Degradation mechanisms of electrocatalysts used in polymer electrolyte fuel cells

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Degradation Mechanisms of Electrocatalysts Used in Polymer Electrolyte Fuel Cells

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Doctor of Sciences

presented by

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2011
A philosopher once said “It is necessary for the very existence of science that the same conditions always produce the same results.” Well, they do not.

Richard Feynman (1918 – 1988)

“The Character of Physical Law”
## Contents

Summary  
Zusammenfassung  
Acknowledgements  

I Introduction  
1. Energy Demand and Research  
2. Fuel Cell  
3. Polymer Electrolyte Fuel Cell (PEFC)  
4. Thermodynamics of a Polymer Electrolyte Fuel Cell  
5. Kinetics of a Polymer Electrolyte Fuel Cell  
6. Components of a Polymer Electrolyte Fuel Cell  
7. Catalyst Layer  
8. Pt/C Corrosion in a PEFC  
4. Pt and C Corrosion  
5. Thermodynamics of Pt/C Corrosion  
6. Kinetics of Pt/C Corrosion  
7. Model Systems for Pt/C Corrosion  
II Methods, Materials and Instrumentation  
30. Analytical Techniques  
30.1. Atomic Force Microscopy (AFM)  
30.2. Cyclic Voltammetry (CV)  
30.3. Scanning Electron Microscopy (SEM)  
30.4. Scanning Tunneling Microscopy (STM)  
30.5. X-ray Photoelectron Spectroscopy (XPS)
III.1.3.2.3. Conclusions                  111
III.1.3.3. Conclusions for Oxidation Experiments        112

III.2. Model Electrodes (Pt/GC) Prepared by Lithography       114
  III.2.1. Introduction             114
  III.2.2. Preparation             115
    III.2.2.1. EUV-IL            114
    III.2.2.2. EBL (GCU)            125
  III.2.3. Oxidation Experiments (Ex Situ)         133
    III.2.3.1. Potentiostatic Hold          133
      III.2.3.1.1. Room Temperature          133
      III.2.3.1.2. Elevated Temperature (60°C)       139
      III.2.3.1.3. Conclusions          147
    III.2.3.2. Cycling                    149
      III.2.3.2.1. Elevated Temperature (60°C)       149
      III.2.3.2.2. Conclusions          156
  III.3. Model Electrodes (Pt/HOPG) Prepared by EBL: In Situ EC-STM 158
    III.3.1. Introduction             158
    III.3.2. Preparation             158
    III.3.3. Oxidation Experiments (In Situ)         169
      III.3.3.1. Stepwise Potential Increase         169
      III.3.3.2. Potential Cycling           180
      III.3.3.3. Oxidation of HOPG without Pt       187
    III.3.4. Conclusions             190

IV  General Discussion and Outlook                   195
V   Outlook                                     201
VI  Appendix                                  202

Bibliography                              202
Contents

Abbreviations 214
List of Publications 217
List of Selected Presentations 218
Curriculum Vitae 219
Summary

The purpose of this work was to improve the scientific understanding of the degradation processes occurring at the support-catalyst-electrolyte interface of an electro-catalyst as observed and controversially discussed for polymer electrolyte fuel cell (PEFC) electro-catalysts. Scanning probe microscopy (SPM) and X-ray photoelectron spectroscopy (XPS) were applied to trace electrochemically induced changes in surface structure and chemical composition. This research goal demanded preparation of so-called model electrodes, ideally comprising a smooth substrate surface with monodisperse Pt particles, i.e. of defined size and arrangement. Untreated glassy carbon (GCU), heat-treated glassy carbon (GCHT) and highly oriented pyrolytic graphite (HOPG) were the substrates of choice as it was found that they were sufficiently smooth and allowed mimicking certain properties of carbon black (CB) which is widely used as support in PEFC electro-catalysts. The non-graphitic, non-graphitised structure of GC, for instance, is comparable to the amorphous “core” of CB while the highly ordered graphitic HOPG has similarities to the graphitic “shell” of primary CB particles. Two methods were chosen for the preparation of model electrodes, the electrochemical Pt deposition and the lithography.

Differences between GC and HOPG as substrates were manifested already in course of electrochemical Pt deposition. Heat-treatment of GC (GCHT) introduced further variation of carbon properties which was shown to exclusively refer to the formation of a porous layer, as discussed in literature, because no changes of the chemical composition and only little of roughness were detected by means of XPS and atomic force microscopy, respectively. Pt particle size and Pt particle size distribution as well as the surface coverage were found to relate to the surface properties of GC modified by heat-treatment. A decrease in particle diameter and an increased Pt coverage was observed after thermal pre-treatment of GC for various deposition pulse lengths.

The lithographic preparation was done in collaboration with the laboratory for micro- and nanotechnology (LMN) and first performed by extreme ultraviolet interference lithography (EUV-IL) on GC substrates. This approach was unique as to our best knowledge no EUV-IL lithography has so far been applied to GC. The first experiments revealed that GC was
indeed suitable for the lithographic preparation. However, certain drawbacks of the EUV-IL process became evident in course of further work, leading to the replacement of EUV-IL by electron beam lithography (EBL). EBL enabled preparation of regular arrays of Pt nanodots with diameter of 30 nm and height of 5 nm on the electrode area of one square centimetre. The pitch, which is the distance between the centres of two dots, could be varied between 70, 100 and 200 nm. This type of preparation of model electrodes was possible due to adjustment and optimisation of different parameters relevant to the EBL process. Although, to our knowledge, HOPG has never been used as a substrate for any lithographic technique, this work shows that Pt dot patterns could be generated on HOPG in combination with Pt deposition via sputtering. Thus-prepared model electrodes turned out to be stable over a long time in air and suitable for in situ STM measurements in sulphuric acid electrolyte.

In order to gain an overview over the stability of GC, GCHT und Pt/GC or Pt/GCHT model electrodes at high anodic potentials, electrodes prepared via electrodeposition were employed for electrochemical oxidation experiments and, subsequently, analysed by means of XPS and SEM. The oxidation experiments were conducted in argon saturated 0.5 M sulphuric acid by either holding the sample at potentials, ranging from 1.2 to 1.9 V vs. SHE or cycling the samples between 0.6 V vs. SHE (the potential of Pt oxide reduction) and varied anodic vertex potential between 1.2 and 1.9 V vs. SHE at room temperature and at 60°C. The XPS study revealed that significant formation of carbon oxides on GCU and GCHT20 occurred at E ≥ 1.7 V vs. SHE and progressed with increasing anodic potentials. The presence of Pt seemed to enhance the carbon oxidation on GCU. The SEM study revealed that the mean diameter of the particles as well as the Pt coverage did not change indicating that the electrochemically deposited Pt was stable on both substrates.

XPS and SEM measurements of lithographically prepared Pt/GCU model electrodes largely confirmed the results obtained for electrochemically prepared Pt/GCU model electrodes. For these samples, tapping mode atomic force microscopy (TM AFM) was additionally used to enable tracing possible height deviation of the well-defined dots. This investigation indicated that the dots’ height increases after both potential hold and potential cycling at 60°C which was ascribed to enhanced carbon corrosion around the dots (in case
Summary

of potential hold) and to enhanced C corrosion and/or dissolution and redeposition of Pt on top of the dots (in case of cycling).

*In situ* visualisation of Pt- and C-degradation was finally realised by measuring EBL Pt/HOPG model electrodes with EC-STM. Stepwise oxidation and corrosion of HOPG, starting at edges and steps, graduate disappearance of Pt dots and their replacement by holes, as well as growing diameter of the holes were traced in 0.5 M sulphuric acid upon application of potentials between 0.6 and 1.9 V vs. SHE. The appearance and propagation of holes was first attributed solely to potential-induced and Pt-enhanced carbon corrosion, further investigations, however, indicated that carbon corrosion in the electrolyte started at pre-formed defects, induced by the sputtering step. Potentials of > 1.6 V vs. SHE were sufficient to induce complete disappearance of the Pt pattern on HOPG. Detachment/peeling of carbon material could also be observed *in situ* on HOPG allowing statements about (Pt-induced) carbon corrosion as the onset of carbon corrosion was shifted by 100-200 mV to lower potentials in presence of platinum; i.e. to 1.5 - 1.6 V vs. SHE.

In general, this work shows that the surface properties of the carbon substrate as well as the choice of preparation strongly influence the degradation mechanisms. Non-graphitic, non-graphitised GC seems to stabilise both electrodeposited and sputtered Pt particles. XPS measurements of these samples imply that there are hints at Pt-induced carbon oxidation in the potential range of 1.3 to 1.7 V vs. SHE and increased amount of oxygen-containing carbon species at potentials above 1.7 V vs. SHE.

The Pt particles, sputtered upon the graphitic surface of HOPG, were stable in sulphuric acid up to a potential of 1.4 V vs. SHE. Further potential increase led to disappearance of the dots and to appearance of holes. At 1.9 V vs. SHE the original dot pattern was completely replaced by a corresponding hole pattern. An explanation might be Pt-catalysed carbon corrosion at the Pt/C/electrolyte boundary, which takes place between 1.4 and 1.7 V vs. SHE. The defects which stabilise Pt dots are the first to corrode, thus disrupting the anchoring of Pt dots. The corresponding processes were not elucidated in detail; the findings however, are in agreement with the published studies which imply that potentials of 1.5 V vs. SHE, which are possible during start-stop processes in an operating PEFC, can induce degradation of Pt and/or its support, depending on the properties of the carbon support.
Zusammenfassung


Zusammenfassung


Um die Stabilität von GC, GCHT, Pt/GC und Pt/GCHT bei hohen Potentialen zu untersuchen, wurden die elektrochemisch herstellten Modelelektroden elektrochemisch oxidiert und deren Eigenschaften mit XPS und SEM untersucht. Die elektrochemischen Oxidationsversuche wurden in einer mit Ar gespülten 0.5 M Schwefelsäure durchgeführt. Entweder wurden die Proben durch das Halten der Proben 30 Minuten lang bei einem Potential zwischen 1.2 und 1.9 V vs. SHE oder durch das Zyken der Pt-oxid-Bildung (1.2-1.9 V vs. SHE) und Pt-oxid-Reduktion bei 0.6 V vs. SHE oxidiert. Beide Versuchsprotokolle wurden bei Raumtemperatur und bei 60°C durchgeführt. Der Vergleich der chemischen Eigenschaften der Modelelektroden vor und nach der Oxidation, der mit XPS gemacht wurde, zeigte, dass bei Potentialen > 1.7 V vs. SHE auf unbehandeltem GC (GCU) und getempertem GC (GCHT) oxidierte Kohlenstoffspezies auftreten, deren Menge sich mit der Erhöhung der Potentiale vergrößerte. Die Anwesenheit von Pt schien die Kohleoxidation weiter zu begünstigen. Detaillierte Auswertung von Rasterelektronenmikroskopieaufnahmen (SEM) zeigte, dass der Durchschnittsdurchmesser der Pt-Teilchen nach der Oxidation weder zu- noch...
Zusammenfassung

abgenommen hat, und dass sich die Menge von Pt auf der Oberfläche nur innerhalb der Fehlergrenze verändert hat, was ein Hinweis auf die Stabilität von Pt auf GCU und GCHT Substraten lieferte.

Die Halte- und Zykelexperimente haben auf lithographisch hergestellten Pt/GCU Proben zu vergleichbaren Ergebnissen geführt. Für diese Proben wurde zusätzlich die Rasterkraftmikroskopie im Tapping Mode (TM AFM) eingesetzt, um mögliche Änderungen der Höhe der gut definierten Pt Teilchen verfolgen zu können. Diese Messungen zeigten, dass die Höhe der Pt Teilchen nach der Oxidation bei 60°C zunahm, was durch die Kohlekorrosion um die Teilchen (im Falle der Halteversuche) bzw. auch durch die Auflösung und Wiederabscheidung von Pt (im Falle der Zykelversuche) erklärt werden konnte.

Abschliessend ist es gelungen, in situ Prozesse der Pt- und Kohlekorrosion auf Pt/HOPG Modelelektroden mit Hilfe der Elektrochemie-STM aufzunehmen. Die schrittweise Oxidation und Korrosion von HOPG, die auf den Stufen und Kanten begann, das allmähliche Verschwinden der Pt Teilchen und das Auftauchen von Löchern, sowie der wachsende Durchmesser der Löcher wurden in der 0.5 M Schwefelsäure beim Anlegen von Potential zwischen 0.6 und 1.9 V vs. SHE beobachtet. Das Auftauchen und die Vermehrung der Löcher wurde zuerst nur der potentialinduzierten und Pt-verstärkten Kohlekorrosion zugeschrieben. Weitere Untersuchungen zeigten allerdings, dass die Kohlekorrosion im Elektrolyten an Defekten anfing, die durch das Pt-Sputtern im Präparationsprozess bereits vorhanden waren. Bei Potentialen oberhalb von 1.6 V vs. SHE war das Pt-Teilchen-Muster komplett verschwunden. Das teilweise Ablösen und Abblättern von HOPG-Basalflächen ohne Pt wurde ebenfalls in situ verfolgt. Diese Untersuchung führte zu den Annahmen, dass die Anwesenheit von Pt die Korrosionspotentiale von Kohle um 100-200 mV erniedrigte, d.h. von 1.7-1.8 V vs. SHE auf 1.5-1.6 V.

Zusammenfassend zeigt die Arbeit, dass die Oberflächeneigenschaften des Kohlesubstrats sowie die Präparationsmethode sehr stark die Degradationsmechanismen der Modelelektroden beeinflussen. Nicht-graphitischer, nicht-graphitisierter GC stabilisiert scheinbar die elektrochemisch abgeschiedenen sowie gesputterten Pt-Teilchen. XPS Messungen dieser Proben zeigen, dass es Hinweise auf Pt-induzierte Kohleoxidation im
Zusammenfassung

Potentialbereiche zwischen 1.3 und 1.7 V vs. SHE gibt, sowie erhöhte Mengen der sauerstoffhaltigen Kohlenstoffspezies oberhalb von 1.7 V vs. SHE.

Die gesputterten Pt Teilchen auf HOPG waren stabil in Schwefelsäure bis 1.4 V vs. SHE. Die Potentialerhöhung führte zum Verschwinden der Teilchen und dem Auftreten von Löchern. Bei dem Potential von 1.9 V vs. SHE wurden das Pt-Teilchen-Muster vollständig durch ein Lochmuster ersetzt. Diese Beobachtungen könnte man durch die Pt-katalysierte Kohlekorrosion an der Pt-C-Elektrolyt-Grenfläche erklären, die bei Potentialen von 1.4-1.7 V vs. SHE bevorzugt an den durch das Sputtern induzierten Defekten stattfindet. Die Defekte, die die Pt-Teilchen auf dem HOPG stabilisieren, korrodieren zuerst, wodurch die Verankerung der Pt-Teilchen aufgelöst wird. Die zugehörigen Prozesse konnten im Rahmen dieser Arbeit nicht im Detail untersucht werden, allerdings stimmen die Beobachtungen mit den Literaturbefunden überein, dass die Degradation von Pt und/oder Kohlenstoffträger stark von den Kohleeigenschaften abhängt. Auch die in der Literatur diskutierte Pt/C Korrosion bei 1.5 V vs. SHE, einem Potential, das auch beim Start/Stop einer PEFC auftreten könnte, wurde beobachtet.
Acknowledgements

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I Introduction

I.1 Energy demand and research

During the last years the energy demands of every country in the world have been constantly increasing and it is highly unlikely that they will regress in the near future. In 2008, total worldwide energy consumption was 474 exajoules, equivalent to an average power consumption rate of 15 terawatts. In 2009, the energy consumption decreased by approximately one percent for the first time in 30 years due to the financial and economic crisis, however, this decline was only short-lived [1].

For a very long time OECD countries have been the major consumers, however, 2009 China became world’s largest energy consumer increasing its consumption by about 8% to 2.234 million tonnes of oil equivalent (Mtoe), while 1 ton of oil equivalent corresponds to 42 GJ [1]. Also India’s (655 Mtoe in 2009) and Russia’s (621 Mtoe in 2009) energy need is quickly growing [1, 2].

Despite numerous efforts to change the trend, combustion of fossil fuels still accounts for the vast majority (80-90%) of worldwide energy consumption, oil remaining the largest source, followed by coal which importance has been steadily growing since 2001 [3-5]. Thus, the amount of emitted carbon dioxide, responsible for the so-called green house effect, has been on the rise from 20.000 million tonnes (Mt) CO\textsubscript{2} in 1990 to almost 30.000 Mt CO\textsubscript{2} in 2010. Environmental concerns related to global warming and sustainability as well as unavoidability of imminent peak-oil lead to intense political discussions and an extensive search for alternative energy sources and carriers [6, 7].

One of the most promising candidates is hydrogen. It can function as an energy carrier in devices such as e.g. a polymer electrolyte fuel cell (PEFC). This type of fuel cells can be used at ambient pressure and low temperature (1-2.5 bar and 50-100°C) and in case of hydrogen/oxygen fuel cell the only exhaust is water. PEFC is based on an electrochemical reaction of hydrogen with oxygen, thus turning chemical energy into electrical energy. To control the process and avoid a possible release of thermal energy via direct combustion,
the oxidation of hydrogen and reduction of oxygen are separated by a proton-conducting but electron insulating membrane. The electrochemical reactions occur at platinum catalyst surface of a three phase boundary (electrode, electrolyte and gas phase). The platinum catalyst consists of carbon supported Pt nanoparticles with a diameter of 3-8 nm. Despite high corrosion resistance of Pt as well as carbon, numerous studies have confirmed that lifetime and stability of PEFC is greatly limited by corrosion and degradation processes occurring on the surface of the catalyst [8-12]. The investigation of the above-mentioned processes in a real PEFC, however, is challenging due to the complexity of the system. Therefore, model systems can be designed for a detailed monitoring of the degradation processes. Moreover, these Pt/C model systems can be made to meet the specific criteria of the investigation technique of choice. For the in situ scanning tunneling microscopy, for instance, which can be employed to pursue e.g. sintering of Pt or carbon corrosion at high resolutions, an extremely flat, well-conducting carbon is required as a support.

The aim of the work is to use Pt/C model electrodes to improve the scientific understanding of the processes occurring at the support-catalyst-electrolyte interface which cause the degradation of the electro-catalysts in PEFCs. The intention is to study the sinter-and corrosion processes of platinum and/or the carbon support in laboratory cells while varying e.g. particle size, support or temperature.

### I.2 Fuel Cell

A fuel cell directly converts chemical into electrical energy. This device can run continuously as long as the necessary reactants are being replenished and has a higher efficiency compared to internal combustion engines as it is not operated on a thermal cycle and is less constrained by the laws of thermodynamics [8, 13, 14]. The theoretical efficiency factor of an electrochemical reaction and, thus, the theoretical efficiency factor of a PEFC is defined by the ratio of Gibbs free energy $\Delta G$ and the reaction enthalpy $\Delta H$ according to (1):

$$\eta_{\text{theoretical, electrochemical}} = \frac{\Delta G}{\Delta H}$$

(1)
Therefore, the theoretical efficiency factor of a PEFC at lower temperatures is slightly larger than at higher temperatures. For operation between 60-100 °C the theoretical efficiency factor of a hydrogen/oxygen PEFC would be 0.81-0.79. The theoretical efficiency factor of a heat engine is defined by Carnot's theorem according to (2):

$$\eta_{\text{theoretical, heatengine}} = 1 - \frac{T_c}{T_h}$$  \hspace{1cm} (2)

where $T_h$ is the temperature of the hot source and $T_c$ is the temperature of the cold sink [15]. Thus, the theoretical efficiency factor of a heat engine strongly decreases with lower temperatures (Figure I-1). These considerations make PEFCs especially attractive for low-temperature applications.

