layered structures: The centerpiece is the membrane which is composed of the phosphoric acid doped organic polymer polybenzimidazole (PBI). Adjacent to the membrane are the anode and cathode. Both electrodes can be subdivided into 3 layers, which are the catalyst layer (CL), microporous layer (MPL) and gas diffusion layer (GDL). This work mainly focuses on the membrane as well as the catalyst layers on both the anode and cathode side.

6.2.2 Investigated samples

In Table 6.1 the three investigated samples are summarized. MEA_t0 is the reference MEA studied before fuel cell operation. MEA_t1 was operated for a deliberately chosen time interval (t1) and MEA_II was operated twice as long (t2). Both MEAs were operated in a continuous operation mode in real fuel cell systems. All three samples are fabricated in the same manner. In this way it is possible to solely study degradation processes that occur with ongoing fuel cell operation time on the micro- and nanometer scale and exclude any influences stemming from different fuel cell preparation and operation procedures.

Table 6.1: Overview of the three investigated samples (MEA_t0, MEA_t1, MEA_t2) and their operation time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Operation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA_t0</td>
<td>Ready-to-use (reference)</td>
</tr>
<tr>
<td>MEA_t1</td>
<td>Continuous operation for one time interval (t1)</td>
</tr>
<tr>
<td>MEA_t2</td>
<td>Continuous operation for two time intervals (t2)</td>
</tr>
</tbody>
</table>
6.2.3 Long-term operation under constant load

Long term operation under constant load was conducted at a current density of 0.2 A/cm² at 160°C in real fuel cell systems. On the anode side, the cells were fueled with reformed natural gas (stoichiometry 1.25), on the cathode side air was supplied (stoichiometry 2.0).

6.3 Characterization methods

6.3.1 Structural and chemical analysis

SEM

Scanning electron microscopy analysis was performed to obtain an overview of the quality and the thickness of the components in the investigated MEAs. For sample preparation, rectangular pieces were cut off each of the three single cells with the help of a scalpel. The sample pieces were fixed in clamp mountings with the MEA cross-section facing up. A JEOL JSM 6490 operated at 15 kV was used. Micrographs exhibiting a high Z-contrast were obtained with the help of a backscattered electron (BSE) detector from JEOL. EDX analysis was performed by use of the attached EDAX detector and the EDAX software. EDX quantification was based on the Cliff-Lorimer equation and the Pt-Lα (9.441 keV), Ru-Lα (2.558 keV), Cl-Kα (2.621 keV) and C-Kα (0.277 keV) lines.

FIB

The preparation of TEM samples was performed by focussed ion beam (FIB) sectioning using the conventional lift-out technique according to Giannuzzi et al. An FEI Helios NanoLab600 with an integrated SEM was applied. Lamellae with dimensions of 10 mm length, 1 mm width and 8 mm depth were fabricated by removing the surrounding material with the help of gallium (Ga) ions with an acceleration voltage of 30 kV and a beam current of 6.5 nA. The exposed lamellae were transferred and attached to a copper (Cu) grid and then thinned by Ga ions until electron transparency (<100 nm). The Ga beam current was reduced gradually to 47 pA. Final polishing was performed with an acceleration voltage of 5 kV and a beam current of 15 pA.

TEM

TEM measurements were performed on an FEI 60–300 Titan Themis which was operated at 300 kV and at 60 kV and a JEOL JEM-2200FS operated at 200 kV. The Titan Themis is equipped with a C₃ corrector for the condenser system. STEM imaging was carried out with the attached high-angle annular dark-field (HAADF), ADF and bright field (BF) detectors simultaneously with a convergence angle of 23.8 mrad and a spot size around 1.5 Å (Spot 6) at 300 kV. For elemental analysis, a Super X-EDX detector from Bruker was used. Diffraction analysis was performed on the JEOL TEM with the attached Gatan camera.
6.3.2 Electrochemical analysis

**Polarization curves**
To record polarization curves, a single cell setup with an active area of 50 cm² and a serpentine channel flow field structure was chosen. The flow rates of the reactants were controlled using mass flow controllers. The cell temperature was fixed at 160°C with the help of electrical heating cartridges and the stoichiometries of the fuel were kept constant at 1.25 for synthetic reformate (76% H₂, 1.2% CO and 22.8% CO₂, Westfalen AG) and 2.0 for air, respectively.

**Electrochemical impedance spectroscopy (EIS)**
Electrochemical impedance spectra were recorded with a Zahner PP241 power potentiostat (Zahner Elektrik) at 0.2 A/cm² in a 50 cm² single cell fed with synthetic reformate at a stoichiometry of 1.25 at the anode and with air at a stoichiometry of 2.0 at the cathode. The frequency range was set between 50 mHz and 50 kHZ. The amplitude was set to 10 mV and the results are shown in Nyquist plots.

**In-situ cyclic voltammetry (CV)**
Cyclic voltammograms were recorded using a Zahner PP241 (Zahner Elektrik) and a Zahner IM6ex electrochemical workstation. The MEAs were tested in a 50 cm² single cell and fed with dry hydrogen on the anode (which was then used as a pseudo-reference electrode) and humidified nitrogen on the cathode. The electrochemical surface area (ECSA) was determined by cycling the cathode 100 times between 0.095 and 1.1 V with 0.1 V/s, followed by an analysis scan with 0.05 V/s. The ECSA was calculated according to Equation 7.1.

\[
\text{ECSA (cm}^2/\text{mg}) = \frac{\text{Charge (µC/cm}^2)}{[210 \times \text{(µC/cm}^2) \times \text{catalyst loading (mg/cm}^2)]} \tag{7.1}
\]

6.4 Results

6.4.1 SEM investigation
SEM overview images of representative cross-sectional areas of the three investigated membrane-electrode-assemblies (MEAs) are displayed in Figure 6.1a – Figure 6.1c. The membrane, anode and cathode are exemplarily marked in Figure 6.1a. The images were acquired using the backscattered electron detector resulting in a high atomic number contrast. Due to the greater amount of Pt at the cathode side and the lower atomic number of Ru at the anode side, the cathode CL appears as the brightest layer in the MEA and can therefore easily be identified. The higher Pt loading at the cathode side is due to the less effectively catalyzed oxygen reduction reaction (ORR) of Pt compared to the hydrogen oxidation reaction (HOR). In all investigated MEAs there are some cracks present in both the anode and cathode CLs originating from the drying process of the electrodes during the MEA
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fabrication. These cracks are mostly filled by the membrane material which is soft at elevated temperatures of 160°C and more.

Figure 6.1: a)-c) SEM overview images of the three investigated samples. The layers from top to bottom in each image are: Gas diffusion layer (GDL), microporous layer (MPL), cathode catalyst layer (CL), membrane, anode CL, MPL and GDL: a) MEA_t0 is ready to use; b) MEA_t1 was operated for a certain time interval t1 in continuous FC operation. The inset on the bottom right corner is a magnification of the rectangular marked region between cathode CL and membrane where a bright band is visible in the membrane; c) MEA_t2 was operated for two time intervals in continuous FC operation; d) Operation times of the investigated MEAs are plotted against the mean thickness of MEA functional layers: cathode CL, membrane and anode CL.