![Figure I-1: Theoretical efficiency factor for a PEFC (H$_2$/O$_2$ operation) and a heat engine with the cold sink temperature $T_c = 90^\circ$C as a function of temperature.](image)

The working principle of a fuel cell has been known for about 150 years and was discovered by C. F. Schönbein and W. R. Grove. The development and quick spreading of the internal combustion engine, however, led to less research in the area in the first half of the 20th century. It was not until the space programs in the 1960s that the interest in fuel cells was rekindled. Nowadays, research is conducted on different types of fuel cells which
can be classified according to the employed electrolyte and the working temperature (Table I-1, adapted from [16]).

Table I-1: different types of fuel cells classified according to the employed electrolyte (adapted from [16])

<table>
<thead>
<tr>
<th>Fuel cell type</th>
<th>Temperature [°C]</th>
<th>Electrolyte</th>
<th>Fuel</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline Fuel Cell (AFC)</td>
<td>&lt; 80</td>
<td>Aqueous alkaline solution (e.g. 30% KOH)</td>
<td>H₂</td>
<td>mobile</td>
</tr>
<tr>
<td>Polymer Electrolyte Fuel Cell (PEFC)</td>
<td>&lt; 120 (Nafion)</td>
<td>Polymer membrane (ionomer e.g. Nafion)</td>
<td>H₂, reformer</td>
<td>mobile, transport, stationary</td>
</tr>
<tr>
<td>Phosphoric Acid Fuel Cell (PAFC)</td>
<td>150 - 210</td>
<td>Molten phosphoric acid</td>
<td>H₂, reformer</td>
<td>mobile, stationary</td>
</tr>
<tr>
<td>Molten Carbonate Fuel Cell (MCFC)</td>
<td>600 - 700</td>
<td>Molten alkaline carbonate</td>
<td>H₂, reformer, methane</td>
<td>mobile, stationary</td>
</tr>
<tr>
<td>Solid Oxide Fuel Cell (SOFC)</td>
<td>750 - 1000</td>
<td>Yttrium stabilized zirconia</td>
<td>H₂, reformer, methane</td>
<td>mobile, stationary</td>
</tr>
</tbody>
</table>

I.3 Polymer Electrolyte Fuel Cell

A special type of fuel cells, proton exchange fuel cells, also known as polymer electrolyte fuel cells (PEFC), is especially well designed for transport, stationary and mobile applications. It can be used in a relatively low pressure (ambient pressure) and temperature range (50-100°C) and in case of hydrogen/oxygen operation the only exhaust is water.
I.3.1 Thermodynamics of a PEFC

A PEFC using hydrogen and oxygen as reactants yields water as a product, according to:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$  \hspace{1cm} (3)$$

The Gibbs-Helmholtz equation defines Gibbs free energy $\Delta G$ of this reaction using reaction enthalpy $\Delta H$ and reaction entropy $\Delta S$ as a function of temperature $T$ [15], according to:

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (4)$$

Gibbs free energy $\Delta G$ at constant pressure and constant temperature can be used to calculate the maximum electric work defined by [8]:

$$\Delta G = -nFE_0$$  \hspace{1cm} (5)$$

With $n$ as the number of electrons, $F$ the Faraday constant and $E_0$ the reversible cell voltage. The negative sign is due to the general convention that the cell voltage is positive for a spontaneously occurring exothermal reaction; however, the Gibbs free energy is negative.

Assuming liquid water as a product of equation (3), it is possible to calculate Gibbs free energy of $-237 \text{ kJ mol}^{-1}$ for (3) by using known reaction enthalpies and entropies for the temperature of 298 K and pressure of 1 bar according to equations (4). Equation (5) can then be used to determine the theoretical value of reversible cell voltage of 1.23 V.

According to the Nernst equation, the cell voltage $E$ is a function of reactants’ and products’ activities, a [15]:

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{H_2O}}{a_{H_2}a_{O_2}^{1/2}}$$  \hspace{1cm} (6)$$

$E^0$ is the standard cell voltage in this equation, it can be defined as the reversible cell voltage if the activities of all components equal to one. $R$ is the gas constant, $T$ - temperature, $n$ - the number of electrons and $F$ - the Faraday constant.
I.3.2 Kinetics of a Polymer Electrolyte Fuel Cell

The value of the cell voltage $E_{\text{cell}}$ can vary from the equilibrium cell voltage $E^{0}$ if there is a current flowing. This deviation is caused by the overpotentials $\eta$. In a fuel cell, the net chemical reaction combines the reaction at the cathode with the one at the anode, thus, different types of overpotentials contribute to the reduced cell voltage [17]:

$$E_{\text{cell}} = E^{0} - \eta_{\text{anode activation}} - \eta_{\text{cathode activation}} - \eta_{\text{anode diffusion}} - \eta_{\text{cathode diffusion}} - U_{\text{ohm}}$$

(7)

Usually, there are three types of overpotentials for a fuel cell, activation overpotentials ($\eta_{\text{anode activation}}$ and $\eta_{\text{cathode activation}}$), diffusion overpotentials ($\eta_{\text{anode diffusion}}$ and $\eta_{\text{cathode diffusion}}$) and Ohmic potential losses $U_{\text{ohm}}$.

Butler-Volmer equation displays the relation between the activation overpotential $\eta_{\text{activation}}$ and the current density $j$ [8]:

$$j = j_{0} \left( \exp \left[ \frac{\alpha n F}{RT} \eta_{\text{activation}} \right] - \exp \left[ - \frac{(1 - \alpha)n F}{RT} \eta_{\text{activation}} \right] \right)$$

(8)

Where $j_{0}$ stands for the exchange current density, defined as the current in the absence of net electrolysis and at zero overpotential and $\alpha$ is the so-called symmetry factor which describes the fraction of potential influencing the activation energy. The exchange current density, which is temperature- and pressure-dependent, describes the electrocatalytic activity of an electrode material. High exchange current density means low activation energy and kinetically favoured reaction, accordingly.

The net reaction of a PEFC, using hydrogen and oxygen as fuel, is a combination of hydrogen oxidation on the anode and oxygen reduction on the cathode side.

Oxidation of hydrogen in an acidic solution can be written as following:

$$H_{2} + 2H_{2}O \leftrightarrow 2H_{3}O^{+} + 2e^{-}$$

(9)

Hydrogen is oxidised fairly easily on a platinum catalyst in an acidic solution at 298 K, due to rather small activation energy which in turn causes high exchange current density of $8 \times 10^{-4}$ A cm$^{-2}$ [8].
Oxygen is reduced in liquid acidic solution according to the following equation:

\[
\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}
\]  

The activation energy for oxygen reduction on a platinum catalyst in an acidic solution at 298 K is fairly high compared to hydrogen oxidation, leading to considerably smaller exchange current density of \(5 \times 10^{-9} \text{ A cm}^{-2}\) [8].

The diffusion overpotential results from a hindered transport of reactants or products and is thus determined by the concentration profile of the species. The concentration gradient is therefore the driving force for the diffusion. The diffusion overpotential \(\eta_{\text{diffusion}}\) can be calculated according to the more detailed equation [8]:

\[
\eta_{\text{diffusion}} = \frac{RT}{nF} \ln\left(1 - \frac{j}{j_{\text{lim}}}\right)
\]

Where \(j\) stands for current density and \(j_{\text{lim}}\) stands for the limiting current density, which increases with growing concentration of reactants and decreasing diffusion layer.

Ohmic voltage losses are linearly increasing with the current flowing through the cell:

\[
U_{\text{ohm}} = iR
\]

The specific resistance \(R\) in a PEFC is defined by contact resistance, resistivity and electrolyte resistance. The contact resistance and resistivity can be minimised by adapting the construction, so that the largest contribution to Ohmic resistance in a PEFC is due to the electrolyte resistance.

The relationship between the cell voltage and the current is dependent on the above-mentioned overpotentials and can be displayed in a so-called polarisation diagram (Figure I-2). It shows that at lower current densities the I-V curve is strongly influenced by activation overpotentials. The Ohmic voltage loss is strongest at medium current densities and at high current densities there are mass transport limitations and concentration overpotentials. The deviation of the open circuit cell voltage from its theoretical thermodynamic value of 1.23 V is due to the formation of mixed potentials, which in turn are caused by different processes, such as e.g. presence of small amounts of hydrogen at
the cathode, due to operation conditions or membrane degradation or formation of hydrogen peroxide.

Usually, a PEFC operates at potentials between 0.5 and 1.0 V, significantly more anodic than the equilibrium potential for carbon corrosion, as will be further elaborated in I.4. During “idling”, when no power is drawn from the PEFC except for auxiliary FC system, the cathode potential is around 0.9 V [18]. The cell could also be at open-circuit voltage (OCV) when no current is drawn from the PEFC and the cathode potential in a cell with a thin membrane increases to 0.95 V [18]. This can happen directly before the PEFC shut-down, immediately after start-up or in PEFC-battery hybrids where battery provides the electric load under low power or idling [18]. However, also cathode potentials up to 1.5 V are possible due to so-called reverse-current during start-up or shut-down of a fuel cell [19-21]. The start-up of a PE fuel cell is usually accomplished by purging the air-filled compartment with hydrogen (vice versa for the shutdown), leading to a formation of a hydrogen-air front which divides the anode compartment in two parts and to polarisation of the electrodes, so that values substantially higher than 1.0 V, e.g. 1.5 V, are possible [20, 22, 23].

![Figure I-2: polarisation curve of a PEFC, illustrating possible voltage loss mechanisms](image)

### I.3.3 PEFC components

Polymer electrolyte fuel cells owe their name to the employed electrolyte which is typically a polymer membrane. An important part of a PEFC is the membrane-electrode-assembly
Introduction

(MEA). MEA contains a polymer electrolyte, sandwiched between catalyst layers, adjoined by gas diffusion layers (GDLs) (Figure I-3). The unity consisting of the catalyst layer and the GDL is herewith defined as the PEFC electrode.

![Figure I-3: Schematic set-up of a PEFC](image)

There are several specifications concerning the properties of a PEFC polymer membrane. The proton conductivity, for instance, should be as high as possible. However, the membrane should be impermeable to electrons (due to a possibility of a short circuit) but also to the reactants, hydrogen and oxygen, to avoid the so-called “gas crossover”. There are several different types of polymer membranes but the most commonly used is the Nafion® membrane, produced by DuPont. It has a fluorinated polymer backbone with sulfonic acid functional groups (Figure I-4).
Introduction

Figure I-4: Chemical formula of Nafion®, used as electrolyte in a PEFC

The catalyst layer usually consists of carbon supported metal nanoparticles, as shown in Figure I-5. The most commonly used metal is platinum (Pt) or a platinum alloy (dark dots in Figure I-5). A more detailed description of the catalyst and its components can be found in the next chapter.

Figure I-5: Pt supported on Vulcan® XC72 (Tanaka) [24]

GDL is usually carbon cloth or carbon paper. It serves several purposes such as even distribution of the gases on the electrode surface but also the contact between the catalyst layer and the current collector situated outside the cell.
A single PEFC unit consists of a MEA, suitable seals and flow fields for the gas channels. One single PEFC, however, does not provide enough voltage to be of any technical relevance. Thus, the fuel cells are joined together in so-called bi-polar stacks of several hundred cells, also called PEFC stacks. Also, for technical applications units for the system support are required.

I.3.4 Catalyst layer

Usually, platinum or platinum alloys are used as effective catalysts for PEFCs [8, 25]. The high activity and efficiency of Pt as a catalyst can be best explained using a so-called volcano plot (Figure I-6). It shows the exchange current density as a function of the enthalpy of lower-higher oxide transition. This type of correlation is equivalent to correlating the catalytic activities of some metal oxides with the standard potential, or Gibbs free energy, for the formation of the higher valency oxide from the lower valency oxide [26, 27]. The maximal catalytic activity is obtained for metal oxides with redox potentials close to the equilibrium potential of O$_2$/H$_2$O electrode [27].

![Figure I-6: Electrocatalytic activity in oxygen evolution at various electrodes as a function of the enthalpy for lower-higher oxide transition. The open symbols represent alkaline conditions, the filled symbols-acidic [26].](image-url)
There are certain requirements for an ideal PEFC catalyst. The electrochemically active surface area of an ideal PEFC catalyst should be as large as possible but consume as little geometric electrode surface area as possible. The reaction sites of the catalyst should be easily accessible to the reactant gases but also to electrons and protons. Therefore, the electrochemically active catalyst surface area is determined by the gas phase, the electronically conducting phase and by proton-conducting phase. The accessibility for electrons and reactant gases is provided by the porous catalyst support structure, the high proton-conductivity by impregnation of the catalyst layer with an ionomer. The mechanical stability of the catalyst and its resistance towards corrosion and/or degradation are likewise an important issue.

Nowadays, most commercially available PEFC electrodes are produced in a wet-chemical process. For this purpose, Pt nanoparticles with sizes of 2.5 to 8 nm [21, 28, 29] are deposited on different carbon materials, such as e.g. carbon black, with different surface areas and varying surface chemistry [18, 28, 30].

An overview of some carbons used as commercial carbon supports is given in Table I-2. So far, largely so-called non-graphitic carbons have been commercially implemented. These carbons have an expanded two-dimensional order of carbon-atoms in sp²-bonded, planar hexagonal networks but without any measurable stacking order of these sheets [31]. According to Franklin, non-graphitic carbons can be further subdivided into graphitising carbons, which can be converted to graphitic carbon by thermal treatment at temperatures between 1700-3000°C and non-graphitising carbons, which cannot [32].
Table I-2: different types of commercially available carbon supports

<table>
<thead>
<tr>
<th>name carbon</th>
<th>BET surface area / m² g⁻¹</th>
<th>Properties</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black pearl 2000</td>
<td>1485</td>
<td>Non-graphitic, non-graphitised carbon</td>
<td>[18]</td>
</tr>
<tr>
<td>graphitised Black Pearl</td>
<td>240</td>
<td>Non-graphitic, graphitised carbon</td>
<td>[18]</td>
</tr>
<tr>
<td>Ketjen Black EC-600JD</td>
<td>1400</td>
<td>Non-graphitic, non-graphitised carbon</td>
<td>[18]</td>
</tr>
<tr>
<td>graphitised Ketjen Black</td>
<td>160</td>
<td>Non-graphitic, graphitised carbon</td>
<td>[18]</td>
</tr>
<tr>
<td>multi-walled carbon nanotubes</td>
<td>&lt; 600</td>
<td>graphitic carbon</td>
<td>[30]</td>
</tr>
<tr>
<td>Vulcan® XC72</td>
<td>232</td>
<td>Non-graphitic, non-graphitised carbon</td>
<td>[18, 28, 30]</td>
</tr>
<tr>
<td>graphitised Vulcan® XC72</td>
<td>80</td>
<td>Non-graphitic, graphitised carbon</td>
<td>[18]</td>
</tr>
<tr>
<td>Vulcan® XC72R</td>
<td>241</td>
<td>Non-graphitic, non-graphitised carbon</td>
<td>[28]</td>
</tr>
</tbody>
</table>

A whole “family” of non-graphitic, non-graphitised carbons can be described by the term “carbon black”. Carbon black consists almost entirely of elemental carbon in form of nearly spherical particles of colloidal size of < 100 nm, that form aggregates of some hundreds nanometers in size [33]. These aggregates can further interact due to van-der-Waals forces and form secondary structures on a scale of several micrometers [33]. The widely accepted model of carbon black was proposed by Heidenreich et al. in 1968 [34] and is of a spherical carbon particle with the concentric organisation of small graphene sheets from the surface to the center, as presented by the authors in Figure I-7.
The concentric arrangement is more pronounced near the outer sphere, leading to the formation of amorphous carbon in the core of the particles. This model was further supported by HRTEM measurements in 2005 [35]. The graphene sheets of the outer shell also contain surface functional groups, such as carboxylic acids or hydroxides [36]. In 2011, Ban et al. [33] confirmed the proposed core-shell structure of CB by their calculations (Figure I-8). The slice view of CB particles, for instance, (Figure I-8a,b) visualises the network of pores created within the material. The interconnected pores form channel-like structures, running from the surface to the core of the CB particles [33]. The porosity of CB depends on the size of the shell units. Particle generation with high density (2 g cm\(^{-3}\)) leads to negligible pore volume of 0.02 ml g\(^{-1}\), larger graphite units prevent closely packed structures and result in higher pore volumes.
The order of CB particles increases from the core to the outer layer, which consists of partially interlaced graphite sheets (Figure I-8c) [33]. This overlap of graphite sheets creates a surface grain pattern formed by the interconnected edges of flakes, as illustrated by dark lines in Figure I-8c. The surface heterogeneity, thus introduced, offers adsorption sites attractive to e.g. metal nanoparticles [33].
The goal of a commercial catalyst is to obtain as much electrochemically active Pt surface area as possible. The catalyst ink, consisting of carbon supported Pt and an ionomer, is sprayed either on GDL [17] or directly onto the polymer electrolyte [37, 38].

I.3.5 Pt/C Corrosion in a PEFC

The use of Pt as a catalyst for PEFC is due not only to its excellent catalytic activity but also to its resistance towards corrosion and sintering under harsh reaction conditions of a PEFC, such as high acidity and elevated temperatures. These qualities, however, have literally a high price: the cost of Pt has been rising steadily during the last decade and it has determined, still determines and will largely determine the price of a PEFC stack [39]. Thus, many efforts are directed towards minimizing the amount of the noble metal while preserving the high electrocatalytic activity, e.g. by spreading Pt nanoparticles on large surface area carbon supports.

Carbon is widely used as a support in PEFCs because of its low price, high availability, high corrosion resistance but also good electric conductivity.

Despite high corrosion resistance of Pt, the stability and lifetime of a PEFC is still largely determined by the catalyst durability during PEFC operation [9]. The loss of Pt active area can be assigned to three fundamental degradation mechanisms such as (i) Pt dissolution and redeposition (Ostwald ripening), (ii) migration and sintering of Pt atoms on the carbon support and (iii) Pt agglomeration triggered by corrosion of the carbon support [9, 40].

Ostwald ripening terms thermodynamically favoured growth of larger particles at the expense of smaller particles (Figure I-9), sintering is a phenomenon which describes diffusion of atoms through / on the microstructure and is caused by a gradient of chemical potential and Pt detachment may signify formation of soluble Pt ions or mechanical separation of Pt from the support (Figure I-9) [9]. The detailed assignment of the above-mentioned degradation processes to reaction conditions is still under investigation.
Figure I-9: schematic representation of the loss of Pt active area due to Ostwald ripening, sintering and corrosion of the carbon support. Adapted from [40]

The degree and the progress of carbon corrosion in PEFC depend on the operation conditions. The combustion of carbon to carbon dioxide is thermodynamically favoured above 0.207 V vs. SHE (also see I.4.1) but is kinetically hindered at potentials below 1 V vs. SHE [19]. The corrosion is considered to proceed via the carbon oxidation or formation of surface oxides at potentials > 0.3 V vs. SHE and further oxidation of these intermediates to CO$_2$ at potentials > 0.6 V vs. SHE [40-42], according to (13) and (14):

\[
C + H_2O \rightarrow CO_{ad} + 2H^+ + 2e^- \quad \text{(13)}
\]

\[
CO_{ad} + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \quad \text{(14)}
\]

All these mechanisms, schematically depicted in Figure I-9, have been discussed as being relevant also for degradation of PEFC catalysts. It was likewise stated that Pt loss on a cathode is significantly larger than on an anode [10, 17].

There are numerous studies dealing with Pt loss in a catalyst; however, less attention has been paid to corrosion and degradation of the carbon support in a PEFC and the interplay of these processes. Nevertheless, these degradation processes are of certain interest and
importance, as loss or agglomeration of Pt particles can be triggered by carbon corrosion. Most of carbon corrosion studies, as described e.g. by Stevens et al. [12] or Maass et al. [42] are performed under working conditions on a real PEFC, a highly complex system, while fundamental research is rarely portrayed and is seldom conducted under conditions which are relevant for a working PEFC. In the following, the fundamental facts of bulk platinum and bulk carbon corrosion will be discussed as well as an approach to better understanding of the corrosion processes.

I.4 Platinum and Carbon Corrosion

I.4.1 Thermodynamics of Pt- and C-corrosion in the bulk

Carbon corrosion is a widely observed phenomenon in an electrochemical system as the thermodynamic potential for the formation of carbon dioxide at standard conditions, shown by equation (15), is only 0.207 V, meaning that the process is possible above 200 mV vs. SHE [40, 43, 44].

\[ C + H_2O \rightarrow CO_2 + 4H^+ + 4e^- \]  \hspace{1cm} (15)

If more water is present, carbon can also be consumed according to the heterogeneous water-gas reaction according to (16), even though under PEFC conditions this reaction is not thermodynamically favoured [12, 42].

\[ C + H_2O \rightarrow H_2 + CO \]  \hspace{1cm} (16)

The corrosion reaction is particularly enhanced in the presence of platinum, as observed by e.g. Maass et al. [42]. The authors state that Pt catalyses the formation of carbon dioxide by accelerating the adjustment of thermodynamic equilibrium according to (17-19):

\[ Pt + H_2O \rightarrow PtOH_{ad} + H^+ + e^- \]  \hspace{1cm} (17)

\[ C + H_2O \rightarrow CO_{ad} + 2H^+ + 2e^- \]  \hspace{1cm} (18)

\[ PtOH_{ad} + CO_{ad} \rightarrow Pt + CO_2 + H^+ + e^- \]  \hspace{1cm} (19)
Pourbaix et al. [45] mapped potential stable phases of an aqueous electrochemical system in the potential-pH diagrams, so-called Pourbaix diagrams. Figure I-10 ([46]) shows a Pourbaix diagram of carbon, visualizing equation (19) by revealing that at low pH-values (in acids, upper left corner of Figure I-10) carbon oxidation/combustion starts above 0.2 V vs. SHE.

Figure I-10: Pourbaix diagram of carbon species, taken from [47]

The studies concerning stability of bulk platinum have likewise been known for a long time. Using a Pourbaix diagram for platinum (or a metal in general), for instance, it is possible to determine the conditions under which a) a metal (in this case Pt) is thermodynamically stable (the potential for corrosion is too low), b) a metal ion is thermodynamically stable (state of corrosion, upon which a metal is dissolved in the electrolyte) and, finally, c) a metal oxide is thermodynamically stable (state of passivation, in which a metal is covered by a – usually protective – metal oxide film) [45]. A Pourbaix diagram for Pt at room temperature in water (also shown in Figure I-11) shows that at room temperature metallic
Pt is stable in a very wide potential and pH range provided the absence of complexing agents, such as e.g. chlorine [45]. It is not attacked by most acids and only with difficulty by oxidising agents [45]. If Pt is used at potentials above 1.4 V vs. SHE (upper part of Figure I-11b), it is usually covered by a film of Pt-oxide or –hydroxide (as expected from diagram in Figure I-11a), which is normally protective (an exception would be the behaviour of platinum black, where the oxide is separated from Pt which, in turn, suffers an anodic attack) [45].

According to DFT calculations, the formation of platinum oxides generally starts above 0.78 V vs. SHE, but potentials around 1.5 V vs. SHE are required for Pt dissolution to become thermodynamically favoured [48]. It has been long suggested in literature [49-52], that there are two types of Pt oxides, namely α- and β-oxides. The α-oxide film is a thin monolayer, while the β-oxide is a thick, highly hydrated, porous, polymer-like material or an aggregate with an open pore structure [49]. Both oxides comprise components of PtO, PtO₂, Pt(OH)₂ and Pt(OH)₄ [40]. The Pt α-oxide is formed under moderate oxidation.
conditions and reduced in the potential range 0.7 to 0.8 V vs. SHE. The Pt $\beta$-oxide is formed under severe oxidation conditions and is reduced at a more negative potential than Pt $\alpha$-oxide [49]. The formation of Pt-oxides is quite crucial to the stability of the noble metal in an electrolyte, as Pt$^{2+}$ ions are easily dissolved in an electrolyte, leading to accelerated Pt-corrosion [49, 53].

XPS studies and electrochemical measurements by Peuckert et al. [54] revealed that the first step for oxidation of Pt in acidic media (1 N sulphuric acid) occurs in the electrochemical double layer region, i.e. between 0.2 and 0.7 V vs. SHE by physisorption of water, which then dissociates and yields an irreversibly adsorbed hydroxyl-species [54]. At 1.2 V vs. SHE the first monolayer is complete and the oxidation continues at higher potentials. In a potential sweep up to 2 V vs. SHE the authors observed a transfer of four charge equivalents which can be interpreted as one monolayer of oxidised Pt$^{4+}$ or two monolayers of Pt$^{2+}$ [54]. Further potential increase of up to 3 V vs. SHE leads to another monolayer of oxidised Pt$^{4+}$ or two monolayers of Pt$^{2+}$. Monitoring the formation of oxidised Pt layers by XPS, revealed no changes of Pt 4f doublet for potentials < 2 V vs. SHE, occurrence of a shoulder at higher binding energies in the Pt 4f spectrum, originating from an oxidised Pt-species, at potentials > 2 V vs. SHE and complete oxidation of the Pt surface after potentiostatic hold of 3 h at 3 V vs. SHE [54]. These findings confirmed authors’ data obtained from CVs, presence of one-two monolayers of oxidised Pt on the bulk-Pt surface at > 2 V vs. SHE and increased amount of Pt-oxide-species at growing potentials [54].

I.4.2 Kinetics of Pt- and C-Corrosion

A good overview of thermodynamic and kinetic stability of Pt and carbon, in particular under conditions relevant for PEFCs was given e.g. by Shao et al. in [40] and will be elaborated in the following.

It is expected that the degradation processes are accelerated at increasing temperatures. Indeed, the carbon corrosion is faster at higher temperatures, as discussed by Shao et al. [40] and Stevens et al. [12]. Also, the rates of coarsening of Pt particles increase linearly with temperature [21, 55]; for Pt dissolution at a certain potential it was estimated that the equilibrium concentration of Pt$^{2+}$ in an acidic solution at 0.9 V vs. SHE increases by two
orders of magnitude during a temperature increase from 25°C to 80°C and an additional order of magnitude for the further increase from 80°C to 120°C [40, 56].

Other factors like the properties of the carbon support, the applied potential, the operation mode or the presence of water in the electrolyte likewise influence the degradation and corrosion processes [40].

**Carbon support**

The degree of graphitisation of carbon, for instance, is a key factor to the thermal and electrochemical stability of the support [44, 57, 58]. It was stated that the enhanced stability is due to a decreased number of defect sites on the carbon surface, where the carbon oxidation is usually initiated [59]. Increasing the degree of graphitisation has additional advantages as it leads to increased strength of π-sites (sp²-hybridised carbon), which act as anchoring centers for Pt ions [60], thus strengthening the metal-support interaction and the resistance of Pt to sintering [58, 61]. Yu and Ziegler showed that catalysts supported on graphitised carbon are more resistant to carbon corrosion than the samples prepared on non-graphitised carbons, despite similar kinetic parameters (Tafel slope and activation energy) for the oxygen reduction reaction, stating that carbon corrosion strongly depends on the properties of the employed carbon [62]. In addition to the structural effects, the corrosion behaviour may be influenced by the concentration of oxygen-containing groups such as ketones, lactones or carboxylic acids on the carbon surface [63, 64]. Antonucci et al., for instance, report that in their papers that the oxidation of carbons only proceeds after a certain critical concentration of oxygenated surface groups is present on the carbon surface [63, 65]. The surface of graphitised carbon consists almost entirely of basal planes, which are most resistant to electrochemical oxidation [64]. Non-graphitised carbon materials, in which graphitised crystallites are mixed with amorphous carbon have a higher density of defects and more unsaturated carbon bonds and hence can be attacked more easily by the electrolyte [64]. The problem is that it is more difficult to deposit platinum on a graphitised carbon surface with less active sites [40].
Introduction

Working conditions

The electrode potential and the operation mode also influence the stability of platinum and/or carbon. It was observed that in an acidic electrolyte the dissolution rate of a Pt wire increases with higher potentials in the range of 0.65 to 1.1 V vs. SHE under potentiostatic conditions and is logarithmically dependent on the applied potential in the region of 0.85-1.1 V vs. SHE [66]. Above 1.1 V vs. SHE, the dissolving rate decreases, which is commonly explained by a formation of a protective oxide layer on the platinum surface [66]. For the Pt/C system, the dissolution of Pt at 0.9 V vs. SHE is comparable to this of a Pt wire [66]; it grows monotonously with increasing anodic potentials (0.6-1.2 V vs. SHE) [40]. Cycling the potential between oxide formation and reduction regions leads to higher (three to four orders of magnitude) dissolution rates than holding the sample at the oxide formation potentials [9, 21, 66-68]. The exact nature of this phenomenon is not yet completely clear, it is hypothesised that the interruption or reduction of relatively corrosion-resistant, steady-state Pt oxide or hydroxide during voltage transients at low potentials leads to accelerated production of oxidised Pt species (Pt$^{2+}$, for instance) which are mobile during subsequent cycling to higher potentials [9]. There are several reasons for increased dissolution rates; one is an electro-reduction of a Pt oxide either via a mechanical detachment of Pt-ions or atoms from the support or via reduction of Pt (IV) oxide formed at higher anodic potentials to soluble Pt (II) oxide [69]. The mechanical detachment of Pt atoms is usually due to surface restructuring during the formation of Pt oxide, which results in an interfacial place exchange of Pt and O-atoms [53, 69]. Another origin of Pt loss is due to the electro-oxidation, related to the formation of Pt$^{2+}$ ions and happens simultaneously with the oxide formation [69].

Presence of water

Another stability issue of Pt and/or carbon is related to the presence of water. As already mentioned in 1.4.1., in the presence of water carbon may be consumed via a heterogeneous water gas shift reaction, reacting to carbon monoxide [40, 57]. Apart from the carbon consumption, this reaction (14) might lead to poisoning of the Pt catalyst. However, there are some contradictions concerning the loss of carbon: the rate of carbon combustion is higher when the samples were held at high temperatures under humidified conditions as compared to dry air [20, 57, 70], however, carbon corrosion of the electro-
catalyst layer was reported to decrease with increasing humidity [21]. It was repeatedly stated, that also Pt dissolution is influenced by the aqueous electrolyte. Stevens et al. showed that no noticeable sintering of Pt particles, supported on Black Pearls (non-graphitic, non-graphitised carbon, see also Table I-2) occurred during long-term (3000 h) exposure to dry air conditions even at high temperatures of 125-195°C [12]. In liquid phase, the Pt nanoparticle size (in case of [71] supported on non-graphitic, graphitised carbon) rapidly increases, even if no external electrochemical force is applied [40, 71]. It was reported that the mass transport mechanism for both unsupported platinum black and Vulcan® XC72 supported platinum is the same in aqueous surroundings, namely via the diffusion of Pt atoms on the crystallite surface [71]. This so-called 2D-Ostwald ripening is independent of the amount of Vulcan® XC72-supported Pt and of the applied potential, as reported by Bett et al. [71]. It was suggested that water molecules were able to penetrate between the metal islands and the support and lower the metal-substrate bonding energy, which in turn resulted in migration of metal crystals [71].

In general, there are multiple reasons and mechanisms for the degradation of the Pt/carbon system, as it comprises the properties of the metal and of the carbon support as well as the metal/carbon interactions. Up to now, however, most of the stability studies, have dealt with a whole highly-complex PEFC system.

I.4.3 Model Systems for Pt/C Corrosion

A possible approach towards better understanding of fundamental Pt and carbon corrosion processes is preparation of model systems, which can be investigated via e.g. in situ methods, thus enabling records of changes in morphology and/or composition of the material during degradation. Some of the requirements for an “ideal” model catalyst were listed by Zoval et al. in 1998 [72]: (i) the particles should be of monodisperse size and shape, (ii) should have an electrical connection to a (catalytically inert) support, which facilitates the characterization of the particles, (iii) should be well-separated from each other, (iv) their structure and the structure of the support should be accessible to certain measurement techniques before, during and after the involved catalytic process and, finally, (v) the particles should be stable for a long time.

In literature, many different methods to prepare Pt/C model electrodes, which meet some of the above-mentioned criteria, are described. Some of them such as e.g. electrochemical
platinum deposition on HOPG and subsequent in situ STM measurements by Matsumoto et al. [73] or platinum arrays on GC prepared by hole mask colloidal lithography for catalyst studies by Lindström et al. [74] will be discussed in the following.

The preparation itself of the model electrodes is quite challenging, as deposition of Pt on a carbon substrate is significantly dependent on the properties of the respective carbon.

Untreated HOPG, for example, is flat on atomic scale, therefore, Pt particles are either immediately deposited on surface defects [75] or agglomerate to form clusters within a short time [76]. Electrochemical Pt deposition on a different carbon substrate, such as glassy carbon [77] or oxidised HOPG [78], results in a very heterogeneous diameter distribution [78]. Cherstiouk et al. [78] as well as Tripkovic et al. [79] used oxidised GC G-type as a substrate, pre-oxidised by pulse application in sulphuric acid. The pre-oxidation was supposed to introduce increased hydrophilicity and surface roughness necessary for stabilization of Pt nanoparticles and, indeed, the authors observed that the size and the amount of Pt particles on the GC substrate varied according to the oxidation degree of GC [78, 79]. Also, Plyasova et al. [80], Martin et al. [81] and Maillard et al. [82] employed electrochemical pre-oxidation of GC to control the properties of electrodeposited Pt. In 2008, Dressick et al. filed a patent [83], describing electrochemically activated GC as an alternative for a stable carbon support for the catalyst in polymer electrolyte fuel cells. Duarte et al. [84] described differences between Pt deposition on carbon fibers and GC, while Jovanovic et al. [85] stressed the influence of (electro)chemically modified GC surface on the activity of supported Pt.

Some techniques enabling to gain more control over the size and spatial distribution of Pt dots on a carbon surface are focused ion beam (FIB) or lithography. FIB, combined with low energy cluster beam deposition (LECBD) has been successfully applied to prepare Co_{50}Pt_{50} clusters on HOPG [86]. Lindström et al. prepared monodisperse Pt discs with diameters of 100, 120 or 140 nm on pre-oxidised GC by hole-mask colloidal lithography [74]. The advantages of employing electron beam (e-beam) lithography (EBL) for catalyst studies, such as using EBL to bridge the material gap between measurements on single crystals and industrial catalysts, have been described by Somorjai et al. in [87]. One of the biggest disadvantages of EBL is the low sample throughput. Extreme-ultraviolet interference lithography (EUV-IL) might be better suited for designing model electrodes as
Introduction

it is an established technique to produce large area periodic arrays with structure size down to 11 nm [88, 89]. However, to the best knowledge, neither EBL nor EUV-IL has been used to pattern GC or HOPG prior to our project.

Characterisation of model electrodes at extremely high resolutions in situ is likewise very challenging, which is confirmed by a small number of publications dealing with this research topic. Siroma et al. [75] investigated Pt induced corrosion of carbon via atomic force microscopy (AFM) in air. They compared AFM images of an HOPG surface containing electro-deposited Pt before and after oxidation at a constant potential for 70 h. However, this study was conducted ex situ, i.e. in air; therefore, it was not possible to monitor the degradation processes in more details. Also, the electro-deposited Pt particles were mainly concentrated on steps and edges of HOPG, which are thermodynamically pre-destined to be oxidised first, independent of the presence of a metal catalyst [73, 90]. A different study by Matsumoto et al. [73], published in 2009, was dedicated to in situ scanning tunneling microscopy (STM) of Pt nanoparticles on HOPG and showed the effect of Pt presence as well as oxygen atmosphere on carbon oxidation. However, also in this study the electro-deposited Pt particles were distributed heterogeneously on the HOPG surface and mainly found on the edges.

Two approaches were investigated in course of this thesis, the electrochemical Pt deposition and lithography. Both techniques have their advantages and disadvantages for fabricating “ideal” model electrodes.

Dissolution of Pt and Ostwald ripening are easier to trace on the surface if the particles have a defined diameter, which does not significantly vary from dot to dot and a strictly controlled arrangement, which is usually true for lithographic preparation. In this case, any deviation from the original sample state, such as increase/decrease of diameter or particle movement can be quickly detected. One of the biggest drawbacks of lithography is its complexity and the need for several processing steps, as can be seen in Figure I-12.
The substrates have to meet certain requirements such as surface smoothness for an even spread of the photoresist, thermal stability up to 200°C required for the soft-bake spincoating step and vacuum compatibility as both EUV and EBL are performed at pressures $< 10^{-6}$ mbar.

The electrochemical platinum deposition from an electroplating solution requires less preparation steps and is, thus, faster and easier. However, the success of the process is likewise dependent on many parameters such as the proper choice of the concentration of the electroplating solution, the deposition technique (potentiostatic or galvanostatic) but also the potential and the length of the electrochemical treatment, such as e.g. the applied pulse. One of the biggest advantages is the ensured electrochemical binding of the deposited particles to the substrate. Some of the major drawbacks are lesser reproducibility and less well-defined size and size distribution of the particles if compared to lithography.

The substrate choice is usually defined by the catalytic process for which the model electrode should be prepared, by the desired measurement techniques and by the measurement conditions, as e.g. *in situ* or *ex situ* mode. In course of this thesis platinum nanoparticles of different sizes were deposited on carbon supports, such as glassy carbon.
Introduction

(GC) and highly oriented pyrolytic graphite (HOPG). The use of the carbon as a support for the PEFCs has already been discussed in I.3.6. Carbon is a good choice for scanning probe microscopy and photoelectron spectroscopy but also electrochemical measurements due to its good conductivity. The important advantages of GC and HOPG as destined substrates for model electrodes are strong similarities of structure and physical and chemical properties to the core (GC) or shell (HOPG) of CB, a carbon typically used in PEFCs.

Also the oxidation and / or degradation conditions for the model electrodes had to be determined. Several protocols for model electrodes are known from literature, some of them will be mentioned in more details in the following examples. Wickman et al. [55], for instance, conducted quartz mass balance measurements on Pt, Pt on C and pure C model electrodes in 0.5 M sulphuric acid at different temperatures, ranging from room temperature to 70°C. The conclusion was that Pt catalyses carbon corrosion and the degradation is faster and stronger at higher temperatures. Oh et al. [91], however, implied that the surface properties of the carbon support play a more important role during the corrosion process than the presence of Pt. Also, the detrimental influence of cycling between different potentials and/or holding the sample at a certain potential was widely discussed. Cherstiouk et al. [92] monitored carbon corrosion during potentiostatic holds at 1.2 V vs. SHE in 2 M sulphuric acid at 80°C. Further, they stated that the corrosion currents increased with rising electrode potential, temperature, water concentration and presence of Pt. Ball et al. [29] described potentiostatic holds at 1.2 V vs. SHE in 1 M sulphuric acid, as carbon corrosion is thermodynamically favoured at this potential. However, they did not observe any influence of Pt on the process and mentioned that pulsed tests or cycling were more aggressive and led to higher degradation rates. Inzelt et al. [69] and Xu et al. [93] confirmed these findings by observing Pt dissolution during cycling between 0.4 and 1.4 vs. SHE and coarsening of Pt nanoparticles during cycling between 0 and 1 V vs. SHE, respectively.