The membrane material shows different surface roughness at anode and cathode side after fuel cell operation. While the PBI surface seems to be smooth at the cathode side, it is rough at the anode side. There are several explanations within the bounds of possibility but none of them are proven so far. One is based on the fact that the phosphoric acid is diluted at the cathode side due to the
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production of water during fuel cell operation. The lack of phosphoric acid could influence the roughness of the membrane material. Another reason could be catalyst dissolution, diffusion and redeposition in the membrane during fuel cell operation; this takes place in the presented samples and will be addressed in section 6.4.4 and discussed in section 6.5. Also, the ratio of the molar flux of \( \text{H}_2 \) and \( \text{O}_2 \) or electric potential across the membrane are possible reasons.

Figure 6.1d addresses the thickness changes of the MEA components with ongoing fuel cell operation times. The unit displayed in y-direction and representing the thickness of the MEA components is arbitrary – yet the relative thickness changes of membrane and electrode CLs are comparable among each other. It is also worth mentioning that the intersection with the x-axis does not equal zero. Membrane and cathode CL continuously decrease in thickness. In the case of the anode, the thickness of the CL stays constant within the error range after \( t_1 \). After \( t_2 \), the width of the anode CL decreased, analogous to that of the membrane and cathode CL. Fluctuations in the thicknesses of the investigated MEA components are possible and could stem from variance in the fabrication of the MEA. Still, it is obvious that the size reduction of the membrane and the cathode CL is more severe than the anode CL. Nevertheless, the reduction in thickness did not result in catastrophic failure of the MEAs investigated.

When taking a closer look at the membrane area next to the cathode CL of MEA_\(_1t_1\), a small band becomes visible (inset in Figure 6.1b). Similar observations in HT-PEMFCs after operation have been reported by Rau et al. \(^9\) In MEA_\(_2t_2\) – after operating the MEA for twice as long – there is no band visible in the SEM image. The reason for this is a combination of the cathode-band distance and the resolution capabilities of the SEM used. The band has moved closer to the cathode and was analysed in detail by TEM (in chapter 6.4.4 and in the discussion part in chapter 6.5).

Qualitative overview EDX measurements were performed in the SEM on the cross-sections of cathode CL, membrane and anode CL of the three investigated MEAs. The EDX spectra show the presence of C, O, P, Cl, Pt and Ru. Carbon can be found in each functional layer of the investigated MEAs. A HSAC is used as catalyst support at both electrodes and the PBI based membrane is mainly consisting of carbon. Phosphoric acid (\( \text{H}_3\text{PO}_4 \)) is used to improve the proton conductivity of the membrane material. Its concentration is highest in the membrane and decreases in direction of both electrodes. A small amount of chlorine (Cl) was detected before fuel cell operation (MEA_\(_0t_0\)) at the cathode side. Obviously, the used Pt precursor was not completely reduced during the fabrication of the MEA. Nevertheless, after the first time interval of fuel cell operation, Cl is removed from the fuel cell and was not detected at later stages. The measured Pt and Ru signals come from the catalyst. Since the catalyst support on both electrodes is a porous HSAC material, the interaction volume of the electron beam within the sample is large in the SEM. A contribution of adjacent layers to the results of the EDX measurements can neither be excluded nor quantified. For this reason, the results obtained by EDX in the SEM are considered as qualitative results. Nevertheless, even though we know that quantification of carbon has a large error bar due to the low fluorescence quantum yield and absorption in the detector, the amounts of Pt and Ru relative to C were calculated for each of the three investigated MEAs. Carbon corrosion is observed, as discussed above, however, the distribution
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of carbon is supposed to be more stable than H$_3$PO$_4$ and the measurement errors of all investigated samples are assumed to contribute equally to the obtained results. A distinct trend regarding the processes that occur on the µm scale during fuel cell operation is observed: A progressively decreasing amount of Pt and Ru in the anode and also a reducing amount of Pt at the cathode side can be detected by EDX measurements in the SEM. The data can be found in Table 6.2.

Table 6.2: Elemental composition of anode CL, membrane and cathode CL of MEA_t0, MEA_t1 and MEA_t2.

The results were obtained by SEM EDX analysis.

<table>
<thead>
<tr>
<th></th>
<th>Anodes [atom%]</th>
<th>Membranes [atom%]</th>
<th>Cathodes [atom%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MEA_t0 MEA_t1 MEA_t2</td>
<td>MEA_t0 MEA_t1 MEA_t2</td>
<td>MEA_t0 MEA_t1 MEA_t2</td>
</tr>
<tr>
<td>CK</td>
<td>73 ± 3 85 ± 2 91 ± 2</td>
<td>100 95 ± 1 95 ± 1</td>
<td>64 ± 5 70 ± 4 79 ± 4</td>
</tr>
<tr>
<td>ClK</td>
<td></td>
<td></td>
<td>4 ± 1</td>
</tr>
<tr>
<td>RuL</td>
<td>10 ± 1 6 ± 1 3 ± 1</td>
<td>1 ± 1 1 ± 1</td>
<td>36 ± 5 30 ± 4 21 ± 4</td>
</tr>
<tr>
<td>PtL</td>
<td>17 ± 2 9 ± 2 6 ± 1</td>
<td>2 ± 2 3 ± 1</td>
<td></td>
</tr>
</tbody>
</table>

### 6.4.2 Nanoparticles in the anode-membrane interface region

In Figure 6.2, TEM and STEM micrographs of the region comprising the anode CLs and the membranes of MEA_t0 (Figure 6.2a), MEA_t1 (Figure 6.2d) and MEA_t2 (Figure 6.2g) are displayed. As mentioned above, the catalyst used at the anode side is a mixture of Pt and Ru. The presence of Ru leads to conglomerates of individual nanoparticles which are grown together forming polycrystalline, worm-like chains of larger sized particles on the carbon support (Figure 6.2b, Figure 6.2e, Figure 6.2h). Similar clusters of nanoparticles were described by Henry et al. who were facing the same problem as we are in our work: The heavy clustering of the Pt/Ru nanoparticles complicates precise studies of their size, crystallinity and elemental composition before and after fuel cell operation. However, an in-depth investigation of the Pt/Ru catalyst nanoparticles is addressed in chapter 5.
Unraveling micro- and nanoscale degradation processes during operation of HT-PEMFCs

Figure 6.2: STEM micrographs of the transition region from the anode catalyst layer to the membrane of a) MEA_t0, d) MEA_t1, g) MEA_t2. b), e) and h) show magnified areas of the anode catalyst layer as marked by dashed, red squares while in c), f) and i) high resolution STEM images of the membrane close to the anode and incorporated particles are displayed (marked by yellow squares).