According to the literature findings, two different types of degradation protocols were determined, potentiostatic hold for a defined time span at potentials ranging from 1.2 V to 1.9 V vs. SHE or cycling the sample between the Pt oxide formation (1.2-1.9 V vs. SHE) and Pt oxide reduction at 0.6 V vs. SHE. The high anodic potentials and sulphuric acid were required in order to be able to imitate the conditions of either OCV (potential hold) or
start/stop (potential cycling) in a real PEFC. The anodic potentials of 1.6 to 1.9 V vs. SHE, at which some of the model electrodes were degraded in this work, cannot be reached in a real PEFC; however, they were chosen to compensate the difference in temperature (according to the Nernst equation, a temperature rise from 22 to 80°C leads to a cell voltage changed by 20%). A real PEFC operates at 80°C, a temperature at which stable measurements within a liquid electrolyte are questionable. Therefore, during this project all measurements were performed either at room temperature or at 60°C. The lower potential of 0.6 V vs. SHE for cycling experiments was chosen according to literature as well to the recommendation of Nicolas Linse who observed that selecting this potential as the lower limit led to enhanced carbon corrosion, if compared to e.g. 0.9 V vs. SHE [20]. The given explanation was that the oxidation state of Pt strongly influences carbon corrosion: elemental Pt enhances the combustion of carbon to carbon dioxide while Pt oxide is rather inert in this respect.

The aim of the project is to improve the scientific understanding of the degradation processes occurring at the support-catalyst-electrolyte interface of an electro-catalyst in a PEFC. For this purpose, model electrodes will be fabricated and treated under conditions comparable to those present in laboratory PEFC cells while being monitored. The degradation processes of Pt and C will be investigated as a function of e.g. carbon support, Pt particle size and distance or temperature. The visualisation of degradation processes will be performed in situ in an electrolyte by scanning probe microscopy (SPM) and changes of chemical properties of the model electrodes will be traced ex situ by X-ray photoelectron spectroscopy (XPS).
II Methods, Materials and Instrumentation

II.1 Analytical Techniques

II.1.1 Atomic force microscopy (AFM)

Atomic force microscopy was first proposed as a method by Binnig, Quate and Gerber in 1986 to measure extremely small forces as well as to investigate bulk insulators [94]. It enables atomic resolution under ambient conditions on conducting as well as insulating samples and provides reliable information about the surface topography [95]. In present project, AFM was used as an auxiliary characterization method to scanning tunneling microscopy (STM) for the samples with low conductivity.

During an AFM measurement, an AFM tip (4 in Figure II-1), mounted to a cantilever spring (3 in Figure II-1), is used as a probe to scan the sample surface (2 in Figure II-1). The spring constant of the tip is chosen as to be smaller than the inter-atomic bonds of the sample, leading to a deflection of the tip upon an interaction with the sample. The deflection of the cantilever is usually monitored by a laser (5 in Figure II-1) which is focused onto an end of the cantilever. The reflected beam is traced by a position-sensitive photodiode (6 in Figure II-1). The sample is continuously scanned in two axes (xy), its position varied by two piezo-elements (1 in Figure II-1). A third piezo is integrated in a scanner and adjusts the z-position, compensating for changes in sample height as well as tip-sample forces [96]. The scanner may be located within a stage (stage-scanning) or at the cantilever (tip-scanning) [97] and references therein.
The operation modes of AFM can be subdivided according to the cantilever dynamics and the tip-surface interaction [95]. If the cantilever is oscillating at or off its resonant frequency during imaging, the process is called “dynamic mode”, if the cantilever is not vibrating, then it is termed “static mode”. The dynamic mode can be subdivided into the amplitude-modulated AFM, also called “tapping mode (TM)”, and frequency-modulated AFM. The tapping mode dynamic AFM is usually used on fragile samples, where there is an imminent danger of damaging or displacing the investigated object.

Both dynamic and static AFM can be operated in contact or non-contact mode, depending on the surface-tip interaction. If the tip is repulsed by the surface (or vice versa), the AFM mode is called “contact”. Imaging in contact mode can be done either by maintaining a constant tip height and recording the cantilever deflection during the xy-scan or maintaining a constant cantilever deflection and adjusting the xy-scan via an electronic feedback loop. If the tip-surface interactions are of attractive nature, the mode is called “non-contact”. The non-contact dynamic AFM mode is usually used to achieve atomic resolution in UHV on surfaces which are too reactive to be imaged in a static mode.
In present work, AFM was used to image low-conducting samples, such as e.g. spin-coated glassy carbon samples. The exposure to the beam, independent on the type of lithography process, requires a special beam-sensitive photoresist on the substrate surface. The proper adhesion and even spread of the photoresist are crucial for the successful exposure. These parameters can be estimated by measuring the average surface roughness (RMS) value before and after the spin-coating with the photoresist. These measurements were performed using contact mode AFM. Oxidised glassy carbon samples were likewise investigated via tapping mode AFM.

The topography measurements were performed under ambient conditions on a Digital Instruments Nanoscope III / Dimension 3100 AFM (Santa Barbara, USA) fitted with a μMasch Ultrasharp tip, type CSC 11 / AlBS / 50 (type B, resonance frequency 100-235 kHz and spring constant 1.5-16.5 Nm$^{-1}$) for tapping mode and type CSC 37 / AlBS / 50 (type B, resonance frequency 17-24 kHz and spring constant 0.1-0.4 Nm$^{-1}$) for contact mode. Both the tapping and the contact mode were used for topographic imaging.

The AFM images were processed using WSxM 5.0 Develop 3.1. software [98].

**II.1.2 Cyclic Voltammetry (CV)**

Cyclic voltammetry (CV) is a widely used form of linear sweep chronoamperometry, in which a potential of an electrode is swept with a constant rate, dU/dt, between two arbitrary values [8].

Usually, CV is used to obtain information about thermodynamics of redox processes and kinetics of heterogeneous electron transfer reactions. The common set-up consists of three electrodes: a working electrode (WE), a counter electrode (CE) and a reference electrode (RE). The observed chemical reactions occur at the WE and the RE establishes a well-defined potential, against which other potentials can be measured. The CE (or auxiliary electrode) is required for a process with a reversed charge with respect to the WE, e.g. the CE functions as a cathode if the WE is an anode and vice versa. There is a current between the WE and the CE, so that a potential measurement, independent of the current flow, is possible between the WE and the RE [99].

In a CV the potential is linearly swept versus time, resulting in a triangular shape of the potential wave (Figure II-2). The area of interest for an experiment is defined by the lower
(E₁ in Figure II-2) and the upper (E₂ in Figure II-2) potential. The potential is applied between the WE and the RE and current is measured between the WE and the CE. The current is plotted against the applied potential to yield a cyclic voltammogram. The speed of sweeping is defined as the scan rate and measured in V s⁻¹.

![Graph](image)

*Figure II-2: potential-time plot for CV*

In this work, mercury-sulfate-electrode (MSE, + 680 mV vs. SHE) served as a RE, glassy carbon (SIGRADUR ®, HTW, Germany) G-type as a CE and the investigated samples/model electrodes as WE. 0.5 M H₂SO₄ (diluted from sulfuric acid 95-97%, pa, Merck) was used as an electrolyte. The solution was prepared using UHQ (ultra high quality, Millipore) water (> 18 MΩ cm).

**II.1.3 Scanning Electron Microscopy (SEM)**

Scanning electron microscopy (SEM) is based on scanning of an object with a focused electron beam. First instrument operating on this principle was built 1935 by Knoll to investigate the charging potential of surfaces under electron bombardment. Its resolution was limited to 100 µm by the final diameter of the electron beam ([100] and references therein). The first real SEM was patented by von Ardenne in 1938, its beam diameter was 100 Å and the recording was carried out by allowing the beam to pass through the specimen and strike the photographic paper which was scanned mechanically in
synchronism with the beam [100]. Later on, the instrument was improved by Professor Sir Charles Oatley and marketed by Cambridge Scientific Instrument Company in 1965.

SEM has a large depth of field which allows more of a specimen to be in focus at a time. High resolution and good control over the degree of magnification are further advantages of this microscope type. In this thesis, SEM was used for characterization of all samples, especially for the evaluation of the size and the geometrical arrangement of nanoparticles on the substrate surface.

The set-up of a typical SEM is shown in Figure II-3. The electron beam (2 in Figure II-3) is thermoionically emitted from an electron gun (1 in Figure II-3), fitted with a tungsten filament cathode. The beam is then focused by one or two sets of condenser lenses (3 and 4 in Figure II-3), until the spot is 1 to 5 nm in diameter. Finally, it passes through a set of deflection coils (6 in Figure II-3) in the electron column (objective lens) and is moved in xy-direction across the sample (8 in Figure II-3).

Interaction of the focused electron beam with the sample results in reflection of high-energy electrons with $E > 50$ eV by elastic scattering (so-called back-scattered electrons, BSE), emission of slow ($E < 50$ eV) secondary electrons (SE) by inelastic scattering and emission of electromagnetic radiation. Each of the three processes can be monitored by a respective detector (7, 10 and 11 in Figure II-3).
The SEM characterization of the samples was carried out with a Zeiss Supra 55 VP Gemini. The detection of back-scattered electrons was carried out by an In-Lens detector in vacuum at acceleration voltages between 2 and 4 kV with a working distance between 2 and 7 mm.

The size of nanoparticles was evaluated using the ImageJ software 1.43 (W. Rasband, NIH, USA).
II.1.4 Scanning Tunneling Microscopy (STM)

Scanning tunneling microscopy (STM), “elder brother” of AFM, was invented by G. Binnig and H. Rohrer in 1981 [101] as a novel technique for surface imaging [102]. This microscopy is based on the concept of quantum tunneling. STM enables atomic resolution so that it is possible to image and manipulate single atoms. Nowadays, STM is used in broad pressure, temperature but also medium range, e.g. in ultra high vacuum or in an electrolyte. In present work, STM was used to characterise nanoparticles on a carbon surface in air as well as \textit{in situ} in sulfuric acid and observe degradation processes occurring upon the contact of the electrolyte with the sample under potential control.

Measurements by STM are possible due to the wave nature of the electrons. Placing two conducting materials within a very short distance, results in a substantial overlap of the respective electron clouds, thus enabling a measurable current between them upon application of a small voltage. This so-called tunneling current is strongly dependent on the distance between the two materials and on the average decay length. The recorded information does not represent directly the topography but the density of states (DOS) of a sample [103].

An STM usually consists of a (commonly) metal tip (2 in \textit{Figure II-4}), piezoelectric z-control (3 in \textit{Figure II-4}), x- and y-scanner, coarse tip-to-sample z-control (6 in \textit{Figure II-4}), vibration isolation system and a computer (7 in \textit{Figure II-4}).
Figure II-4: schematic set-up of an STM. 1 – sample surface, 2 – STM tip, 3 – STM scanner (piezoelectric tube with electrodes), 4 – control voltages for piezo tube, 5 – tunneling current amplifier, 6 – distance control and scanning unit, 7 – data processing and display. Adapted from M. Schmid, TU Wien

A special application is electrochemical STM (EC-STM), developed by Hansma and Tersoff in 1987 [104]. It enables visualisation of surface processes in an electrolyte while electrochemical processes take place. Usually, a four-electrode-assembly is used to control the tip and the sample potentials. Two working electrodes, the tip and the sample, as well as the CE and the RE, are connected to a bipotentiostat, which can independently control both working electrodes (Figure II-5). A bias voltage results in a difference between the tip potential and the sample potential.
The STM measurements were conducted in a modified STM cell with a three electrode arrangement where the sample acted as WE and two annealed high purity Pt wires with a diameter of 0.5 mm (FG 999.5, Carl Schaefer AG) as quasi-reference and counter electrodes, respectively (Figure II-6).

![Figure II-5: Schematic set-up of the EC-STM, taken from [105]](image)

![Figure II-6: A PEEK EC-STM cell with sample acting as a WE and Pt-wires as CE and RE, respectively](image)
The quality of an STM image strongly depends on the vibration insulation as well as on the quality of the tips. Usually, the tips are home-made by etching or mechanical shearing of tungsten, platinum-iridium or gold wires. For this project, a tip-etching set-up, according to [105], was constructed (Figure II-7a). The metal of choice for the tips was gold, as it can be etched rather quickly and comparably easy and is inert under chosen electrochemical STM conditions (0.5 M sulphuric acid). For tip preparation a gold wire with a diameter of 0.25 mm (FG 999.9, Carl Schaefer AG) was pulled through a Pt ring with a diameter of 0.5 mm (FP 999.5, Carl Schaefer AG). An electrolyte lamella (36% HCl, Baker Analyzed™ Reagent, Germany) was used as a contact between the gold wire and the Pt ring. A DC voltage of 1.68 V was applied, leading to the tip etching in the region of the electrolyte lamella. After approximately five minutes, the Au wire broke in two and its lower part was collected into one of the holes in a self-made tip-holder. Figure II-7b displays an SEM image of an etched, non-coated Au-tip. After etching, the tips were immersed into hot ultra high quality (UHQ) water (Millipore, > 18 MΩ cm) and partially coated with apiezon wax (B7276, Plano GmbH, Germany) in a modified copper soldering iron, made at the PSI workshop. For this purpose, the tips were fixed in a holder, made from a needle and slowly pulled through an apiezon film between two ends of the modified soldering iron, heated to 180°C.

Figure II-7: a) scheme of a tip-etching set-up, adapted from [105] and b) SEM image of an etched tip
STM measurements were conducted using an Agilent PicoLe microscope with a 10 µm STM scanner in constant current mode with the set point current of 1 nA.

*In situ* STM images were recorded in an electrochemical cell (*Figure II-6*), exposing 0.7 cm$^2$ of the working electrode to the electrolyte (0.5 M H$_2$SO$_4$, diluted from sulfuric acid 95-97%, pa, Merck). The solution was prepared using UHQ (ultra high quality, Millipore) water (> 18 MΩ cm).

The STM images were processed using WSxM 5.0 Develop 3.1. software [98].

**II.1.5 X-Ray Photoelectron Spectroscopy (XPS)**

X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), is a highly surface-sensitive technique which enables measurements of elemental composition, empirical formula and chemical as well as electronic states of the elements in the investigated sample. In presented work, XPS was used to trace changes of the chemical state of carbon and platinum upon oxidation and/or degradation but also to ensure that the samples are not contaminated after multiple lithography and metal deposition steps.

XPS relies on the photoelectric effect, discovered by Hertz in 1887 and explained by Einstein in 1905 [106]. The photoelectric effect describes the ejection of electrons from the sample surface upon hitting it with electromagnetic radiation of very short wavelength, i.e. sufficiently high energy [107].

In XPS, the electromagnetic radiation, highly focused X-rays, are emitted either by a monochromatic source (usually Al Kα) or non-monochromatic magnesium source. The elemental composition of the sample is determined by measuring the kinetic energy of the ejected electrons, according to (1):

$$E_b = E_{\text{photon}} - E_{\text{kin}} - \phi$$

where $E_b$ is the binding energy (BE) of an electron, $E_{\text{photon}}$ – the photon (X-ray) energy, $E_{\text{kin}}$ – the kinetic energy of electrons and $\phi$ – the work function of the spectrometer. The X-ray energy and the work function of the spectrometer for a specific XPS are known, thus, BE
of an ejected electron can be calculated by measuring its kinetic energy. The number of ejected electrons also determines the signal intensity of an element and, therefore, relates to its amount within a certain sample area. Figure II-8 displays a schematic XPS set-up as well as a typical XPS spectrum for elemental platinum (7 in Figure II-8).

The high surface-sensitivity of XPS relies on the fact that only those electrons are analysed, which have managed to escape into vacuum, thus restricting their origin to the upper 5-10 nm of the sample.

Figure II-8: Schematic XPS set-up: 1 – sample surface, 2 – focused X-ray beam from the anode, 3 – ejected electrons, 4 – electron collection lens, 5 – analyzer, 6 – electron detector, 7 – recorded Pt 4f spectrum

XPS measurements for this work were performed by a VG ESCALAB 220i XL spectrometer equipped with a monochromatic Al anode as an X-ray radiation source operating at 150 W, spot size of 500 μm and a base pressure of <2 x 10^-8 mbar. The survey and the high resolution spectra were obtained, using a pass energy of 50 eV (step
size 0.5 eV, step dwell time 50 ms) and a pass energy of 20 eV (step size 0.1 eV, step dwell time 50 ms), respectively.

II.2 Materials

II.2.1 Glassy Carbon (GC)

Glassy carbon is a non-graphitic, non-graphitisable carbon produced by pyrolysis of phenolic resins and allowing mimicking an activated carbon – also non-graphitisable carbon. It has a mirror-like surface which shows high resistance towards chemicals and high temperatures but also impermeability to gases and liquids. Due to these properties it can be used in electrochemistry as an electrode material and its smooth surface is expected to be easily probed by SPM (Figure II-9a).

There are two types of glassy carbon, high temperature (or G-type) and low temperature (K-type). The GC samples (SIGRADUR, HTW, Germany), discussed in this work were either left untreated (GCU) or were heat-treated in air at 450°C for 10 (GCHT10), 20 (GCHT20) or 30 (GCHT30) minutes. Moreover, the capacity of glassy carbon can be tuned via electrochemical or thermal treatment by opening the pores. It is known from literature, that heating the low-temperature GC K-type at 450°C in air results in opening of the micropores (1-2 nm in diameter) already present in the material and formation of a porous layer with a thickness of up to 40 µm (Figure II-9b), depending on the temperature and the length of the thermal pre-treatment [108].
Figure II-9: a) a picture of GC and b) a drawing of opening of the pores and formation of porous layer and subsequent transformation of GCU to GCHT, adapted from [109].

On one hand, this opening of the pores and the presence of the porous surface layer are supposed to improve the adhesion of the platinum catalyst to the support. On the other hand, the layer should not be too thick, as the increased double layer capacitance (from 10 \( \mu \text{F cm}^{-2} \) up to 100 mF cm\(^{-2} \)) complicates the electrochemical Pt deposition and the characterisation of the samples due to significant capacitive currents during pulsed deposition and in the respective cyclic voltammograms (CV). This behaviour may be of importance for platinum deposition, as the pores can increase the adhesion of the metal to the carbon surface.

Prior to any preparation steps, the GC substrates were characterised by cyclic voltammetry, XPS and contact mode AFM to determine the extent to which the heat-treatment has an influence on porosity, chemical composition and roughness of the substrate.

The difference between GCU and GCHT is best visible if the capacity values of the substrates are compared. The capacity was evaluated by recording cyclic voltammograms in 0.5 M sulphuric acid with scan rate of 50 mV s\(^{-1} \) and measuring the current flowing in the double layer region. Figure II-10 displays the dependence of capacity on the length of heat-treatment. The values rise exponentially from approximately 7 \( \mu \text{F cm}^{-2} \) for GCU and
20 µF cm\(^{-2}\) for GCHT10 over 0.8 mF cm\(^{-2}\) for GCHT20 to 18 mF cm\(^{-2}\) for GCHT30. The capacity of 100 mF cm\(^{-2}\) is reached after heat-treating the sample for 60 minutes. These results are in good agreement with data published by Braun et al., who showed an exponential growth of capacity \(C\) with time \(t\) for heat-treatment of GC at 450°C [110]. Same authors stated that the highest capacity value of GC, measured for different temperatures and varying length of the heat-treatment is 100 mF cm\(^{-2}\) [110].

The BET surface area of powdered GCU K-type measures 2 m\(^2\) g\(^{-1}\) and can increase to up to 900 m\(^2\) g\(^{-1}\) upon heat-treatment of 2 h at 450°C [111].

![Figure II-10: Capacity of GC as a function of the length of heat-treatment](image)

The XPS analysis, however, shows that the chemical properties of GC do not change upon heat-treatment. The carbon C1s spectra for GCU as well as GCHT10, GCHT20 and GCHT30 are exemplarily shown in **Figure II-11**. All the substrates, GCU (black dotted line in **Figure II-11**), GCHT10 (red solid line in **Figure II-11**), GCHT20 (blue dashed line in **Figure II-11**) and GCHT30 (olive short dashed line in **Figure II-11**) are characterised by a narrow carbon peak at 284.4 eV and do not feature further well-defined peaks at higher binding energies, which could be ascribed to oxygen-containing surface groups, except for a slight shoulder at BE > 286 eV, highlighted by an oval in **Figure II-11**. However, it is already present on the GCU. The possible oxygen-containing moieties would be carbonyl
and/or quinone at BE 286-288 eV and carboxyl at 288-290 eV [109]. The oxygen content is determined to be 7.9 +/- 1.0 at % for all measured samples. The type of surface functionalities and the oxygen content correspond to the ones determined for carbon black [36, 112].