Besides being located on the HSAC support, Pt/Ru nanoparticles were also detected in the membrane material close to the anode catalyst layer of MEA_t1 and MEA_t2 but not in MEA_t0. Overview images showing the homogeneous distribution of these particles in the membrane are displayed in Figure 6.3a and Figure 6.3b. This confirms what we have already concluded from our SEM analysis: an instability of the Pt/Ru catalyst in the electrochemical environment of the fuel cells during operation leads to catalyst dissolution and diffusion of the Pt and Ru ions into the membrane where they precipitate and form nanoparticles. This process is promoted by the elevated operation temperature of 160°C present in HT-PEMFCs. The diameters of the catalyst NPs in the membrane close to the anode CL were measured. In MEA_t1, NPs with a mean size of 2.4 ± 0.5 nm were observed (Figure 6.2f). With ongoing fuel cell operation time (MEA_t2) two different sizes of the spherical catalyst NPs are present in the membrane: 2.7 ± 0.7 nm and 5.5 ± 0.8 nm (Figure 6.2i).
Unraveling micro- and nanoscale degradation processes during operation of HT-PEMFCs

Figure 6.3: a) HAADF STEM micrographs of the interface region of anode CL and membrane of MEA_t1; b) HAADF STEM micrograph of the membrane of MEA_t2; c) – e) EDX map of nanoparticles in the membrane adjacent to the anode CL of MEA_t2; a) STEM micrograph; b) Pt distribution; c) Ru distribution.

Quantitative EDX analysis was performed in the TEM. A detailed insight into specific areas of the catalyst layers, the membrane and the composition of single catalyst NPs was obtained. The Pt/Ru catalyst particles in the anode catalyst layers are worm-like, about 30 nm long chains, which consist of individual nanoparticles with varying Pt/Ru content. An exemplary Pt/Ru catalyst network is displayed in Figure 6.4, where the amount of Ru locally varies in the range of 19 atom% and 78 atom%; the amount of Pt is vice versa. Although the Pt/Ru catalyst particles contain up to 78 atom% Ru, they still adopt the Pt fcc structure as demonstrated by electron diffraction experiments (see Figure 6.4d and Table 6.3). However, the phase diagram\(^{192}\) would predict a phase separation in Pt fcc and Ru hcp in the presence of high Ru contents. This is most likely another driving force for the observed dissolution.

Figure 6.4: Insight into the anode of MEA_t2: a) HRSTEM micrograph of a Pt/Ru catalyst agglomerate on its carbon support; b) and c) elemental distribution of Pt and Ru in a catalyst NP; d) Electron diffraction pattern of the anode of MEA_t1. Indicated are the hkl values of the fcc lattice of Pt.

Table 6.3: Space group, d-spacing (in Å) and hkl values of fcc Pt and hcp Ru.

<table>
<thead>
<tr>
<th></th>
<th>Space group</th>
<th>d-spacing and hkl values of fcc Pt and hcp Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>Fm3m</td>
<td>2.26 (111) 1.96 (200) 1.39 (220) 1.18 (311) 1.13 (222)</td>
</tr>
<tr>
<td>Ru</td>
<td>P6_3/mmc</td>
<td>2.34 (100) 2.14 (002) 2.05 (101) 1.58 (102) 1.35 (110) 1.22 (103) 1.17 (200) 1.14 (112)/(201)</td>
</tr>
</tbody>
</table>
Overview EDX STEM measurements covering a large area of the anode side reveal a progressively decreasing Ru/Pt ratio with increasing operation time: In the as-prepared state (MEA_t0), 42 ± 4 atom% Ru and 58 ± 4 atom% Pt are present in the anode. After fuel cell operation, MEA_t1 exhibits 38 ± 4 atom% Ru and 62 ± 4 atom% Pt while in MEA_t2 29 ± 4 atom% Ru and 71 ± 4 atom% Pt are found (Table 6.4). These results indicate a lower stability and thus preferential dissolution of Ru during fuel cell operation compared to Pt. Yet also Pt dissolution is likely to take place (see also Table 6.2).

Table 6.4: Mean ratio of Ru/Pt in the anode CLs of MEA_t0, MEA_t1 and MEA_t2.

<table>
<thead>
<tr>
<th>Anode CL</th>
<th>MEA_t0</th>
<th>MEA_t1</th>
<th>MEA_t2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/Pt</td>
<td>0.72 ± 0.11</td>
<td>0.62 ± 0.10</td>
<td>0.42 ± 0.08</td>
</tr>
</tbody>
</table>

Quantitative STEM EDX analysis of the nanoparticles in the membrane close to the anode catalyst layer of MEA_t2 was also performed. During the acquisition, the membrane material at the anode side was heavily prone to electron-beam-induced damage. For this reason the EDX acquisition time had to be kept short, thus resulting in higher noise levels and reduced visibility of the particles in the obtained EDX map. The spherical nanoparticles located within the membrane between the anode and the band in MEA_t2 (see Figure 6.3c – Figure 6.3e) were found to be composed of 66.2 atom% Pt and 33.8 atom% Ru. This result seems to stand in contrast with the EDX measurements in the anode CL which clearly show that the amount of Ru decreases more rapidly in the anode compared to Pt. TEM investigations can explain this finding as will be shown below in section 6.4.4.

6.4.3 Nanoparticles in the cathode

In Figure 6.5, STEM micrographs of the interface area between cathode CL and membrane of MEA_t0, MEA_t1 and MEA_t2 are displayed. Compared with the anode side, the catalyst NPs exhibit a spherical shape rather than worm-like chains. The mean size of the Pt catalyst NPs in the cathode CL before fuel cell operation is in the range of 2.0 ± 0.3 nm (Figure 6.5b). With ongoing operation time a coarsening of the Pt NPs can be observed which is more severe than at the anode side. This is due to the harsher conditions at the cathode. After the first time interval of fuel cell operation, the mean diameter of the Pt NPs in the cathode CL is in the range of 5.0 ± 2.3 nm and after the second time interval, the Pt NPs exhibit a size of about 8.0 ± 2.4 nm. These values are listed in Table 6.5.
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Figure 6.5: STEM micrographs of the transition region between membrane and cathode catalyst layer of a) MEA_t0; c) MEA_t1; g) MEA_t2; b) magnified area of the cathode CL of MEA_t0; d) and h) STEM micrographs of the band in the membrane of MEA_t1 and MEA_t2; e), f), i) high resolution STEM micrographs of single particles in the membrane of MEA_t1 and MEA_t2.

Table 6.5: Mean size distribution of catalyst nanoparticles in the cathode and the adjacent membrane.

<table>
<thead>
<tr>
<th></th>
<th>MEA_t0 [nm]</th>
<th>MEA_t1 [nm]</th>
<th>MEA_t2 [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt NP in cathode</td>
<td>2.0 ± 0.3</td>
<td>5.0 ± 2.3</td>
<td>8.0 ± 2.4</td>
</tr>
<tr>
<td>Pt/Ru NP in membrane adjacent to cathode CL</td>
<td>/</td>
<td>14.7 ± 4.7</td>
<td>16.1 ± 4.1</td>
</tr>
</tbody>
</table>
The histogram in Figure 6.6 displays the relative number of Pt NPs as a function of their diameter in MEA_t0, MEA_t1 and MEA_t2 in the cathode CL. The measurements are grouped in bins of 0.5 nm. Before fuel cell operation, the sizes of the catalyst NPs vary only in a small range (between 1 nm and 4 nm). With ongoing fuel cell operation time the spread in the size of the catalyst NPs increases. Also, the onsets of MEA_t1 and MEA_t2 are shifted to larger particle size values compared to MEA_t0, proportional to the fuel cell operation times.

![Figure 6.6: Size distribution of Pt catalyst nanoparticles in the cathode catalyst layer of MEA_t0, MEA_t1 and MEA_t2.](image)

### 6.4.4 Membrane region with nanoparticle-band

As membrane material, crosslinked polybenzimidazole was used and impregnated with phosphoric acid to improve the material’s proton transport ability. STEM measurements of the membrane of MEA_t0 show a constant contrast due to the amorphous structure of PBI (left side of Figure 6.5a). Nanoparticles were detected in the membrane after fuel cell operation. Depending on the distance to the cathode CL, two different types of NPs are present in both MEA_t1 and MEA_t2: spherical, monocrystalline NPs with sizes in the range of 2 – 3 nm are located in the membrane area that is close to the cathode interface (Figure 6.5f and Figure 6.7). A large amount of starlike shaped, polycrystalline NPs was detected within the membrane at the band and close to it. In MEA_t1, the average size of these NPs is in the range of 14.7 ± 4.7 nm and in MEA_t2 their mean diameter was found to be 16.1 ± 4.1 nm. These values are displayed in Table 6.5. Representative STEM micrographs of these NPs are presented in Figure 6.5e (MEA_t1) and Figure 6.5i (MEA_t2), and also for the case of MEA_t2 in Figure 6.8.
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Figure 6.7: HAADF STEM micrograph of the membrane area between the cathode catalyst layer (right) and the band (left). Bright nanoparticles can be seen; b) HRTEM micrograph of Pt nanoparticles (dark spots) in a membrane area as it is exemplarily marked by a pink square in a).

Figure 6.8: STEM overview micrograph of the membrane between band and anode CL of MEA_t2.
In both operated MEAs, the discussed NPs accumulate to form a band (Figure 6.5d and Figure 6.5h). In vicinity to this band, the previously mentioned spherical nanoparticles that are observed adjacent to the membrane-cathode interface markedly increase in size (right side in Figure 6.5d). The distance between this band and the cathode CL decreases with increasing fuel cell operation time. In MEA_t1, the band is on average $2.3 \pm 0.2 \mu m$ away from the cathode CL while in MEA_t2, the mean distance was found to be $0.4 \pm 0.1 \mu m$. According to the model of Zhang et al., the position of the band in the membrane is determined by the ratio of 2/1 of the molar flux of crossover H$_2$ and O$_2$ and the gas permeability of the membrane material. The authors claim that with unchanged permeability characteristics of the membrane, the relative location of the band is independent of the membrane thickness. Zhang et al. also state that in an H$_2$/air operation condition – which is the case for our fuel cells – the position of the band is expected to be close to the membrane/cathode interface. Our results are in good agreement with these statements. A detailed discussion regarding the degradation behavior of the membrane as well as formation and final position of the band in the electrolyte can be found in the discussion part in section 6.5.

In Figure 6.9 the elemental distribution of Pt and Ru in a representative area of the cathode CL and the membrane of MEA_t2 is displayed. The results of the elemental quantification are summarized in Table 6.6. The membrane in the displayed micrograph can be subdivided into three regions: the area at the cathode side, the Pt/Ru band and the area in direction of the anode side. Cathode CL (EDX_1) and membrane between the cathode side and the band (EDX_2) are free of Ru. The presence of Pt in the discussed membrane section indicates a small, periodically repeated cathodic Pt catalyst dissolution, migration and precipitation during fuel cell operation. This is confirmed by qualitative SEM EDX analysis (Table 6.2).

**Figure 6.9:** a) - c) Elemental distribution of Pt and Ru in the interface region of cathode CL (upper part) and membrane (lower part) of MEA_t2. The distribution of Pt and Ru is marked in red and blue. d), e) Electron diffraction patterns of d) the band and e) several Pt/Ru particles in the membrane area between anode and band.
The band in the membrane contains 62 atom% Ru and 38 atom% Pt (see Table 6.6). On average the starlike shaped NPs near the band in direction of the anode side contain 82 atom% Ru and 18 atom% Pt while the spherical Pt/Ru nanoparticles closer to the anode have only ca. 34 atom% Ru (see section 6.4.2). This suggests that the dissolution and diffusion velocity of Ru are higher than that of Pt. The Pt amount in the band is higher than in the star-like shaped NPs. This is most likely due to Pt stemming from the cathode side. Pt and Ru from the anode side dissolve at elevated fuel cell operation temperatures in the electrochemical environment of HT-PEMFCs. The ions diffuse into the membrane where they are periodically redeposited and dissolved with intermittent diffusion. Similarly the same process happens with Pt in the cathode CL. Thus the catalyst material stemming from both the anode and cathode side is periodically dissolving, diffusing and reprecipitating until it reaches a certain equilibrium point where the molar flux of H₂/O₂ equals 2/1. At this point dissolution, diffusion and precipitation proceed within the band area. Taking all EDX results in the different membrane regions into consideration, ca. 47% of the Pt in the band stems from the cathode catalyst layer and 53% from the anode catalyst layer. The detected Ru is solely coming from the anode side.

Table 6.6: Pt/Ru ratio in the area shown in Figure 6.9.

<table>
<thead>
<tr>
<th></th>
<th>EDX_1 Cathedral</th>
<th>EDX_2 Membrane</th>
<th>EDX_3 Band</th>
<th>EDX_4 Star-like particles in the membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuL [atom%]</td>
<td>0</td>
<td>0</td>
<td>62 ± 3</td>
<td>82 ± 4</td>
</tr>
<tr>
<td>PtL [atom%]</td>
<td>100</td>
<td>100</td>
<td>38 ± 3</td>
<td>18 ± 4</td>
</tr>
</tbody>
</table>

Electron diffraction experiments were carried out on several starlike shaped Pt/Ru nanoparticles in the membrane and on the band of MEA_t1 and MEA_t2. All obtained diffraction patterns consist of spots that form circular rings due to the selected area diffraction aperture capturing contributions from several nanoparticles. The diffraction pattern displayed in Figure 6.9e is representative for measurements on several starlike shaped nanoparticles in the membrane of MEA_t1; the one shown in Figure 6.9d is typical of those obtained from the band. Diffraction analysis revealed that the starlike shaped Pt/Ru particles in the membrane containing a high amount of Ru mainly crystallize in the hcp lattice which is in accordance to the bulk phase diagram. The nanoparticles forming the band were found to crystallize in the Pt fcc lattice due to the lower amount of Ru and the high amount of Pt which is stemming from both anode and cathode CLs. Depending on the amount of Ru and Pt present, the Pt fcc or Ru hcp lattice is adopted.
HRSTEM micrographs reveal different shapes of the catalyst particles in the membrane region between anode and band after the two different operation times (Figure 6.10). In the case of MEA_t1 (Figure 6.10a – Figure 6.10d) the particles exhibit a starlike shape while in MEA_t2, after twice the operation time, the particles are formed by several, randomly overlapping, facetted discs (Figure 6.10e – Figure 6.10h). This can also be seen nicely in the overview STEM image in Figure 6.8. EDX maps reveal the elemental distribution of Pt (red) and Ru (blue) within the Pt/Ru nanoparticles in the membranes of the two operated MEAs. In MEA_t1 (Figure 6.10d), both elements are distributed uniformly within each of the nanoparticles. This was found to be in contrast to MEA_t2 (Figure 6.10h) where Pt seems to gather in one region while Ru is distributed more uniformly. Henry et al.\textsuperscript{190} describe in their work that Pt-Ru NPs in the Nafion membrane of low temperature PEMFCs exhibit a Pt-core Ru-shell structure. Although this is not the case in MEA_t1, the particles in MEA_t2 might be in an intermediate state before reaching a similar core-shell structure. The average composition of the NPs in MEA_t1 is 71 atom% Ru and 29 atom% Pt, while in MEA_t2 the average amount of Ru was found to be 82 atom%. A detailed analysis of the degradation behavior of the anodic Pt/Ru catalyst in simulated accelerated fuel cell operation tests is addressed in chapter 5.
6.4.5 Electrochemical analysis

Figure 6.11: Results of electrochemical measurements: a) Polarization curves of MEA_t0, MEA_t1 and MEA_t2; b) Cyclic voltammetry (CV) of all MEAs.