![C1s spectrum of GCU (dotted black line), GCHT10 (solid red line), GCHT20 (dashed blue line) and GCHT30 (short dashed olive line)](image)

Figure II-11: C1s spectrum of GCU (dotted black line), GCHT10 (solid red line), GCHT20 (dashed blue line) and GCHT30 (short dashed olive line)

The comparably low values of BET surface area (e.g. 160 m² g⁻¹ for Ketjen Black), the non-graphitic, non-graphitisable nature of GCU, its behaviour upon heat-treatment and the chemical properties show strong similarities to the “core” part of carbon black as it was observed e.g. by Heidenreich et al. [34] and Avila-Brande [35], described by Donnet [36, 113] and modeled by Ban et al. [33] (see also chapter I.3.4). Especially, the porous layer (or the active layer) obtained upon heat-treatment shows certain similarities to carbon blacks, as discussed by Sullivan et al. in [114].
The surface of GC before and after heat-treatment was probed by AFM to trace any treatment-induced deviations of the surface roughness. The AFM images revealed that despite low RMS values of < 1 nm, even before heat-treatment, the surface was not completely flat, but covered with slightly protruding, irregularly shaped nubs of different sizes on nanometer scale (Figure II-12a). This structure did not change upon heat-treatment; the “nano-roughness” remained for samples heat-treated for 30 min (Figure II-12b) and even 60 min.

Figure II-12: TM AFM images of a) GCU and b) GCHT30. The Δz-range is 5 nm.

Even though no big change could be observed at a first glance at the AFM images, their detailed evaluation showed that the length of GC heat-treatment slightly changed the surface roughness. Indeed, the mean roughness, root mean square roughness, maximum peak height and depth as well as the mean height (or z-value) slightly increased with
thermal treatment (Table II-1). The numbers shown in Table II-1 are mean values and were determined as following: for each sample AFM images of different sizes (100nm, 500nm, 1µm and 5µm) were recorded, RMS was measured using WSxM 5.0 Develop 3.1. software [98] and the mean value for all four images was calculated.

Table II-1: roughness analysis (mean roughness Ra, root mean square RMS, average maximum height Rpm, average maximum depth Rvm and mean height mean z-value) of GCU, GCHT10, GCHT20 and GCHT30

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Ra / nm</th>
<th>RMS / nm</th>
<th>Rpm / nm</th>
<th>Rvm / nm</th>
<th>Mean z-value / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCU</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
<td>-0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>GCHT10</td>
<td>0.7</td>
<td>0.6</td>
<td>1.0</td>
<td>-1.0</td>
<td>0.4</td>
</tr>
<tr>
<td>GCHT20</td>
<td>0.7</td>
<td>0.6</td>
<td>1.3</td>
<td>-1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>GCHT30</td>
<td>0.8</td>
<td>0.7</td>
<td>1.4</td>
<td>-1.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The presence of the micropores, which could be measured with small angle X-ray scattering (SAXS) and which are largely responsible for the increased double layer capacity of GC after heat-treatment, could not be resolved with contact mode AFM.

The results of both, XPS and AFM show that the surface properties, such as the chemical composition and roughness, are not significantly changed by the thermal treatment. Consequently, the larger capacity values result largely from an increased surface area of the GC support.

In current work both, GCU and GCHT were used as substrates for the preparation and subsequent oxidation of Pt/C model electrodes.

II.2.2 Highly Oriented Pyrolytic Graphite (HOPG)

Highly oriented pyrolytic graphite (HOPG) is a graphitic material with a high degree of certain crystallographic orientation of the c-axis perpendicular to the surface of the
Methods, Materials and Instrumentation

substrate, obtained by hot working of pyrolytic graphite by annealing under compressive stress at approximately 3300 K. Thus, HOPG is a highly-ordered form of high-purity pyrolytic graphite (impurity level is of the order of 10 ppm ash or better) [115, 116].

HOPG is characterised by the highest degree of three-dimensional ordering. The density, parameters of the crystal lattice, preferable orientation in a plane (0001) and anisotropy of the physical properties of the HOPG are close to those for natural graphite mineral. In particular, HOPG belongs to lamellar materials because its crystal structure is characterised by an arrangement of carbon atoms in stacked parallel layers – the two-dimensional and single-atom thick form of carbon that is called graphene. The lattice of graphene consists of two equivalent interpenetrating triangular carbon sub-lattices A and B (Figure II-13), each one contains a half of the carbon atoms. Each atom within a single plane has three nearest neighbours: the sites of one sublattice (A, marked by red in Figure II-13) are at the centres of triangles defined by three nearest neighbours of the other one (B, marked by blue in Figure II-13). The lattice of graphene thus has two carbon atoms, designated A and B, per unit cell, and is invariant under 120° rotation around any lattice site. A network of carbon atoms connected by the shortest bonds has a honeycomb-structure, but in bulk HOPG, A- and B-sites C-atoms become non-equivalent (including those on the surface): two coupled hexagonal lattices on the neighbour graphene sheets are arranged according to Bernal ABAB stacking, when every A-type atom in the upper (surface) layer is located directly above an A-type atom in the adjacent lower layer, whereas B-type atoms do not lie directly below or above an atom in the other layer, but sit over a void – a centre of a hexagon. Figure II-13 illustrates the assumed non-equivalent types of carbon atoms. Thus in each layer the atoms form a grid of correct hexagons with distances between atoms equal to 0.1415 nm. The distance between layers is equal 0.3354 nm [116].
Figure II-13: Schematic representation of the structure of the bulk hexagonal graphite crystal. The dashed lines show the axes of bulk unit cell. Side insets: top view of the basal plane of graphite and schematic representation of the surface structure (carbon atoms) of graphite most viewed by SPM, where every other atom is enhanced (right-side inset) and viewed under ideal conditions, where every single atom is seen (left-side inset). Taken from [116]

HOPG terminated with graphene layer is an excellent tool for using in scanning probe microscopy as a substrate or calibration standard at atomic levels of resolution. It is an easily renewable material with an extremely smooth surface. It has an ideal atomically flat surface and provides a background with only carbon in the elemental signature thus making results in a featureless background. This is vital for SPM measurements that require uniform, flat, and clean substrates [116]. An exemplarily STM image of HOPG in sulphuric acid is shown in Figure II-14a. The flat surface can be comfortably scanned by the STM tip and its quality tested by measuring e.g. the height of the steps. In this case, the determined value is approximately 0.7 nm, which corresponds to two graphene layers Figure II-14b.
HOPG specimens are layered polycrystals. Each bulk polycrystal looks like mosaic of microscopic monocrystal grains of different sizes. The structure is columnar, the columns run vertically within the flat slab of the material, and the grain boundaries can be seen on the lateral surfaces. The grains are slightly disoriented with respect to each other. An angular spread of the c-axes of the crystallites is of the order of 1 degree. The surface of specimen consists of many randomly placed steps – result of the cleaving process: single atomic steps and steps of several or dozens of atomic layers. Although the heights of multilayer hills and valleys are not calibrated, single steps have the well defined height of 0.34 nm and can be used for calibration in z direction. To characterise the angle of deviation of the grain's boundaries from the perpendicular axis of the columnar structure, a measure of the parallelism of grains – “perfectness” of HOPG samples – a "mosaic
spread" term is used. The lower the mosaic spread, the more highly ordered the HOPG. The term originates from X-ray crystallography. The disorder results in broadening of the (002) diffraction peak: the higher the disorder, the wider the peak. Therefore, perfectness of HOPG can be easily related to a Full Width at Half Maximum (FWHM) of the Cu-K\(\alpha\) rocking curve (radiation peak) measured in degrees – "mosaic spread angle". Thus, the smaller this angle, the higher the quality of HOPG. The size of grains also varies with the mosaic spread. The lower mosaic spread results in a freshly cleaved surface that exhibits a smaller number of steps due to the bigger size of grains. The higher the quality, the smaller the roughness of the surface. The lower level grade material is also more "cleavable" allowing the bigger number of cleavings per sample [115, 116].

All the other physical characteristics of graphite, including atom-to-atom distance or the surface properties are independent of its grade and remain the same for all types of HOPG. Due to the anisotropic nature of HOPG such characteristics as thermal conductivity and electrical resistivity are different in different directions: along the basal plane and along the principal axis c (perpendicular to the basal plane) [115, 116].

HOPG is a highly stable material. It remains stable at the temperatures up to 500°C in air and up to 2000-3000°C in a vacuum or an inert environment. It also exhibits high chemical inertness [116].

The highly-ordered HOPG structure and its surface properties may serve as a model for the outer shell of carbon black as it provides the “perfect” basal planes and step edges as described for CB e.g. by Heidenreich et al. [34], Avila-Brande [35], by Donnet [36, 113] and modeled by Ban et al. [33] (see also chapter I.3.4.).

In current work HOPG was used as a substrate for preparation of Pt/C model electrodes, in particular for \textit{in situ} STM measurements.

\section*{II.3 Electrode Preparation}

\subsection*{II.3.1 Potentiostatic Platinum Deposition}

The potentiostatic electrodeposition is one of the best-studied deposition methods due to its high degree of reproducibility and controllability, as it is possible to vary e.g. the size or
the shape of Pt particles by changing e.g. the deposition pulse length. Also the support itself is of importance, as it is known from literature [117-119] that its surface chemistry and/or surface morphology influence the deposition process. Paoletti et al., for instance, used carbon black and multi-walled carbon nanotubes to obtain Pt particles of spherical, dendritic or lamellar shapes [120], while Cherstiouk et al. prepared spherical Pt nanoparticles with narrow size distribution upon highly oriented pyrolytic graphite (HOPG) and oxidised glassy carbon (GC) G-type, pre-oxidised by pulse application in sulphuric acid [78]. The pre-oxidation was supposed to introduce increased hydrophilicity and surface roughness necessary for stabilization of Pt nanoparticles and, indeed, the authors observed that the size and the amount of Pt particles on the GC substrate varied according to the oxidation degree of GC [78].

In this project, the electrochemical platinum deposition was performed on untreated and thermally treated GC as well as HOPG with various deposition pulse lengths to monitor the size dependence of nanoparticles on the pulse length but also the influence of the porosity of the substrate. The goal was to prepare Pt/carbon model electrodes for electrochemical oxidation/corrosion experiments.

Prior to the electrochemical platinum deposition, the glassy carbon samples K-type (SIGRADUR, HTW, Germany) were placed in an oven and heated at 450°C in air for 10 (GCHT10), 20 (GCHT20) or 30 (GCHT30) minutes, respectively. The electrochemical deposition of platinum upon GC and HOPG was performed in a glass cell, in which a polyether ether ketone (PEEK) sample holder exposed a 1 cm² circular area of glassy carbon to the plating solution containing aqueous 5 mM hexachloroplatinic acid (Fluka) and 0.5 M sulfuric acid (diluted from sulfuric acid 95-97%, pa, Merck). The solution was prepared using UHQ (ultra high quality, Millipore) water (> 18 MΩ cm). Glassy carbon or HOPG was employed as working electrode (WE), glassy carbon as counter electrode (CE) and mercury/mercury sulfate (MSE; +680 mV vs. hydrogen standard electrode) as reference electrode (RE). The working electrode was immersed into the platinum plating solution at a potential of +200 mV vs. MSE (to avoid electroless platinum deposition). For Pt deposition the potential was stepped from this value to the deposition potential of -700 mV vs. MSE. After application of the deposition potential for a given time (0.5 s, 1 s, 2 s, 5 s, 7 s), the electrode potential was stepped back to +200 mV vs. MSE and the working electrode was removed from the solution under potential control. The pulse train
was applied using a computer controlled (PARcontrol 0.86) potentiostat / galvanostat (EG&G Princeton Applied Research A 370).

II.3.2 Extreme Ultraviolet Interference Lithography (EUV-IL)

Interference Lithography (IL) is commonly used for making large-area patterns. Its advantages are practically unlimited depth of focus, large exposure areas and no need for complicated and very expensive numerical aperture optics [89]. The smallest possible period/pitch equals to half the wavelength of the employed coherent light. Therefore, extreme ultraviolet light from undulators at the synchrotron radiation facilities is used to produce structures smaller than 75 nm [89]. Due to frequency multiplication, the created interference pattern has twice the frequency of the diffraction grating. Thus, the choice of diffraction grating defines the created pattern, e.g. two-beam interference results in line-structure and four-beam interference in a hole-structure. The EUV-IL set-up at the X-ray Interference Lithography (XIL) beamline at the Swiss Light Source (SLS) synchrotron at Paul Scherrer Institut (PSI) is schematically depicted in Figure II-15.

Set-up for X-ray Interference Lithography

![EUV-IL schematic set-up](image)

Modern synchrotrons like the Swiss Light Source provide the light necessary to illuminate the grating mask with coherent light.

The synchrotron light is diffracted at gratings created with either e-beam lithography or with XIL itself.

Frequency multiplication: The created interference pattern has twice the frequency of the diffraction grating.

Figure II-15: EUV-IL schematic set-up. 1 – synchrotron-generated focused X-rays, 2 - pinhole, 3 - diffraction gratings, 4 – a sample spincoated with a photoresist. Taken from [121]
In this project, EUV-IL was performed to create periodic dot arrays with diameters between 50 and 100 nm on carbon substrates. The ultimate goal was to use the created model electrodes for electrochemical studies on platinum dissolution and carbon corrosion.

The sample exposure was performed at the XIL beamline which uses undulator light with a central wavelength of 13.4 nm (92 eV) and 4% spectral bandwidth. The incident EUV power on the sample was several mW/cm\(^2\) and the delivered dose was controlled in the range of 25-107.5 mJ cm\(^{-2}\) using a fast beam shutter. Sample irradiation was performed according to the methods described by Solak et al. [89]. Silicon nitride masks with gratings of various periods were used to create interference patterns with periodicity in the range of 141 to 1410 nm.

On each sample, nine fields were exposed using EUV doses of 25-107.5 mJ cm\(^{-2}\). After the EUV exposure, the samples were developed using the 3:1 mixture of methyl-isopropyl-ketone and isopropanol for 30 s at the Hamatech Steag machine in the PSI LMN cleanroom.

Prior to the exposure at the XIL beamline, the glassy carbon samples K-type (SIGRADUR®, HTW, Germany) were spin-coated with a “positive” photoresist poly(methyl-methacrylic acid) (PMMA). Two different photoresist thicknesses, 65 and 44 nm were chosen. The 15x15x1 mm\(^3\) pieces of glassy carbon were first cleaned by immersion into isopropanol, ultrasonicing for 5 min and drying in nitrogen flow. The procedure was repeated for acetone and afterwards again for isopropanol. The cleaned samples were then spin-coated with an 1:6 PMMA:chlorobenzene (CB) solution the reaction conditions displayed in Table II-2.

**Table II-2: Spin-coating conditions**

<table>
<thead>
<tr>
<th>Thickness / nm</th>
<th>Velocity / rpm</th>
<th>Acceleration / rpm/s</th>
<th>Time / s</th>
<th>Softbake</th>
</tr>
</thead>
<tbody>
<tr>
<td>44</td>
<td>4000</td>
<td>2000</td>
<td>45</td>
<td>1 min @ 450°C</td>
</tr>
<tr>
<td>65</td>
<td>2000</td>
<td>1000</td>
<td>45</td>
<td>1 min @ 450°C</td>
</tr>
</tbody>
</table>

The diameter of obtained structures varied between 60 and 110 nm (also see III.2.2.). An additional process step was introduced to further decrease the diameter. For this purpose,
an additional chromium/silver mask was evaporated on the exposed structures during a glancing angle deposition (GLAD) process. This bi-metallic combination was chosen as chromium alone leads to a good constriction of the holes but the layers have a grainy appearance while smooth layers of pure silver clog the holes [122]. For the deposition of the metal mask a Balzers BAE 250 (Oerlikon Balzers, Liechtenstein) evaporation system was used. The metal deposition was performed according to the methods described by F. A. Zoller et al. in [122]. For the chromium deposition the substrates were tilted to a highly oblique angle of 65°C relative to the incident flux and were continuously rotated about an axis normal to the substrate at 120 rpm s\(^{-1}\) (Figure II-16). The deposition rate was set to 0.1 nm s\(^{-1}\). For the silver deposition the substrates were tilted to a highly oblique angle of 70°C relative to the incident flux and were continuously rotated about an axis normal to the substrate at 120 rpm s\(^{-1}\). The deposition rate was set to 2 nm s\(^{-1}\). After the platinum deposition via sputtering the bi-metallic mask and the photoresist were wet-etched in the solution “Chrom etch n°1” (Microchemicals GmbH), containing ammoniumceriumnitrate, perchloric acid and water.

\[\text{EUV-IL patterned} \quad \text{glancing angle} \]

*Figure II-16: Scheme of evaporation of additional Cr/Ag mask upon EUV structures using glancing angle deposition (GLAD) technique, adapted from [122]*

**II.3.3 Electron Beam Lithography (EBL)**

Electron beam lithography (EBL) refers to a lithographic process that uses a focused beam of electrons to form patterns on a substrate, as opposed to optical lithography that uses light for the same purpose. Herein lie some of the advantages of this technology such as higher patterning resolution due to shorter electron wavelength (compared to longer-waved optical lithography) or absence of a lithographic mask which is used in optical lithography to project the patterns. The patterns are “drawn” on the sample surface using electron beam as a “pen”. This “serial” manner of pattern creation causes the major drawback of EBL, if compared to optical lithography: the low sample throughput.
In this project electron beam (e-beam) lithography was used as an alternative to EUV-IL to create periodic dot arrays on carbon substrates. The ultimate goal was the model electrodes, already mentioned in II.3.1.

The typical electron beam components are the electron source (1 in Figure II-17), which determines the ultimate beam diameter and current density, the electron optics (2, 3, 4, 5 in Figure II-17), used for beam formation and position control, a vacuum system (9 in Figure II-17), pattern generator, which transfers the pattern data to the beam for exposure (6 in Figure II-17), the stage system (8 in Figure II-17), which steps/moves the substrate for large area exposure, control electronics for hardware and software and, finally, correction systems (7 in Figure II-17) to measure and compensate system distortions.

Figure II-17: Schematic set-up of E-beam. 1 – electron source, 2 – extractor/focus, 3 – gun alignment coils (tilt and shift), 4 – magnetic lens, 5 – beam blanking aperture/spray aperture, 6 – beam deflection system (pattern generator), 7 – fast focus and stigmation, 8 – substrate on a stage, 9 – vacuum system (adapted from Vistec EBPG5000+ manual)
The movement of the stage is constantly controlled by a two-axis laser interferometer system, while the electronics generates analogue and digital signals which control the whole e-beam. The layout patterns are split into fields, consisting of several sub-fields, which are filled up by the pattern generator by guiding the e-beam.

The correction systems are very important, as scanning the beam almost always results in errors such as raster pincushion, off-axis de-focus, off-axis astigmatism as well as errors created by height differences on the substrate surface. Another important factor for successful e-beam patterning is the beam-substrate interaction which leads to scattering of incident electron beam within the photoresist and the substrate. The beam penetration increases with higher intensity of the e-beam and lower molecular weight of the substrate. Also the proximity effect is important. It describes the fact that small isolated areas on a substrate receive lower exposure dose than larger, denser patterns.

In this project, exposures of the dot arrays were performed using a Vistec EBPG5000Plus electron beam lithography tool, operated at 100 keV. This e-beam writer is equipped with a pattern generator which can be operated at beam stepping frequencies up to 50 MHz, and a deflection system, capable of deflecting the beam to large angles so that a writing field as large as 512×512 µm² can be exposed without any stage movements. The Gaussian shaped beam was focused to approximately 10 nm in diameter at a beam current of 10 nA. Rectangular dot arrays were generated by setting the beam step size equal to the dot pitch, so that the exposure of each dot was performed within a single “beam shot” with a dose of 105, 75 and 14 µC cm⁻² for the 70, 100 and 200 nm pitch, respectively. The exposed samples were developed in the isopropanol (IPA):methyl-isobutylketone (MIBK) 3:1 mixture for 45 s, rinsed in IPA for 30 s and dried by centrifugation at 3000 rpm (for more details refer to [123]).

Prior to the exposure to the electron beam, the samples were spin-coated with a so-called “positive” photoresist (the photoresist exposed to light is afterwards soluble to the photoresist developer). Before spincoating, 15×15×1 mm³ pieces of glassy carbon were first cleaned by immersing them into isopropanol, ultrasonicating for 5 min and drying in nitrogen flow. The procedure was repeated for acetone and afterwards again for isopropanol. In case of HOPG, the sample was freshly cleaved with a scotch-tape. As photoresist, two-layers of a poly(methyl-methacrylic acid) (PMMA) / ethyl lactate solution, an 2% solution of PMMA with the molecular weight of 50k (lower layer) and 1% solution of
PMMA with the molecular weight of 950k (upper layer), was used (Figure II-18). For the upper layer PMMA with a higher molecular weight is used due to its low sensitivity towards the e-beam. This way, only relatively small holes are created on the photoresist surface. The lower substrate-near PMMA layer has a smaller molecular weight, remains less exposed and maintains a high development rate. Therefore, it is possible to obtain a reproducible, pronounced undercut (the distance between the upper PMMA layer and GC in Figure II-18). Such an undercut helps to prevent the photoresist sidewalls from being coated with metal, making the lift-off easier.

The samples were first spin-coated with a 35 nm PMMA layer (MW 50k). The acceleration was 2000 rpm/s and the rotation velocity 4200 rpm. The rotation time was 60 s. Afterwards, the samples were soft-baked on a hot plate at 175°C for 5 min. Then, the second PMMA layer (MW 950k) of approximately 30 nm was spincoated upon the first layer. The acceleration was 2000 rpm/s and the rotation velocity 4500 rpm. Also after this step the sample was soft-baked on a hot plate at 175°C for 5 min to remove all traces of the solvent.
Deposition of a Pt layer on the developed samples was performed by Michael Horisberger (LDM) with a DC magnetron-sputtering device TIPSI with an Ar pressure of $10^{-3}$ mbar and a power of 30 W. After Pt deposition the lift-off process was accomplished by soaking the samples overnight in acetone and ultrasonicating them for five minutes in acetone (GC samples) or rinsing them with acetone and isopropanol (HOPG samples) the following day.
II.4 Degradation/Oxidation Experiments

II.4.1 Potentiostatic Hold

The potentiostatic hold experiments were conducted in deaerated 0.5 M sulphuric acid (diluted from sulfuric acid 95-97%, pa, Merck). The solution was prepared using UHQ (ultra high quality, Millipore) water (> 18 MΩ cm). Glassy carbon or HOPG was employed as working electrode (WE), glassy carbon G-type as counter electrode (CE) and mercury/mercury sulfate (MSE; +680 mV vs. hydrogen standard electrode) as reference electrode (RE). The time was varied between 10-60 min and the potential kept constant at 1.9 V vs. SHE or the time was kept constant at 30 min and the potential varied between 1.2 V and 1.9 V (vs. SHE). The potential was applied using a computer controlled (PARcontrol 0.86) potentiostat/galvanostat (EG&G Princeton Applied Research A 370).

The potential was first held at OCV for 20s and then stepped to the oxidation potential for 10 to 60 minutes. The samples were removed from the electrolyte after switching off the potentiostat. Afterwards, the model electrodes were rinsed with deionised water, blown dry with argon and used for further SEM and XPS measurements.

In case of experiments performed at 60°C, the whole set-up was placed into a Binder thermo-chamber and left therein for 40 minutes to reach the required temperature of 60°C, prior to the potentiostatic hold.

II.4.2 Potential Cycling

The potential cycling experiments were conducted in deaerated 0.5 M sulphuric acid (diluted from sulphuric acid 95-97%, pa, Merck). The solution was prepared using UHQ (ultra high quality, Millipore) water (> 18 MΩ cm). Glassy carbon or HOPG was employed as working electrode (WE), glassy carbon G-type as counter electrode (CE) and mercury/mercury sulfate (MSE; +680 mV vs. hydrogen standard electrode) as reference electrode (RE). The potential was cycled between 0.5 V and 1.2, 1.4, 1.6 or 1.8 V (vs. SHE) for 500 cycles at a scan rate of 100 mV s⁻¹. The potential was applied using a computer controlled (PARcontrol 0.86) potentiostat / galvanostat (EG&G Princeton Applied Research A 370). The samples were removed from the electrolyte after switching off the
potentiostat. Afterwards, the model electrodes were rinsed with deionised water, blown dry with argon and used for further SEM and XPS measurements.

In case of experiments performed at 60°C, the whole set-up was placed into a Binder thermo-chamber and left therein for 40 minutes to reach the required temperature of 60°C, prior to the oxidation experiment.
III Results and Discussion

III.1 Model Electrodes (Pt/GC) Prepared by Potentiostatic Pt Deposition

III.1.1 Introduction

The need for better understanding of corrosion and/or degradation of the catalyst in a PEFC has already been described in chapter I. However, a real catalyst is a highly complex system and it is difficult to observe the above-mentioned processes in details. Therefore, Pt/C model electrodes can be employed to gain better insight into electrochemically induced reactions such e.g. Pt dissolution. The different ways to prepare model electrodes were already discussed in chapter I., in following the focus will be on potentiostatic platinum deposition on carbon, i.e. GC and GCHT.

Electrochemical platinum pulse deposition on glassy carbon was already performed by different groups, for instance, see [78-85, 120, 124].

In this project, potentiostatic deposition upon untreated (GCU) and heat-treated (GCHT) GC was performed in order to prepare model electrodes but also to monitor the influence of heat-treatment of GC on the electrodeposition process.

For oxidation experiments, two different oxidation protocols were considered (see also I.4.3. and II.4.). One was holding the model electrode for a certain time at potentials between 1.2 and 1.9 V vs. SHE and the second, cycling it between 0.5 V and 1.2 to 1.8 V vs. SHE.

The following chapters will describe the fabrication, subsequent characterization and oxidation of model electrodes prepared by potentiostatic platinum deposition. Afterwards, the obtained results will be discussed.
### III.1.2 Preparation

Prior to Pt deposition, the GC substrates were characterised by cyclic voltammetry, XPS and contact mode AFM to determine the extent to which the heat-treatment has an influence on porosity, chemical composition and roughness of the substrate (see also II.2.1.).

As already described in II.2.1., the XPS analysis showed that the chemical properties of GC did not change upon heat-treatment. All the substrates were characterised by a narrow carbon peak at 284.4 eV and did not feature further well-defined peaks at higher binding energies, which could be ascribed to oxygen-containing surface groups. Also, Pt deposition did not influence the C1s spectra, as can be concluded from the normalised C1s spectra of GCU before/after Pt deposition (deposition pulse length was 2 s) and GCHT30 after Pt deposition (likewise pulse length of 2 s) which are displayed in Figure III-1. A slight shoulder at BE > 286 eV, highlighted by an oval in Figure III-1 is the only indication for the presence of oxygen-containing carbon moieties, however, there is no change to it either upon Pt deposition or on heat-treatment.
Figure III-1: XPS spectrum of carbon (C1s) for GCU before electrochemical deposition (black solid line), GCU after Pt deposition (deposition pulse length 2 s, red dashed line) and GCHT30 after Pt deposition (deposition pulse length 2 s, blue dash-dotted line). The oval indicates the BE region with oxygen-containing carbon moieties.

The detailed normalised Pt4f spectra of different pulse lengths for the same substrate (exemplarily shown for GCU the pulse length of 2 s (dashed black line), 3 s (solid red line) and 5 s (dash-dotted blue line) in Figure III-2a) as well as of the same pulse length of 2 s for different GC pre-treatments (exemplarily shown for GCU (dashed line), GCHT20 (solid line) and GCHT30 (dash-dotted line) in Figure III-2b) show no differences, displaying the Pt (0) low energy and high energy components at 70.9 (Pt4f\(_{7/2}\)) and 74.2 (Pt4f\(_{5/2}\)) eV, respectively.

The normalised C1s spectra (Figure III-3), corresponding to the Pt4f spectra shown in Figure III-2, likewise indicate that the chemical properties of carbon do not depend on either the length of the deposition pulse (Figure III-3a) or thermal pre-treatment of the carbon support (Figure III-3b). All spectra feature a sharp main C1s signal at 284.4, indicating a C-C bonded carbon and a slight shoulder at BE > 286 eV, indicated by an oval, attributed to oxygen-containing carbon moieties.
Figure III-2: XPS spectra of platinum (Pt 4f) a) on GCU with deposition pulse length of 2 s (black dashed line), 3 s (red solid line) and 5 s (blue dash-dotted line) and b) electrodeposited Pt with a pulse length of 2 s on GCU (black dashed line), GCHT20 (red solid line) and GCHT30 (blue dash-dotted line).
Figure III-3: XPS spectra of carbon (C1s) a) on GCU with deposition pulse length of 2 s (black dashed line), 3 s (red solid line) and 5 s (blue dash-dotted line) and b) for electrodeposited Pt with a pulse length of 2 s on GCU (black dashed line), GCHT20 (red solid line) and GCHT30 (blue dash-dotted line). The oval indicates the BE region with oxygen-containing carbon moieties.
In general, the prepared samples contained not only carbon, platinum and oxygen, as could be expected, but also traces of impurities. The survey, displayed in Figure III-4, revealed that there was also a certain amount (approximately 1.9 at%) of nitrogen (BE 400.8 eV for N 1s), sulfur (BE 168.4 eV for S 2p), silicon (BE region 98-108 eV) and chlorine (BE region 194-204 eV) on the model electrode surface.

![Figure III-4: XPS survey spectrum of electrodeposited Pt on GCU, deposition pulse length is 2 s.](image)

Table III-1 summarises the chemical composition of Pt/GCU and Pt/GCHT20 with a pulse length of 2 s and compares the results to the elemental abundance on pure GCU or GCHT20 substrate. It shows that prior to the deposition the substrate contained carbon, oxygen and some nitrogen (< 1 at%). Continued measurements of the as-received GCU as well as heat-treated GC repeatedly displayed certain amounts (< 1 at%) of nitrogen, thus, we concluded that the presence of this element is due to an impurity in as-received glassy carbon substrate.

After the electrochemical deposition, there are also traces of sulfur, chlorine and silicon, as already discussed for the survey spectrum shown in Figure III-4.
Results and Discussion

Table III-1: Elemental abundance calculated from an XPS spectrum of GCU, GCHT20 and electrodeposited Pt on GCU and GCHT20, pulse length 2 s

<table>
<thead>
<tr>
<th>Sample</th>
<th>C  / at%</th>
<th>O  / at%</th>
<th>Pt / at%</th>
<th>Si / at%</th>
<th>S  / at%</th>
<th>N  / at%</th>
<th>Cl / at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCU</td>
<td>91.3</td>
<td>7.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>GCHT20</td>
<td>90.2</td>
<td>9.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
</tr>
<tr>
<td>Pt/GCU (2s)</td>
<td>80.7</td>
<td>15.7</td>
<td>0.5</td>
<td>0.7</td>
<td>0.3</td>
<td>1.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Pt/GCHT20 (2s)</td>
<td>79.1</td>
<td>16.8</td>
<td>1.1</td>
<td>0.6</td>
<td>0.4</td>
<td>1.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The binding energies of the sulfur species (BE = 168.4 eV) detected on Pt/GCU or Pt/GCHT20 samples suggest that there is a certain amount of sulfate adsorbed on the surface, which has not been removed by rinsing the sample in bi-distilled water. To some extent, the sulfate also allows for increased amount of oxygen on electrodeposited samples (1.4 at% for Pt/GCU and 1.6 at% for Pt/GCHT20). The traces of chlorine can also be easily explained as originating from the electroplating solution. The silicon signal most probably comes from the silicone sealing which is used to press the glassy carbon tighter against the walls of the electrochemical cell.

The current transients recorded during platinum deposition show similar current values for untreated glassy carbon (GCU) and increased values for thermally treated GC (GCHT) (Figure III-5). The reduction charge for GCU and GCHT10, for instance, shows similar values, while for higher heat-treatment lengths it rises to one or two orders of magnitude for GCHT20 and GCHT30, respectively (Table III-2).
Table III-2: reduction charges for pure carbon support as well as reduction charges, deposition charge and amount of platinum for Pt/GC samples for the pulse length of 2s in 0.5 M sulphuric acid.

| Substrate | \(|Q_{\text{red, no Pt}}| / \text{C}\) | \(|Q_{\text{red, Pt}}| / \text{C}\) | \(\Delta Q_{\text{Pt}}\) | \(m_{\text{Pt}} / \mu\text{g cm}^{-2}\) |
|-----------|---------------------------------|---------------------------------|-----------------|----------------|
| GCU       | 6.8*10^{-5}                    | 4.5*10^{-3}                    | 3.7*10^{-3}    | 1.8            |
| GCHT10    | 3.2*10^{-4}                    | 2.4*10^{-3}                    | 6.8*10^{-3}    | 3.1            |
| GCHT20    | 1.6*10^{-3}                    | 6.2*10^{-2}                    | 2.1*10^{-2}    | 8.7            |
| GCHT30    | 1.3*10^{-3}                    | 1.2*10^{-1}                    | 5.2*10^{-2}    | 14             |

The latter high charge values, however, are largely due to the double layer charging, to the reduction of oxygen-containing functional groups on the carbon substrate surface, created in the process of thermal treatment, and/or the evolution of hydrogen in the active layer.

These processes were investigated by recording current transients for pulsing GC in 0.5 M sulphuric acid which did not contain any platinum and observing similar trend in reduction charges, i.e. smaller charge values for GCU and higher charge values for GCHT, as shown for the data in Table III-2 (for \(Q_{\text{red, no Pt}}\)). The Pt loading grows with increased thermal treatment length, for the pulse length of 2s it varies approximately between 2 \(\mu\text{g cm}^{-2}\) for GCU and 14 \(\mu\text{g cm}^{-2}\) for GCHT30 (Table III-2). The amounts of deposited Pt were calculated using the current transient data obtained during the deposition. Here, the charge \(\Delta Q\) (\(\Delta Q = |Q_{\text{red}}| - Q_{\text{ox}}\)) was employed to determine first the molar amount and then the mass of deposited platinum.
Results and Discussion

Figure III-5: Current transients recorded during platinum deposition on GCU (solid line), GCHT20 (dashed line) and GCHT30 (dotted line).

The SEM images recorded for Pt deposition upon HOPG, GCU and GCHT show similarities, but also differences which are dependent on the substrate. Figure III-6 displays the deposited Pt particles on various substrates, showing the typical size, size distribution as well as coverage and shape of the Pt particles. Typically, deposited Pt particles are desert-rose shaped (Figure III-6b), featuring an irregular round shape with crystalline “petals” protruding at the edges. This form hints at a second, gas-evolving process in parallel with Pt-deposition, as described by Penner et al. in [125].

The deposition pattern, however, is dependent on the support. Pt deposition on HOPG, for example, usually takes place at step edges and other defects [76, 126, 127]. Thus, the particles are clustered on the edges (Figure III-6c).
GCU, on the contrary, offers a surface without steps or other well-defined defects so that there is a more unitary dispersal of Pt particles. Still, the distribution of Pt particles is random (Figure III-6d). Finally, GCHT offers homogeneously distributed surface defects,
where the nucleation sites are evenly spread. This surface property of GCHT also explains the smaller size and denser package of deposited Pt particles (Figure III-6e, f).

The particle size changes as well. Smaller, more densely packed particles are formed on GCHT if compared to GCU (exemplarily shown for deposition pulse length of 5s on GCU in Figure III-7 and GCHT30 in Figure III-8) where the diameter but also the particle distance is larger. However, despite the smaller size, the surface coverage of deposited Pt is larger for GCHT (compare Figure III-7 and Figure III-8).

Figure III-7: SEM image of electrochemically deposited Pt on GCU (pulse length 5s) with different magnifications. a) 25 k, b) 50 k, c) 150 k and d) 250 k.
Figure III-8: SEM image of electrochemically deposited Pt on GCHT30 (pulse length 5s) with different magnifications. a) 25 k, b) 50 k, c) 150 k and d) 250 k.

One possibility for increased number of Pt particles can be found in literature [58, 60]. It is stated that higher amount of oxygen-containing groups such as carboxylic acids or phenolic groups on carbon blacks may be responsible for higher hydrophilicity of the surface which in turn is better accessible by the electroplating solution and offers more anchoring sites for the Pt ions [58, 60]. In our case, however, we found no significant deviation of chemical surface composition after heat-treatment. XPS measurements of GCU and GCHT, in particular C1s spectra, revealed that the amount of oxygen-containing carbon moieties such as, for instance, ketones or carboxylic acids, typical for oxidised GC, remains unchanged for GCU and GCHT (also see II.2.1., Figure II-11 or Figure III-3b).
Results and Discussion

Also Pt deposition does not influence the C1s spectra (and, thus, chemical composition) of either GCU or GCHT (also see Figure III-3a).

The particle distribution on the substrates, especially GCU, was not completely homogeneous so it was important to evaluate several regions and to obtain statistical information about the surface coverage as well as the average particle size and size distribution. The diameter as well as the amount of Pt dots on the support was estimated from SEM images using image software ImageJ 1.43 (W. Rasband, NIH, USA). For each sample four different locations were investigated with SEM and for each location images with 8 different magnifications were obtained. For the statistical information at least 3 different magnifications for each location were evaluated with ImageJ (at least 12 data sets). The results were compared and the average particle diameter or coverage was calculated. The presented diameter distributions are shown for one location and a chosen magnification of 50k for the location with the most representative distribution. Thus, not only representative statements about each substrate were possible but also the comparison between them.

Figure III-9: Diameter distribution of Pt particles for the pulse length of 2 s on GCU (filled bars) and GCHT20 (striped bars)
Results and Discussion

Freshly cleaved HOPG, GCU and GCHT10 display quite a wide range of particle diameters; for the pulse length of 2s it is possible to find particles with a diameter of 25 but likewise 300 nm (Figure III-9, filled bars). On the contrary, particles on GCHT20 and GCHT30 show a narrower size distribution with a better defined “mean diameter” value (exemplarily shown for GCHT20 in Figure III-9, striped bars).

A decrease in Pt particle diameter and an increased Pt coverage was observed for GCHT for various deposition pulse lengths. For the pulse length of 2 s, for instance, the average Pt particle diameter on GCU is 120 nm and on GCHT30 it is 50 nm (Figure III-10a).

Also, for GCHT, pulses longer than 2 s do not lead to any strong growth of the particles’ mean diameter (contrary to the growth observed for GCU, Figure III-10a). The amount of platinum on the surface, i.e. the surface coverage, however, significantly increases for longer thermal treatment. For the pulse length of 2 s, for example, the surface coverage for GCU is approximately 5 % as opposed to 10 % for GCHT30 (Figure III-10b). Moreover, on GCU the slightly increased surface coverage due to longer pulses seems to originate from a larger diameter. On GCHT the increased surface coverage resulting from longer pulses is due to larger number of Pt particles, as the particle diameter is always smaller than for GCU and does not significantly change once a certain pulse length of 2 s is reached.
Results and Discussion

The change in Pt particle size as a function of GC pre-treatment may be explained by the opening of the pores. It is known from literature [108], that heating GC K-type at 450°C in air results in opening of the micropores (1-2 nm in diameter) already present in the material. This pore-opening process leads to enhanced density of defects, which offer more nucleation sites for crystallization. The micropores at the surface also suppress surface diffusion of platinum atoms and, thus, further 2 D crystal growth which obviously occurs on GCU.