In Figure 6.11a, polarization curves of the MEAs are displayed. During the acquisition, the anode was fed with synthetic reformate and the operation temperature was 160°C. In all three MEAs, the open circuit voltage (OCV) stays constant within the error range around 900 mV. This indicates that no short circuit or gas leakage is occurring during fuel cell operation which conforms to the results from SEM analysis presented in chapter 6.4.1. With increasing operational time the internal resistance of the MEAs increase as can be seen in the ohmic part of the polarization curves.

The extent of the accessible surface area of the Pt NPs on the HSAC support in the cathode CLs of the MEAs was measured by the hydrogen underpotential deposition (H_{UPD}) charge in cyclic voltammetry experiments. The obtained curves, as displayed in Figure 6.11b, are comparable in shape. The first peak at low potential and positive current arises from desorption of adsorbed H\_2 and is therefore used for the calculation of the ECSA. The other peaks are related to Pt oxidation, Pt-O-reduction and hydrogen adsorption and are not considered for the ECSA calculation. With excess of H\_3PO\_4 the Pt (111) and Pt (100) surfaces are blocked by PO\_4\textsuperscript{3-} anions. Therefore no designated Pt-H features on the different surfaces can be observed. This is also described by He et al.\textsuperscript{274} In Table 6.7, the ECSAs of the three investigated MEAs are summarized.
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Table 6.7: Electrochemical surface area (ECSA) of the Pt catalyst at the cathode of all MEAs obtained from the hydrogen underpotential deposition (H_{UPD}) charge from the CV experiments.

<table>
<thead>
<tr>
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<th>ECSA (m² Pt/g Pt)</th>
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<tbody>
<tr>
<td>MEA_t0</td>
<td>12.2 ± 0.6</td>
</tr>
<tr>
<td>MEA_t1</td>
<td>8.1 ± 0.4</td>
</tr>
<tr>
<td>MEA_t2</td>
<td>7.1 ± 0.4</td>
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</table>

Compared to the reference MEA_t0 which has not been operated, a gradual decrease of the ECSA in MEA_t1 and MEA_t2 has been observed. The ECSA of Pt in the cathode CL of MEA_t0 was calculated to be 12.2 ± 0.6 m²/g. After the first time interval of fuel cell operation (MEA_t1) the accessible surface area of Pt was found to be 8.1 m²/g and after twice the operation time (MEA_t2), 7.1 m²/g. This result is the consequence of several reasons: As presented in Figure 6.6, the size of the Pt nanoparticles in the cathode catalyst layer increases with fuel cell operation time and, accordingly, the overall catalyst surface area decreases. Additionally, a small part of Pt was found to diffuse into the membrane making it inaccessible for the cathode’s oxygen reduction reaction and lowering the ECSA value. Also, thinning of the cathode CL due to oxidation of the carbon support (SEM analysis, Figure 6.1) causes the Pt catalyst NPs to form agglomerates or detach from the electrode. The loss in ECSA during the first operation time interval (MEA_t1) represents about one third of the accessible catalyst area. Nevertheless, the losses after another time interval (MEA_t2) of operation are only about 10%. This shows that the first thousands of operating hours have the highest impact on particles’ coarsening.

Figure 6.12: Nyquist plots of EIS measurements of all investigated MEAs.

Figure 6.12 shows the Nyquist plots obtained by electrochemical impedance spectroscopy (EIS). The diameters of the semicircles at medium frequencies are dominated by the activity of the cathode catalyst for the ORR. The formation of a semicircle at high frequencies is indicative for a decrease of anode catalyst activity with increased operation time. In MEA_t0, the resistances measured are slightly higher than in MEA_t1, indicating a better performance after the first interval of fuel cell operation. This is related to the fact that the test for MEA_t0 was performed directly after MEA...
production. During the conditioning phase of the fuel cell, the $\text{H}_3\text{PO}_4$ is redistributed and the performance of the fuel cell is improving. The resistances in MEA_t2 increased compared to MEA_t0 and MEA_t1. This can be explained by the loss of carbon material and a decreased accessible catalyst surface area due to Ostwald ripening and nanoparticle dissolution. We found this result to be in good agreement with our SEM and TEM analysis in chapter 6.4.1–chapter 6.4.4. The ionic membrane resistance was found to stay constant within the error range.

6.5 Discussion

The present work reveals micro- and nanoscale degradation processes that occur during long-term operation of HT-PEMFCs. SEM investigation of cross-sections of the three investigated MEAs − where MEA_t0 was not operated while MEA_t1 and MEA_t2 were operated for specific time intervals t1 and t2 − revealed an operation-related thickness decrease of the anode and cathode catalyst layers and the membrane. This effect is strongest for the membrane and the cathode CL and almost negligible for the anode CL. The membrane, which is composed of the organic polymer polybenzimidazole, is known to be susceptible to weight loss during fuel cell operation and a lot of effort has been, and is still being put in to increase its stability further.35–36, 107 Also, carbon corrosion in the electrochemical environment of the fuel cell during operation is a known and well-documented process in literature and many research activities are focusing on overcoming this issue by either stabilizing the carbon support or replacing it by other promising materials.1 Nevertheless, even though we observe a thickness decrease of our MEA components, our system does not experience a catastrophic failure. All MEA specific components like the membrane, anodic and cathodic catalyst layers, microporous layers and gas diffusion layers were investigated in the SEM to a great extent and over large areas. No holes could be detected in any membrane section, suggesting that neither a short circuit nor a gas leak was occurring. The catalyst layers reveal holes at regular intervals, which is due to the drying process of the electrodes during their fabrication and partly due to operation-related loss of the carbon support.

The formation of a Pt band has been discussed in literature to a great extent for Nafion membranes of PEMFCs. Most authors agree in their explanations on how Pt catalyst dissolution and precipitation take place, why there is a band forming and where the band is located: A potential effect at the cathode side is proposed to account for the Pt particle dissolution while residual oxygen oxidizes the catalyst, resulting in $\text{Pt}^{2+}$ ions and Pt oxides which dissolve in water.155, 157, 275 Diffusion of these ions and oxides takes place as a consequence of the concentration gradient between cathode and membrane,156, electro-osmotic drag and chemical diffusion144, 276. Cross-leaked hydrogen stemming from the anode is supposed to reduce these $\text{Pt}^{2+}$ ions and oxides in the membrane to metallic Pt and it itself is forming protons. The mechanism described is assumed to be a repetitive one. Following this explanation, the final position of the Pt band in the membrane depends on the partial pressures of oxygen and hydrogen, and the gas permeability of the membrane.115, 156–157, 277–279 Zhang et al.116 present
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a theoretical model and experimental proof that the exact location of the Pt band in the membrane is in the position where the ratio of the molar flux of H₂ vs. O₂ equals 2/1. The authors state this to be the critical value of H₂ excess to create a reducing environment that prevents a repeated dissolution of the previously redeposited catalyst. The amount of dissolved Pt depends on the operation time, rather than the potential conditions. Only a few reports can be found in which Pt dissolution at the anode is described. Moreover, many authors claim an inhibition of anodic Pt dissolution due to the low anodic potential compared to the Pt redox potential, and also that the anodic hydrogen oversupply reduces all eventually formed Pt-oxides. However, Xie et al. pointed out in their work that this only accounts for Pt bulk material. Since the catalyst normally used in PEMFCs is in the form of nanoparticles, which are designed to exhibit a high surface area, their electrochemical thermodynamics differ from Pt bulk characteristics. This was also later confirmed by Tang et al. Additionally elevated operation temperatures promote dissolution.

Several research works analyzing the activity and stability of Ru compared to RuO₂ and Pt can be found in literature. The results show a relatively low stability of Ru in an electrochemical environment. On the other hand, a good activity of Ru and an improved performance when using the Pt-Ru/C system in PEMFCs and HT-PEMFCs was found. Henry et al. presented a detailed TEM study of Pt-Ru precipitates in the membrane of aged PEMFCs which were operated at 75°C: Similar to the work in hand, the authors observed a band in the membrane formed by Pt/Ru particles adjacent to the cathode catalyst layer. The authors describe the shape of these precipitates as flower- and star-like. Size and elemental distribution of these catalyst particles are different than the ones presented here. The authors found Pt-core, Ru-shell polycrystalline particles in the membrane and state that their elemental distribution is a result of their formation process: After operation-related dissolution and migration of Pt from the cathode CL and Ru from the anode CL, the dissolved Pt ions are first reduced by crossover hydrogen and accordingly form Pt nanoparticles. These nanoparticles are then proposed to catalyze the reduction of dissolved Ru which precipitates around them, thus forming the observed core-shell structures.

The nano- and micrometer scale observations in our fuel cell system slightly differ from the one described above. The differences can be attributed to the fact, that in the present work HT-PEMFCs are studied with an operation temperature of 160°C. A schematic drawing of the processes that take place in our system is presented in Figure 6.13. Unlike Henry et al., we found both Pt and Ru dissolving from the anode side and, similar to their work, we also found a small amount of Pt dissolving from the cathode side. These elements firstly form spherical shaped nanoparticles with a size of a few nanometers in the membrane area close to the anode and cathode catalyst layers respectively. During fuel cell operation, a repetitive dissolution, migration and precipitation of the catalyst seems to take place. The Pt/Ru catalyst stemming from the anode side was found to form 14 – 16 nm sized, starlike shaped particles in the membrane area adjacent to the cathode CL. The elemental distribution within these particles is homogeneous after the first time interval (MEA_t1) of fuel cell operation. After the second operation time interval (MEA_t2) a Pt accumulation within the observed particles was found while Ru is distributed uniformly. It was also observed that, apart
from the Pt rich region, the particles embedded in the membrane of MEA_t2 are composed of faceted, overlapping discs. The diffraction patterns obtained from these structures in MEA_t1 and MEA_t2 reveal that the Pt/Ru nanoparticles adopted the hcp lattice due to the high Ru content. The diffusion direction of the anode catalyst is in accordance with the protons constantly forming at the fuel cell’s anode and travelling to the cathode side. Pt catalyst dissolution and migration from the cathode CL into the membrane was detected as well. Pt and Pt/Ru from the cathode and anode catalyst layers diffuse into the membrane and form nanoparticles which accumulate into a band.

Figure 6.13: Schematic drawing of the nano- and micrometer scale processes that take place during fuel cell operation. Unintentional H\textsubscript{2} and O\textsubscript{2} diffusion into the membrane occurs as outlined by the yellow arrows. Instead, only diffusion of H\textsuperscript{+} (indicated by white arrows) is desired. For simplification, the reduction of O\textsubscript{2} at the cathode is not drawn.

The distance between this band and the cathode catalyst layer was found to decrease from 2.3 ± 0.2 µm (MEA_t1) to 0.4 ± 0.1 µm (MEA_t2) with ongoing fuel cell operation time. Since the average thickness decrease of the whole membrane after the operated time intervals of the investigated MEAs is larger than the difference of 1.9 µm (as was found by SEM analysis), the position of the band in the membrane is determined by other parameters (than the thickness). Rather, as mentioned before, it is dependent on the ratio of the molar flux of H\textsubscript{2}/O\textsubscript{2} which was found by Zhang et al. to be 2/1 at the position of the band and the gas permeability characteristics of the membrane.\textsuperscript{116} It is also worth mentioning that according to the authors the position of the band is independent of the membrane thickness. We believe that the band of catalyst nanoparticles in the membrane might be beneficial for the fuel cell’s performance. The catalyst particles in the membrane act as an active filter for cross-
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leaking O₂ and H₂. O₂ reacts with metallic Pt or Ru to form the related oxides, while water is formed in the presence of H₂ and metallic Pt or Ru is redeposited. In the absence of the catalyst material in the membrane, H₂ and O₂ would be free to migrate all the way to their counter electrode in the MEA and, while doing so, omit the key processes of the fuel cell operation steps. Our results have shown that the relative position of the band in relation to the decreasing membrane thickness changes with ongoing fuel cell operation time. This indicates that the O₂ and/or H₂ permeability of the PBI-based material has changed due to degradation. This can be minimized by chemical and/or mechanical strengthening of the membrane and most efficiently by using a PBI with a small distribution of the polymer chain length.³⁶ Ru crossover from the anode through the membrane into the cathode side has been reported previously, not only in PEMFCs, but also in direct methanol fuel cells (DMFCs) where Ru was detected in the cathode catalyst layer after fuel cell operation.²⁸²-²⁸³ The presence of Ru at the cathode side is known to inhibit the oxygen reduction reaction kinetics which are already among the limiting factors in fuel cell performance.²³⁵ In our case the catalyst material stays in the membrane. As long as this status is preserved, a catastrophic failure of the fuel cells is prevented. We also found that the amount of Ru and Pt dissolving at the beginning of fuel cell operation is higher than that with ongoing operation time. This may be because smaller particles in the anode dissolve at an early state while bigger agglomerates of Pt/Ru particles are more stable. Furthermore, most of the catalyst material is still present at the anode side and only a comparably small amount of catalyst dissolved and diffused into the membrane. Nevertheless, these stability issues are not to be neglected and a lot of efforts are made to prevent catalyst dissolution at all and improve the fuel cells’ performance.