The question, whether the recorded high current values for GCHT were due to a considerably higher amount of electrodeposited Pt or to different factors like e.g. the double layer charging, was further pursued by calculating the amount of electro-deposited platinum. For this purpose, the data was extracted from the SEM images and the recorded current transients. Then, both values were compared.

The calculation of amount of deposited Pt using SEM images was done with the following assumptions: the particles are regular hemispheres, there is a certain mean particle diameter (**Figure III-10a**) and the investigated substrate region is representative for the whole substrate (homogeneous surface coverage). The mean particle diameter was calculated applying the ImageJ software, the amount of platinum on the surface was calculated by taking into account Pt mass and the number of Pt particles. This value was compared to the one obtained from the transients’ data.

Discrepancies were found for all substrates (**Figure III-11**); however, the nature of discrepancies differed. For GCU the calculated Pt amount is slightly higher for the SEM evaluation (**Figure III-11a**), while in case of GCHT the Pt amount calculated from SEM images is smaller for GCHT20 (**Figure III-11b**) and considerably smaller for GCHT30 (**Figure III-11c**). This fact would mean that the high current values of thermally treated samples are due not only to higher amount of Pt, but also to double layer charging and surface reactions like reduction of surface oxygen groups, hydrogen evolution and probably deposition of Pt in the porous layer, where it cannot be detected by SEM.

The results of SEM measurements concerning the amount of Pt on the surface were confirmed by XPS measurements (**Table III-3**). For all investigated pulse lengths, the amount of deposited Pt increased with longer heat treatment (**Table III-2, Table III-3**). Also, the amount of Pt increased with growing deposition pulse length for both GCU and
Results and Discussion

GCHT (Table III-3). The same pulse length, for instance, leads to higher Pt loadings if GCHT is used, such as 0.5 at % for GCU and 2 at % for GCHT30 for the pulse length of 2 s (Table III-3). There are also differences between GCHT20 and GCHT30, e.g. 1.1 at % for GCHT20 and 2 at % for GCHT30.

Figure III-11: Amount of electro-deposited platinum calculated by evaluating the recorded current values or SEM images for a) GCU, b) GCHT20 and c) GCHT30.

The only exception is the deposition pulse of 0.5 s for GCHT20 and GCHT30, here there is more Pt on the sample heat-treated for a shorter period. Also, the SEM results repeatedly display this discrepancy (Figure III-11). A closer look at the normalised Pt4f elemental spectra for both carbons (Figure III-12) reveals the difference: the reduction of Pt (IV) salt (from PtCl$_6^{2-}$) to Pt (0) is obviously faster on the GCHT20 (Figure III-12a). Already after 0.5
Results and Discussion

s almost all Pt on the surface is Pt (0), as confirmed by the narrow, well-defined Pt (0) doublet with the low energy component at 70.9 eV (Pt4f\textsubscript{7/2}) and high energy component at 74.2 (Pt4f\textsubscript{5/2}) eV, respectively.

Figure III-12: Pt4f spectra for a) GCHT20 and b) GCHT30 for different deposition pulse lengths

For the same deposition pulse length, Pt on GCHT30 is still partially oxidised (Pt (0) / Pt (II) mixture), evident from the broad, ill-defined Pt-doublets with low energy Pt4f\textsubscript{7/2}
components at 70.9 (Pt (0)) as well as 72.9 (Pt (II)) eV and high energy Pt$^{4f_{5/2}}$ components at 74.9 (Pt (0)) as well as 75.9 (Pt (II)) eV.

One explanation for the above-mentioned findings might be that some electrodeposited Pt (0) particles on the surface of GCHT30 are smaller than on the surface of GCHT20 and, thus, are supposed to oxidise to Pt (II) as soon as they are exposed to the ambient conditions [90].

Alternatively, this behaviour may result from morphology changes during the heating procedure: after thirty minutes a thick porous layer is formed on the GC surface and the capacity is increased by approximately an order of magnitude compared to GCHT20 (Figure II-10), and, respectively, so is the RC constant ($RC_{\text{GCHT30}} = 10 \times RC_{\text{GCHT20}}$). Thus, the deposition pulse length of 0.15 s is not sufficient to reduce the entire Pt deposited on GCHT30 surface to Pt (0). Also, a deposition time of 0.5 s is too short, however, this deposition pulse length seems to be the threshold, for longer pulses the time obviously suffices to reduce all of platinum (IV) to platinum (0).

The increased Pt amount due to longer pulse lengths, which has already been described above using the SEM and transient data, is also confirmed by the XPS measurements. For GCU, e.g., the Pt content rises from almost non-detectable (< 0.1 at %) for the deposition pulse length of 0.5 s to almost 3 at % for 7 s (Table III-3).

Table III-3: The amount of Pt on the surface determined with XPS in (Pt in at %) and with SEM ($m^* \text{ in } \mu\text{g cm}^{-2}$) as a function of deposition pulse length ($t_p \text{ in s}$)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>GCU</th>
<th>GCHT20</th>
<th>GCHT30</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_p \text{ / s}$</td>
<td>0.5s</td>
<td>1 s</td>
<td>2 s</td>
</tr>
<tr>
<td>Pt / at %</td>
<td>&lt;0.1</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>$m^*(\text{ Pt})$ / $\mu\text{g cm}^{-2}$</td>
<td>0.2</td>
<td>1.4</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Results and Discussion

Also the Pt growth mode seems to depend on the substrate. A comparison of transients (Figure III-5) reveals that the 2s pulse on GCU displays non-monotonous transients and additional features (Figure III-5, solid line) which can be interpreted as a sign for 2D nucleation and growth [128]. This transient form can be explained by adsorbed metal ion charge transfer and bulk diffusion as the rate determining step [128-130]. Also, 2D growth is considered to happen via coalescence of small Pt particles, which are supposed to be quite mobile on a smooth substrate with RMS < 1 nm [131]. For GCHT, however, a monotonous curve and, thus, a 3D nucleation and growth are observed, which is probably due to higher local density of imperfections and surface defects which enable better Pt adhesion [128].

Summarising the results of characterised Pt/GCU and Pt/GCHT model electrodes, a model for electrochemical Pt deposition on these substrates can be proposed.

The GCU surface possesses a certain “nano-roughness”, which was already discussed in chapter II, however, there are no protruding features such as steps or plane edges which would serve as preferable sites for Pt deposition. Therefore, the distribution of nucleation centres is random, as is the distribution of particle diameters (Figure III-13a). The deposition is “restricted” to the GC surface exposed to the electrolyte as there was no indication for the penetration of the electrolyte into the material.

The opening of the pores in the heat-treated material leads to strongly increased surface area which influences Pt deposition in terms of e.g. coverage and particle size. The porous structure creates more nucleation centres (pores) which are finer dispersed on GCHT. In contrast to GCU, the porous layer, formed during the heat-treatment, is supposed to be wetted by the electroplating solution, which was clearly indicated by the current response, which increased by more than two orders of magnitude after heat-treatment which was longer than 10 min (Table III-2, Figure III-5). As a consequence, the deposited Pt particles are partially trapped or “anchored” in the porous GCHT layer (Figure III-13b,c) or at the low-coordinated carbon species which are probably present in the micropores. Also deposition of Pt in the porous layer can be considered. The thickness of the porous layer and the consequent penetration depth of the electroplating solution (Figure III-13b,c) are dependent on the length of thermal pre-treatment of GC.
Results and Discussion

Figure III-13: A sketch of electrochemical Pt deposition upon a) GCU, b) GCHT10 and c) GCHT30. It indicates the changes upon longer heat-treatment: growth of the porous layer, the penetration of the electrolyte into the layer as well as increased surface coverage and smaller particle size.

The differences between GCU and GCHT will be further observed and discussed in course of electrochemical oxidation experiments.

III.1.3 Oxidation Experiments

III.1.3.1 Potentiostatic Hold Experiments

III.1.3.1.1 Room Temperature

III.1.3.1.1 Untreated GC (GCU)

In order to quantify oxidation upon electrochemically prepared model electrodes, the length of the pulse applied to the glassy carbon substrate to deposit platinum from the solution was set to 2 seconds. This time span is sufficient to produce model electrodes
with 2-4 \( \mu \text{g} \) of platinum per \( \text{cm}^2 \). The diameter of most dots under these conditions is 114 nm +/- 20 nm. The 2s-pulsing experiment on GCU was repeated approximately 40 times with very similar results so that it can be stated that at least the diameter of the obtained dots and amount of Pt remained in the same range.

First, 1.9 V vs. SHE was chosen as it was supposed to represent a potential high enough to induce the corrosion of platinum and/or its carbon support. The time span was varied between 20 minutes and one hour. Before and after the electrochemical experiment the samples were measured with SEM and XPS. The SEM images did not show any significant changes, regarding the mean diameter of the particles (Figure III-14).

![Figure III-14: Mean diameter of platinum dots determined from SEM images of electrochemically prepared GCU model electrode (pulse length 2s) as a function of oxidation length (oxidation potential 1.9 V vs. SHE)](image)

The XPS results, however, revealed a strong oxidation of carbon (Figure III-15). The normalised C1s spectra of “oxidised” samples (lines with symbols in Figure III-15), for instance, show a strong increase of \(-\text{COOH}\) and \(-\text{CO}\) bands at higher binding energies when compared to an untreated model electrode (solid black line in Figure III-15). For determination of possible platinum effect, pristine glassy carbon samples were oxidised in the same manner (lines with empty symbols in Figure III-15). They also showed an
increase in the intensity of oxygenated carbon bands, this change was nevertheless smaller than for GCU/Pt electrodes oxidised for the same amount of time.

The results showed that carbon oxidation took place at this potential at room temperature and seemed to be enhanced by the presence of platinum.

![C1s spectra](image)

**Figure III-15:** C1s spectra of GCU electrodes with (filled symbols) and without Pt (empty symbols) before (solid line) and after (line with symbols) the potential hold.

The evaluation of respective normalised Pt4f spectra recorded for the same sample before and after the electrochemical experiments revealed a curious trend, for samples with a holding time of 20 and 40 min there was an additional doublet at higher binding energies which usually indicates changes in Pt oxidation state (**Figure III-16**). This oxidation pattern, however, was not regular; as no oxidation was observed for a hold of 10 or 60 min at 1.9 V vs. SHE. The spectra were similar at every of the four measured areas of the sample, confirming that the obtained data was not restricted to any specific corners of the model electrodes.
Results and Discussion

Figure III-16: Pt4f spectra of Pt/GCU model electrodes before (black lowest line) and after electrochemistry (10, 20, 40 or 60 min at 1.9 V vs. SHE).

The experiments were repeated, however, the results (the additional doublet) could not be reproduced. The same observations were made on GCU when varying the oxidising potential; the findings are discussed at the end of this chapter.

The next step was to keep the oxidation time constant and vary the potentials at which the sample was held. The chosen potential range was between 1.2 and 1.9 V vs. SHE.

The oxidation/corrosion currents recorded at varying potentials (Figure III-17) revealed, that the current values were smaller at lower holding potentials, the difference between the current values at e.g. 1.2 V and 1.7 V vs. SHE was in the range of two orders of magnitude (black solid line in Figure III-17 and blue solid line in Figure III-17). A typical transient at potentials < 1.6 V vs. SHE was best described by an exponential decay. At potentials > 1.6 V vs. SHE a different behaviour was observed, the current first decayed (region A in Figure III-17) to a certain value, then the values started to increase (region B in Figure III-17).
The SEM images of the electrodes after oxidation did not show any significant changes, regarding the mean diameter or the number of the particles ([Figure III-18](#)); the evaluation showed that it still remained within the error margin (standard deviation) of the mean diameter before electrochemical experiments.
However, the XP spectra revealed a strong oxidation of carbon, especially for potentials > 1.7 V vs. SHE. In order to validate this first impression, the XP spectra were used to determine the amount of carbon and oxygen and plot it against the oxidation potentials (Figure III-19). The plot was likewise used to trace the influence of Pt presence on the oxidation of GC. Figure III-19 shows a difference between the model electrodes containing platinum and the ones without: Especially at elevated potentials the electrodes with platinum contain visibly less carbon (filled triangles) and more oxygen (filled squares), respectively. The carbon and oxygen content of model electrodes both with and without platinum before the oxidation were 91 +/- 2 at% and 9 +/- 2 at%, respectively. This kind of evaluation, however, is not sufficiently precise as the amount of oxygen on the sample surface is likewise dependent on impurities (also coming from electrolyte and storage under ambient conditions).
Figure III-19: Carbon (triangles) and oxygen (squares) content of the model electrodes after oxidation at different potentials determined from XP spectra.

For this reason, additional attention was paid to C1s spectra. The normalised C1s spectra of oxidised samples (Figure III-20), for instance, show a strong increase of –COOH and –CO bands at higher binding energies (BE > 285.5 eV) when compared to an untreated model electrode. Also, it seems that the electrodes containing Pt (solid lines / filled symbols in Figure III-20) are stronger oxidised if compared to plain carbon electrodes (dashed lines / empty symbols in Figure III-20). These results again suggest that the oxidation process seems to be enhanced by the presence of platinum.
To prove this fact, the XP spectra underwent a Shirley background removal and the component peaks were separated by the VG Avantage 3.70 program (Thermo VG Scientific), using mixed Gaussian-Lorenzian functions (Figure III-21). Four C-peaks were fitted into the existing C1s-spectrum: C1s is the main C-peak at 284.5 +/- 0.2 eV, its FWHM was allowed to vary between 1.0 and 1.2; C1s Scan A and C1s Scan B, at 287.2 +/- 0.3 eV and 289.0 +/- 0.3 eV, respectively, correspond to carbon atoms attached to different oxygen-containing moieties (oxidised carbon), their FWHM was set to 1.5. Finally, the C1s Scan C with varying binding energy and fixed FWHM of 1.0 was required due to broadening of the main peak with increasing oxidation potential. The peak-broadening can be explained by apparition of so-called β-carbon, carbon attached to phenolic groups or to other oxygen-containing carbon moieties, such as e.g. –CO [132]. The above-mentioned fitting parameters were a product of several tries to find the best and most reliable set of parameters to describe the XP spectra of GCU and, later on, GCHT20 with and without platinum.
Results and Discussion

Figure III-21: An example of the deconvolution procedure applied to the C1s XP spectra of the oxidised model electrodes (i.e. oxidised at 1.6 V vs. SHE for 30 min).

After the fitting, the atomic percentage ratio between oxidised carbon species (area of C1s C=O and COOH species) and total carbon was plotted versus the applied potential for the thermally treated GC samples both with and without platinum (Figure III-22). This plot shows that the amount of oxidised carbon on the sample surface, which is 0.09 for non-oxidised GCU and 0.11 for non-oxidised Pt/GCU, grows with increasing corrosion potential for electrodes both with and without platinum, strong oxidation starting at potentials above 1.75 V vs. SHE. This plot revealed that the amount of oxidised carbon on the surface is higher for model electrodes containing Pt (filled squares in Figure III-22) at all investigated potentials. It suggests that in case of model electrodes with untreated glassy carbon as a support the presence of platinum enhances the carbon oxidation for potentials ranging from 1.2 V to 1.9 V vs. SHE.
Figure III-22: Atomic percentage ratio of oxidised carbon to “undamaged” carbon for GCU with (filled squares) and without (empty diamonds) platinum (deposition pulse length 2 s) at different potentials. The value of non-oxidised GCU with and without Pt is 0.11 and 0.09, respectively.

The evaluation of respective normalised Pt4f spectra recorded for the same sample before and after the electrochemical experiments revealed an additional doublet at higher binding energies, which usually indicates changes in Pt oxidation state (Figure III-23). The oxidation pattern, however, was not regular; it seemed that there is a strong oxidation of Pt already at potentials > 1.5 V but no oxidation at 1.9 V Figure III-23. The spectra were similar at every of the four measured points of the sample, confirming that the obtained data was not restricted to any specific corners of the model electrodes. This behaviour was the same as already observed for Pt4f spectra of some samples with varying length of the potentiostatic hold.
Results and Discussion

Figure III-23: XPS Pt4f spectra for Pt/GCU samples (deposition pulse length 2 s) held for 30 min at 1.2 V, 1.3 V, 1.4 V, 1.5 V, 1.7 V, 1.8 V and 1.9 V vs. SHE

The potential hold experiments were repeated to confirm the results. However, the data could not be reproduced; upon the repetition, the Pt 4f spectra displayed only the doublet corresponding to elemental Pt, irrespectively of the applied potential (exemplarily shown for potentials of 1.5, 1.7 and 1.8 V vs. SHE in Figure III-24).
This behaviour, in turn, has been explained in detail by Peuckert et al. [54], who implied that at potentials below 2.2 V vs. SHE only one or two oxidation monolayers are formed on the bulk platinum surface so that only traces of Pt$^{2+}$ can be detected by XPS. Also, Xu et al. [93] published 2008 their EC-STM studies which described a formation of a “passivation” layer on bulk Pt surface at potentials higher than 1 V vs. SHE, which considerably slowed down further platinum corrosion.

From these literature studies as well as from the experimental findings it was concluded that the shift of Pt to higher binding energies, which was observed for some samples in Figure III-23 was due to partial charging. Probably on some oxidised Pt/GCU model electrodes there was poor Pt adhesion to the GCU substrate after the oxidation or corrosion of GCU upon application of a potential, which in turn led to partial charging of the Pt$4f$ spectra. On the same samples, however, no charging was observed for other elements, such as e.g. carbon or oxygen.
III.1.3.1.1.2 Heat-treated GC (GCHT20)

The pulse length for electrochemical platinum deposition upon GCHT20 was equally set to 2 seconds, producing model electrodes with 6-10 µg of platinum per cm². The mean diameter of the dots under these conditions is 53 +/- 15 nm. The 2s-pulsing experiment with GCHT20 was repeated approximately 30 times with the same results so that it can be stated that at least the diameter of the obtained dots remained in the same range.

The current transients looked similar to the ones obtained for GCU, smaller current values for lower potential values, exponential decay and subsequent increase of the current for potentials above 1.7 V vs. SHE, as is exemplarily shown for potential hold at 1.2 V, 1.65 V, 1.8 V and 1.9 V vs. SHE in Figure III-25.

![Figure III-25: Oxidation /corrosion transients recorded for Pt/GCHT20 (deposition pulse length 2 s) during the potentiostatic hold at 1.2 V, 1.65 V, 1.8 V and 1.9 V vs. SHE](image)

As in the case of GCU, the SEM images of the electrodes after oxidation did not show any significant changes, regarding the mean diameter of the particles; it still remained within the error margin (standard deviation) of the mean diameter before electrochemical experiments (Figure III-26).
The XP spectra, however, again revealed a strong oxidation of carbon. The C1s spectra of oxidised samples, for instance, show a strong increase of –COOH and –CO bands at higher binding energies. After the fitting procedure described in III.2.2.1.1.1, the atomic percentage ratio between oxidised carbon species and total carbon was plotted against the applied potential for the GCHT20 samples both with and without platinum (Figure III-27).
Results and Discussion

Figure III-27: Atomic percentage ratio of oxidised carbon to “undamaged” carbon for GCHT20 with (filled squares) and without (empty diamonds) platinum (deposition pulse length 2 s) at different potentials. The value of non-oxidised GCHT20 with and without Pt is 0.12 and 0.10, respectively.

This plot shows that the amount of oxidised carbon on the sample surface grows with increasing potential for electrodes both with and without platinum. Strong oxidation starts at potentials above 1.6 V vs. SHE. At very low potentials, like 1.2 V vs. SHE for instance, there is a small difference between the glassy carbon with and without platinum. At very high potentials (> 1.8 V vs. SHE) the situation is similar, so there seems to be Pt enhanced oxidation. On the other hand, for a potential between 1.4 and 1.65 V the oxidation seems to be stronger for the samples containing no Pt. The conclusion which can be drawn from the evaluation is that there is no evident influence of Pt on the oxidation behaviour of GCHT20.