6.6 Conclusion

The work in hand presents an in-depth study of nano- and micrometer scale processes that take place during operation of high-temperature polymer-electrolyte-membrane fuel cells. As catalyst material, Pt was used at the cathode side and a mixture of Pt and Ru at the anode side to counteract CO poisoning effects. Altogether, three MEAs were investigated: MEA_t0 was not operated while MEA_t1 and MEA_t2 were operated for specific time intervals. MEA_t2 was operated for about twice as long as MEA_t1. SEM investigation reveals a thinning of all MEA components with ongoing fuel cell operation time. Since the operation conditions at the cathode side are harsher than at the anode side, mainly due to the presence of oxygen, the cathode was found to be more susceptible to corrosion than the anode. TEM investigation of the membrane/cathode and membrane/anode transition areas revealed a band of Pt and Pt/Ru nanoparticles in the membrane area adjacent to the cathode catalyst layer. Additionally, nanoparticles were detected in the membrane area between the anode catalyst layer and the band. The catalyst material forming the band originates from both catalyst layers. The band-forming particles containing 71 – 82 atom% Ru on average, depending on the operation time, exhibit a starlike shape with a size distribution of 14 – 16 nm and possess a hexagonal
crystal structure. Additionally, a small amount of nearly spherical Pt nanoparticles was observed. The position of the band within the membrane is determined by the partial pressures of oxygen and hydrogen and by the gas permeability of the membrane. Its location is not permanent since the thinning of the membrane gives a stronger effect than the distance decrease between band and cathode catalyst layer. Instead, its position is dependent on the 2/1 ratio of the molar flux of H\textsubscript{2} and O\textsubscript{2}. Even though the catalyst material in the membrane is inactive for the fuel cell’s ORR or HOR, the material does act as an active barrier for cross-leaking H\textsubscript{2} and O\textsubscript{2}; this might even benefit the fuel cell’s performance.
Summary & Outlook

The scope of this thesis is the investigation of alternative catalysts and support materials and the analysis of their operation-related degradation characteristics in HT-PEMFCs. A detailed knowledge of factors that accelerate, decelerate or even prevent altering mechanisms of materials helps to continue with targeted fuel cell optimization and guarantee an extended life-time. The standard composition of anodes and cathodes is a high-surface-area carbon used as support, which is decorated with highly dispersed, spherical Pt catalyst particles of a few nanometers in size.\textsuperscript{120, 135} In the present work, two strategies were implemented and investigated independently to improve operation related degradation of the anode side: the replacement of the high-surface-area carbon support by tungsten suboxide (WO\textsubscript{3-x}) and the utilization of a Pt/Ru catalyst alloy rather than pure Pt. WO\textsubscript{3-x} is rendered a suitable Pt catalyst support material at the anode side where it fulfills all necessary criteria: electron and proton conductivity, a strong anchorage for the catalyst particles, a high surface area to guarantee their widespread distribution and a good stability over an extended life-time at elevated temperatures in the electrochemical environment of HT-PEMFCs.\textsuperscript{130, 197-199} At the cathode, WO\textsubscript{3-x} would be oxidized to the insulating WO\textsubscript{3} and as such, the fuel cell’s performance would deteriorate. The distribution of the Pt catalyst on the surface of WO\textsubscript{3-x} was studied in this work and found to differ markedly from Pt loaded HSAC, even though the synthesis route is the same for both material systems: firstly, the deposition of the Pt based precursor onto the support material via a wet chemical approach and subsequently the thermal reduction of the precursor salt in a second step. Instead of dispersed, spherical nanoparticles, on the WO\textsubscript{3-x} support there are micrometer sized, octahedral shaped, highly porous 3D networks of crystalline Pt nanorods developing. The formation process of these catalyst morphologies is analyzed as a function of the reduction time of the catalyst precursor in the second step of the synthesis route (chapter 4).\textsuperscript{227} SEM and TEM analyses revealed that firstly octahedral shaped bulk crystals from the Pt-based precursor salt H\textsubscript{2}PtCl\textsubscript{6} are formed on WO\textsubscript{3-x}, which subsequently reduce to metallic Pt. This reduction process is starting from the outside of the Pt-precursor bulk crystal and is progressively penetrating to its core. Since the shape of the previously formed octahedral bulk morphologies remains unchanged, a highly porous Pt network is developing concomitantly. The connectivity of a 100 nm x 100 nm sized section of the Pt network was analyzed using electron tomography and the accessible surface area was calculated to be 32.5 m\textsuperscript{2}/g. For comparison, cyclic voltammetry experiments were performed to measure the overall extent of the accessible Pt catalyst surface over a large area. Depending on the reduction time, the
accessible Pt surface area was found to be in the range of 7.5–10.4 m²/g, which is in good agreement with the results obtained from electron tomography. The WO₃ₓ supported, high-surface-area Pt networks had been implemented as anodes in MEAs and their performance and degradation behavior were investigated depending on different fuel cell operation modes and times. Detailed TEM analyses were performed before and after continuous fuel cell operation (600 h and 2000 h respectively) as well as after 35 start-stop cycles. Besides the slightly lower cell voltages of the Pt/WO₃ₓ material system compared toPt/HSAC, a good stability of Pt on the WO₃ₓ grains was found and only minor degradation occurred.¹

The second scope of this thesis is dedicated to the reduction of the CO poisoning effect of the anode catalyst using a Pt/Ru alloy with a nominal ratio of 1, rather than pure Pt. A detailed (S)TEM analysis of the structure, the chemical composition and the stability of overview areas and single Pt/Ru catalyst morphologies on HSAC support during two specific operation conditions was performed (chapter 5).²⁴⁹ For one, fuel cell reversal conditions were simulated by performing a cyclic voltammetry experiment in the potential range of [0–1.2] V_RHE. Additionally, the ramping up procedure of fuel cells, starting from room temperature and an air open circuit voltage of 1 V_RHE, was simulated by performing cyclic voltammetry experiments in the potential range of [0–1.0] V_RHE. Therefore, CO stripping experiments were performed intermittently before and after up to 25000 potential cycles to analyze the CO tolerance and the accessible surface of Pt. While CO was removed easier from the surface of Pt in the beginning of the experiment, a second contribution was found to evolve after 500 potential cycles where the CO tolerance measured was similar to pure Pt nanoparticles. The accessible surface area of Pt in the investigated Pt/Ru particles increased in the beginning of the experiment, supposedly because Ru on the surface of the catalyst particles dissolved and exposed underlying Pt. However, with ongoing potential cycling, the overall surface area of Pt progressively decreased due to degradation. A detailed STEM study of identical locations was performed before and after 5000, 15000 and 25000 cycles in the potential range of [0–1.0] V_RHE and after 2000 and 7000 cycles in the range of [0–1.2] V_RHE. Additionally, the surface and volume evolution of single Pt/Ru catalyst morphologies was monitored and visualized using electron tomography. Dissolution was found to be the main degradation mechanism with Ru being dissolved preferably, but also agglomeration was demonstrated to take place. Generally, the stability of the Pt/Ru catalyst was found to be higher with the maximum potential value being lower.²⁴⁹

Carbon supported Pt/Ru catalyst alloys were employed as anode in HT-PEMFCs and their degradation behavior during regular long-term fuel cell operation was analyzed (chapter 6).²⁵⁵ At the cathode side, a standard Pt loaded HSAC was used and the membrane was cross-linked polybenzimidazole. Degradation analysis was performed on both the micro- and the nanometer scale using SEM and TEM, respectively. SEM revealed a progressive thinning of electrodes and membrane, however, all layers remained, thus preventing a catastrophic failure of the fuel cell. Using TEM, after fuel cell operation, nanoparticles were found in the whole membrane area, their size and composition depending on the distance to the electrodes. Near the cathode catalyst layer, pure Pt nanoparticles with a size of ca. 2–3 nm were present. Farther inside the membrane, star-like shaped particles with
a mean diameter of ca. 14–16 nm were found. EDX analysis revealed that these particles are composed of ca. 71–82 atom% Ru and 18–29 atom% Pt. In between these two characteristic membrane sections, a part of the described nanoparticles accumulated to form a band, composed of ca. 62 atom% Ru and 38 atom% Pt. The position of the band in the membrane is assumed to be determined by the 2/1 ratio of the molar flux of crossover H₂/O₂. Near the anode catalyst layer, Pt-rich (ca. 66 atom% Pt and ca. 34 atom% Ru) nanoparticles with a size in the range of 2–3 nm were detected. The presence of nanoparticles in the membrane can be explained by a periodically repeated dissolution, diffusion of ions and precipitation. Migration of whole particles is very unlikely to take place. From these results several conclusions can be drawn: Both Pt from the cathode side and Pt/Ru from the anode side are dissolving and diffusing into the membrane. At the anode side, the diffusion velocity of Ru is larger due to its lower stability in the electrochemical environment of HT-PEMFCs. Considering only the Pt content in the nanoparticle band, ca. 47 atom% Pt is stemming from the cathode catalyst layer and ca. 53 atom% Pt from the anode catalyst layer.

In summary, in this PhD work, the influence of new MEA components on the whole HT-PEMFC performance was investigated by changing always one part at a time: HSAC was replaced by WO₃ₓ and instead of pure Pt, a Pt/Ru alloy was used. Both changes, when performed independently, revealed an improvement of the resulting fuel cell stability or performance. A next step would be the combination of WO₃ₓ as long-term stable support material and Pt/Ru alloy as CO tolerant catalyst to use as anode for newly designed HT-PEMFC MEAs. Their performance analysis will show in which way the independently investigated materials will interact and if their observed positive effects will compensate or add up when combined.

A further important aspect that influences both fuel cell performance and its economic viability is the catalyst loading on anode and cathode side. A certain amount of catalyst material needs to be implemented into the catalyst layers in order to guarantee extended fuel cell operation. The specific amount is depending on the activity of the catalyst with respect to the catalyzed reaction. Since the efficiency of the cathodic oxygen reduction reaction is about 6 orders of magnitude slower than the anodic hydrogen oxidation reaction, the amount of Pt used at the cathode side is significantly higher. Accordingly, this is not only a matter of higher expenses, but also increasing degradation. Due to the larger amount of Pt nanoparticles present in the cathode CL, they are in closer vicinity, thus agglomeration is expected to occur increasingly. This can only be circumvented by improving the reaction kinetics of the cathodic ORR, either by increasing the Pt activity or finding an alternative, more active catalyst material.

The work in hand demonstrates the high value of electron microscopy to understand the formation and growth behavior of new catalyst structures as well as degradation mechanisms occurring during fuel cell operation. Electrochemical analysis methods give a general view of the overall fuel cell performance, the evolution of the catalyst surface or the changing internal resistances. However, the results obtained are averaged and always based on a conglomerate of different influences during fuel cell operation and their itemization is hardly possible. Electron microscopy on the other hand is a very local analysis method that gives detailed insight into micro- and nanometer scale processes. SEM
can be used to study surfaces and the evolution of the functional layers with ongoing fuel cell operation. FIB was successfully applied to cut site specific samples of well-defined regions of interest, including the delicate PBI-based membrane. TEM investigations helped to obtain information of the processes taking place on the nanometer scale range, including degradation of catalyst nanoparticles and their support material. The combination of both electrochemical analysis and electron microscopy enables the user to assign occurring fuel cell deterioration to specifically observed degradation mechanisms. This knowledge can be used to study the influence of single parameters on the overall fuel cell performance and continue with targeted fuel cell optimization.
8 List of publications and presentations

8.1 Scientific publications

8.1.1 Journals

Contributions: TEM analysis performed by Katharina Hengge, TEM sample preparation done by Katharina Hengge and Thomas Gänslcr, tomography done by Katharina Hengge and Thomas Gänslcr, with the help of Michael Beetz, cyclic voltammetry and CO stripping done by Enrico Pizzutilo, anode preparation done by the cooperation partners at ELCORE GMBH, XRD measurements done by Benjamin Breitbach, written by Katharina Hengge. The manuscript was revised by all authors.

Contributions: FIB sectioning done by Katharina Hengge, SEM analysis performed by Katharina Hengge and Daniel Varley, TEM analysis performed by Katharina Hengge, MEA preparation done by the cooperation partners at ELCORE GMBH, electrochemical analysis done by Tim Lochner, Markus Perchthaler, Christoph Heinzl, written by Katharina Hengge. The manuscript was revised by all authors.

Contributions: Samples prepared by Markus Perchthaler, SFC measurements done by Simon Geiger, TEM sample preparation done by Katharina Hengge (partially with the help of Ramona Hoffmann and Sonja Matich), SEM analysis performed by Katharina Hengge, TEM analysis performed by Katharina Hengge and Christoph Heinzl, tomography done by Katharina Hengge with the help of Michael Beetz, written by Katharina Hengge. The manuscript was revised by all authors.

Contributions: TEM analysis performed by Christoph Heinzl, SEM analysis performed by Katharina Hengge and Steffen Schmidt, XRD measurements done by Benjamin Breitbach, FIB sectioning performed by Katharina Hengge (partially with the help of Ramona Hoffmann and Sonja Matich and Tristan Harzer), electrochemical analysis done by the cooperation partners at ELCORE GMBH, written by Christoph Heinzl and Katharina Hengge. The manuscript was revised by all authors.

### 8.1.2 Conference proceedings


### 8.2 Conference contributions

#### 8.2.1 Oral presentations


2. Template-free synthesized high surface area 3D networks of Pt on WO$_{3-x}$ – a promising alternative for H$_2$ oxidation in fuel cell application, MRS Fall Meeting 2016, Boston, Massachusetts.


8.2.2 Poster presentations


2. Growth of novel Pt 3D networks on WO$_{3_x}$ electrodes and their effect on the performance of fuel cells, 16$^{th}$ European Microscopy Congress (EMC 2016), Lyon, France.

3. Degradation analysis of high-temperature polymer-electrolyte-membrane fuel cells via electron microscopic techniques, 15$^{th}$ TEM-UCA European Summer Workshop 2015, Cadiz, Spain.


5. Electron microscopy characterization of platinum on WO$_x$ support material in high-temperature polymer-electrolyte-membrane fuel cells, Nanosciences: Great Adventures on Small Scales, CeNS Workshop 2013, Venice, Italy.
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