The evaluation of respective normalised Pt4f XP spectra gave little information about the platinum oxidation state (exemplarily shown for potential hold values of 1.3 V, 1.6 V, 1.8 V and 1.9 V vs. SHE in Figure III-28); however, this behaviour was expected. Also, no partial charging was ever observed for the Pt4f spectra after oxidation, implying better Pt adhesion to GCHT20. Obviously, the penetration of the electroplating solution into the
Results and Discussion

porous layer present on the GCHT20 surface indeed led to better anchoring of the Pt particles to the substrate.

![Figure III-28: XPS Pt4f spectra for Pt/GCHT20 samples (pulse length 2 s) held for 30 min at 1.3 V, 1.6 V, 1.8 V and 1.9 V vs. SHE](image)

**Figure III-28:** XPS Pt4f spectra for Pt/GCHT20 samples (pulse length 2 s) held for 30 min at 1.3 V, 1.6 V, 1.8 V and 1.9 V vs. SHE

**III.1.3.1.1.3 Conclusions**

Oxidation experiments at room temperature were performed on untreated and heat-treated GC electrodes without and with platinum, prepared by electrochemical Pt deposition, by holding the samples for 30 minutes at potentials ranging from 1.2 V to 1.9 V vs. SHE at room temperature.

The SEM images did not show any potential-related changes of the diameter and abundance of the particles.

The XP spectra revealed that for all electrodes the carbon oxidation grew with increasing anodic potentials. The evaluation of C1s spectra showed that for GCHT there is no difference between the oxidation of pure carbon electrodes and the ones containing Pt. For GCU, however, there seem to be a platinum enhanced oxidation of the support. Also, the oxidation of GCU electrodes starts at higher potentials ($E_{\text{Cox}} = 1.75$ V) than for
Results and Discussion

GCHT20 electrodes (E_{Cox} = 1.6 V), irrespectively of the presence of platinum. This difference in the oxidation behaviour is most probably due to the formation of a porous layer on the GC surface and low-coordinated C-atoms within the pores during the heating at 450°C [114]. This layer, combined with an increased number of defects on the GC surface, is probably also responsible for altered platinum behaviour as it suppresses the surface movement of the platinum atoms and modifies the platinum deposition process. The influence of substrate properties on Pt adhesion was further manifested in XPS measurements of electrodeposited Pt after the oxidation. Partial charging, probably due to worsened contact between the substrate and the metal, was observed for some GCU samples while for Pt/GCHT20 there was no change of the Pt4f signal after the oxidation (as compared to the before-state).

The oxidation process which occurs during the potentiostatic hold obviously influences the chemical properties of the substrate. However, there is no evidence for any potential-induced change in diameter of Pt particles, as was measured by SEM.

III.1.3.1.2 Elevated Temperature (60°C)

III.1.3.1.2.1 Untreated GC (GCU)

As already mentioned in III.1.1., several studies from literature, for instance Wickman et al. [55] or Cherstiouk et al. [92], to name few of them, reported that carbon degradation is faster and stronger at elevated temperatures (as compared to room temperature) and that the corrosion currents increased with rising electrode potential, temperature, water concentration and presence of Pt. The influence of temperature on the oxidation of carbon was first monitored for electrochemically prepared Pt/GCU model electrodes.

The recorded transients showed that the currents were indeed larger than the ones obtained at room temperature (exemplarily shown for 1.4 V and 1.8 V vs. SHE in Figure III-29). Also at 60°C the course of the line at potentials below 1.5 V vs. SHE is characterised by an exponential decay (Figure III-29) while the transient at higher potentials shows an exponential decay followed by rising values (Figure III-29) (also see III.1.2.1.1.).
Results and Discussion

Figure III-29: Oxidation/corrosion transients recorded for Pt/GCU (deposition pulse length 2 s) during the potentiostatic hold at 1.4 V and 1.8 V vs. SHE at RT and at 60°C

The SEM images of the electrodes after potentiostatic hold at elevated temperatures do not show any significant changes, regarding the appearance or distribution of the particles on the surface as is exemplarily shown in Figure III-30 for the potential of 1.8 V vs. SHE.
Results and Discussion

Figure III-30: SEM images of Pt/GCU model electrodes a) before and b) after potential hold at 1.8 V vs. SHE at 60°C

The evaluation of mean diameter values before and after oxidation experiments revealed that the particles have become slightly larger (Table III-4); however, the increase is within the error margin (much smaller than the SD value calculated for the mean diameter) if all the assumptions, e.g. regular hemispheres and homogeneous surface coverage, for calculation of mean diameter are considered.

Table III-4: Mean diameter values before and after potentiostatic hold experiments at 60°C, determined using SEM

<table>
<thead>
<tr>
<th>Holding potential / V vs. SHE</th>
<th>d before oxidation / nm</th>
<th>d after oxidation / nm</th>
<th>Δd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>72 +/- 16.8</td>
<td>77 +/- 17.1</td>
<td>5</td>
</tr>
<tr>
<td>1.6</td>
<td>71 +/- 19.9</td>
<td>74 +/- 20</td>
<td>3</td>
</tr>
<tr>
<td>1.8</td>
<td>67.5 +/- 14.3</td>
<td>70 +/- 17.3</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The evaluation of respective XP Pt 4f spectra recorded for the same sample before and after the electrochemical experiments reveals no obvious change in Pt oxidation state. No partial charging, described in the previous chapters, was observed for the model electrodes.
The C1s spectra revealed a strong oxidation of carbon, especially for potentials > 1.6 V vs. SHE. In order to validate this first observation, XP spectra were deconvoluted according to the procedure described in III.1.3.1.1.1. After fitting, the atomic percentage ratio between oxidised carbon species and total carbon was plotted versus the applied potential for the untreated GC samples both with and without platinum (filled symbols in Figure III-31). This plot shows that the amount of oxidised carbon on the sample surface grows with increasing potential for electrodes both with and without platinum. The amount of oxidised carbon on the surface is higher for electrodes containing Pt (filled red squares in Figure III-31) at all investigated potentials. Thus, in case of model electrodes with GCU as a support the presence of platinum enhances the carbon oxidation for investigated potentials. For comparison, the plot also contains values for the same type of experiments at room temperature (empty symbols in Figure III-31).

Figure III-31: Atomic percentage ratio of oxidised carbon to “undamaged” carbon for GC samples with (red filled squares) and without (black filled diamonds) platinum at different potentials at 60°C and room temperature (empty symbols).
Results and Discussion

### III.1.3.1.2.2 Heat-treated GC (GCHT20)

As in case of GCU, the SEM images of the Pt/GCHT20 model electrodes after potentiostatic hold at elevated temperatures do not show any significant changes, regarding the appearance or distribution of the particles on the surface as is exemplarily shown in Figure III-32 for the holding potential of 1.8 V vs. SHE.

![SEM images of Pt/GCHT20 model electrodes](image)

**Figure III-32**: SEM images of Pt/GCHT20 model electrodes a) before and b) after potential hold at 1.6 V vs. SHE at 60°C

The evaluation of mean diameter values before and after oxidation experiments revealed again that the particles have become slightly larger (**Table III-5**); however, this change was likewise smaller than the value of standard deviation calculated for the samples.

**Table III-5**: Mean diameter values before and after potentiostatic hold experiments at 60°C, determined using SEM

<table>
<thead>
<tr>
<th>Holding potential / V vs. SHE</th>
<th>d before oxidation / nm</th>
<th>d after oxidation / nm</th>
<th>Δd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>33.3 +/- 8.5</td>
<td>39.2 +/- 12.5</td>
<td>5.9</td>
</tr>
<tr>
<td>1.6</td>
<td>40.1 +/- 12.6</td>
<td>43.6 +/- 14.8</td>
<td>3.5</td>
</tr>
<tr>
<td>1.8</td>
<td>35.2 +/- 10.9</td>
<td>37.8 +/- 10.7</td>
<td>2.6</td>
</tr>
</tbody>
</table>
Results and Discussion

The Pt4f XP spectra showed no oxidation, however, C 1s did. The spectra were deconvoluted and the information about oxidised carbon plotted according to the procedure described above. Figure III-33 displays the results for the hold experiments at 60°C (filled symbols) but also at room temperature (empty symbols).

![XPS C1s deconvolution GCHT20](image)

**Figure III-33:** Atomic percentage ratio of oxidised carbon to “undamaged” carbon for GC samples with (red filled squares) and without (black filled diamonds) platinum at different potentials at 60°C and room temperature (empty symbols).

The plot reveals that the amount of oxidised carbon is higher for the samples containing Pt, both at room temperature and at 60°C; however, this Pt influence seems to be more pronounced at elevated temperatures. The values are comparable to those obtained for GCU; however, the increase in the amount of oxidised carbon is steeper for GCHT20. Also, for GCHT the difference between GCHT without Pt at room temperature and at 60°C is almost within the error margin, while it is quite substantial for GCU. One possible explanation might be the presence of a porous layer on the surface of GCHT, which acts passivating up to a certain oxidation threshold [114]. The presence of Pt and elevated temperature enhances the oxidation but to a lesser extent than for GCU.
III.1.3.1.2.3 Conclusions

Oxidation of Pt/GCU, prepared by electrochemical Pt deposition and Pt/GCHT20 was investigated by applying potentiostatic hold at elevated temperatures (60°C). The size or the shape of Pt dots – investigated via SEM – has not substantially changed. XPS analysis of the model electrodes has revealed that the amount of oxidised carbon on the surface increased with temperature and that in all cases the samples containing platinum were stronger oxidised than the ones without platinum. This difference was larger at elevated temperatures (60°C), than observed at room temperature (see also III.1.3.1.1.).

III.1.3.2 Potential Cycling (GCU as substrate)

III.1.3.2.1 Room Temperature

The model electrodes have proven to withstand potentiostatic hold oxidation experiments; additionally, their stability towards oxidation was further tested during cycling experiments. Some authors [66, 93, 133, 134] indicate that cycling between the platinum oxide formation and reduction regions leads to higher dissolution rates than holding alone due to formation and reduction of a platinum oxide film and resulting mobile Pt\(^{2+}\) species. For these reasons, cycling experiments between 0.5 and varying upper potentials (up to 1.8 V vs. SHE) at room temperature as well as at 60°C were conducted on model electrodes with and without platinum.

A typical CV, obtained for the electrochemically prepared Pt/GCU model electrode, is shown in Figure III-34a. The characteristic platinum features in hydrogen (around 0 V vs. SHE) and oxygen (at potentials > 1.7 V vs. SHE) evolution regions, usually clearly visible for e.g. a platinum wire or disc as shown in Figure III-34b, cannot be clearly discerned in this CV. This observation is due to a small amount of electrodeposited Pt on the surface (2-4 μg cm\(^{-2}\)), as a result almost all Pt features are obscured by the electrochemical response of GCU. Indeed, if a CV of Pt/GCU model electrode (Figure III-34a) is compared to a CV of GCU (Figure III-34c), many similarities are visible, such as for instance for the region between 0.7 V and 1.6 V vs. SHE. The recorded current values for Pt/GCU are likewise in between the values for pure GCU and pure Pt.
Results and Discussion

a) $\mathrm{H}_2$ evolution

b) $\mathrm{O}_2$ evolution

Double layer

PtOx formation

PtOx reduction
Figure III-34: CVs recorded on a) Pt/GCU model electrode (deposition pulse length 2 s), b) Pt-disc and c) GCU. Scan rate 50 mV s\(^{-1}\)

Recording CVs during potential cycling (Figure III-35) showed that the current values increased with growing upper vertex potential.
Figure III-35: Cycles 400-450 for Pt/GCU model electrodes. The samples were cycled between 0.5 V and 1.4 V (black), 1.6 V (red) and 1.8 V (blue) vs. SHE at room temperature. The scan-rate is 100 mV s\(^{-1}\).

The SEM images before and after cycling at room temperature did not show any differences regarding the diameter or the distribution of the particles (Figure III-36), further more detailed evaluation of the mean diameter, however, yielded an increased dots size, as shown in Table III-6. This difference, however, was again smaller or equal to the calculated standard deviation.
Figure III-36: SEM images of Pt/GCU model electrodes a) before and b) after potential cycling between 0.5-1.6 V vs. SHE (500 cycles, scan-rate 100 mV s\(^{-1}\)) at RT

Table III-6: Mean diameter values before and after cycling experiments at room temperature, determined using SEM

<table>
<thead>
<tr>
<th>Upper (anodic) potential limit with lower potential limit of 0.5 V vs. SHE / V vs. SHE</th>
<th>d before cycling / nm</th>
<th>d after cycling / nm</th>
<th>(\Delta d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>104 +/- 20</td>
<td>107 +/- 20</td>
<td>3</td>
</tr>
<tr>
<td>1.4</td>
<td>131 +/- 30</td>
<td>143 +/- 30</td>
<td>12</td>
</tr>
<tr>
<td>1.6</td>
<td>100 +/- 10</td>
<td>127 +/- 27</td>
<td>27</td>
</tr>
<tr>
<td>1.8</td>
<td>121 +/- 35</td>
<td>125 +/- 26</td>
<td>4</td>
</tr>
</tbody>
</table>

The Pt4f XP spectra again showed neither obvious oxidation, nor partial charging; however, C1s displayed some changes. The spectra were deconvoluted and the information about oxidised carbon plotted according to the procedure described in previous chapters. The results are shown in Figure III-37.
Results and Discussion

III.1.3.2.2 Elevated Temperature (60°C)

The CVs recorded for cycling Pt/GCU at 60°C (Figure III-38) showed that the current values increased if compared to the ones observed at RT (Figure III-35), otherwise the same trend towards higher current values with increasing upper vertex potential was found (Figure III-38).

Figure III-37: Atomic percentage ratio of oxidised carbon to “undamaged” carbon for GCU samples with (red squares) and without (black diamonds) platinum at different potentials at room temperature.

The amount of oxidised carbon for electrodes containing Pt are slightly higher at potentials > 1.8 V vs. SHE, meaning that also in case of cycling the oxidation is enhanced by the presence of Pt.

If the amount of oxidised carbon for the cycling experiments is compared to potentiostatic hold experiments, it may be concluded that cycling does not seem to lead to higher oxidation rates.
Figure III-38: Cycles 400-450 for Pt/GCU model electrodes. The samples were cycled between 0.5 V and 1.4 V (black), 1.6 V (red) and 1.8 V (blue) vs. SHE at 60°C. The scan-rate is 100 mV s\(^{-1}\).

The SEM images before and after cycling at 60°C did not show any significant differences regarding the diameter or the distribution of the particles, however, the sample with the positive vertex potential of 1.8 V vs. SHE displayed severely damaged carbon in some areas (Figure III-39b).

The detailed evaluation of the particle diameter revealed a smaller mean diameter after the cycling (Table III-7). This behaviour is different from the results obtained from hold or cycling experiments of electrochemically produced Pt/GCU samples at room temperature (Table III-4, Table III-5 and Table III-6); however, also in this case the difference in diameters before and after the oxidation is much smaller than the standard deviation calculated for these samples.
Results and Discussion

Figure III-39: SEM images of Pt/GCU model electrodes a) before and b) after cycling between 0.5 and 1.8 V vs. SHE (500 cycles, scan-rate 100 mV s\(^{-1}\)) at 60°C

Table III-7: Mean diameter values before and after cycling experiments at 60°C, determined using SEM

<table>
<thead>
<tr>
<th>Upper (anodic) potential limit with lower potential limit of 0.5 V vs. SHE / V vs. SHE</th>
<th>d before cycling / nm</th>
<th>d after cycling / nm</th>
<th>Δd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>77.2 +/- 24.8</td>
<td>71.4 +/- 27.2</td>
<td>5.8</td>
</tr>
<tr>
<td>1.4</td>
<td>59 +/- 30.2</td>
<td>56.2 +/- 30</td>
<td>3.2</td>
</tr>
<tr>
<td>1.6</td>
<td>78.9 +/- 20.6</td>
<td>68.2 +/- 30.7</td>
<td>10.7</td>
</tr>
<tr>
<td>1.8</td>
<td>66.4 +/- 18</td>
<td>60.8 +/- 14</td>
<td>5.6</td>
</tr>
</tbody>
</table>

The Pt4f XP spectra showed no obvious oxidation, however, C1s did. The spectra were deconvoluted and the information about oxidised carbon plotted according to the procedure described in previous chapters. The results are shown in Figure III-40.
Figure III-40: Atomic percentage ratio of oxidised carbon to “undamaged” carbon for GCU samples with (red filled squares) and without (black filled diamonds) platinum at different potentials at 60°C and room temperature (empty symbols).

Also in case of cycling at 60°C the amount of oxidised carbon for electrodes containing Pt are higher; showing that the oxidation is enhanced by the presence of Pt. If the amount of oxidised carbon for the cycling experiments at elevated temperatures is compared to cycling experiments at room temperature, it may be concluded that higher temperature indeed influences the oxidation for electrodes both with and without Pt, especially at voltages < 1.8 V vs. SHE.

III.1.3.2.3 Conclusions

Oxidation experiments were performed on GCU model electrodes without and with platinum, prepared by electrochemical Pt deposition, by cycling the samples for 500 cycles between 0.5 V at a scan-rate of 100 mV s\(^{-1}\) and varying anodic potentials, 1.2 V to 1.8 V vs. SHE at room temperature and at 60°C.

The XP spectra revealed that for all electrodes the carbon oxidation grew with increasing anodic potentials. The evaluation of C1s spectra showed that there seemed to be a slight
effect of platinum on the oxidation of the support. Comparison to the values obtained for the potentiostatic hold experiments (chapter III.1.3.1.) implies that cycling indeed leads to higher oxidation rates, at least at 60°C. Also higher temperature seems to lead to slightly higher amount of oxidised carbon, as already noticed for potential hold experiments (chapter III.1.3.1.3.).

III.1.3.3 Conclusions for Oxidation Experiments

The oxidation experiments, in particular potentiostatic hold, revealed certain similarities and differences between the untreated and heat-treated GC. For both substrates, the chemical properties of carbon change upon oxidation.

In case of GCU and Pt/GCU, there is increasing carbon oxidation with increasing value of the holding potential as detected by XPS. There are also hints at Pt-enhanced carbon oxidation. These oxidised carbon species are considered to be intermediates for the subsequent carbon corrosion. Information concerning (Pt-induced) carbon corrosion itself, usually quantified by detection of CO$_2$ was not gathered in course of the above measurements; however, there were certain hints at it. One came from the XPS analysis of electrodeposited Pt, a partial charging was observed for certain Pt4f spectra which might be provoked by loose contact of Pt to the GCU, perhaps as a result of carbon corrosion underneath the particles (Figure III-41).

Figure III-41: a sketch of proposed mechanism of carbon oxidation for electrochemically prepared Pt/GCU model electrodes

According to the SEM measurements, the diameter of the particles did not change after oxidation. No information was obtained concerning the particle height, which might have been changed after the oxidation, due e.g. to carbon corrosion directly at the
Results and Discussion

edges/corners of the dots (as schematically shown in Figure III-41). Also the movement of particles, indicating, e.g. Ostwald ripening, could not be visualised by the ex situ techniques.

In case of GCHT20 and Pt/GCHT20, there was likewise oxidation of carbon; it grew stronger with higher holding potentials. Neither strong indication for Pt-induced carbon oxidation nor partial charging was observed, though. The absence of partial charging for Pt/GCHT20 model electrodes might hint at better adhesion of Pt particles to the substrate. The presence of the porous layer, which soaks up electroplating solution might indeed lead to better anchoring of the particles, which then have an improved electric contact to the substrate (if compared to GCU) (Figure III-42). Another explanation, resulting from the presence of a porous layer, would be “blocking” of some pores by electrodeposited platinum, so that no complete enveloping of the particles by the electrolyte and subsequently less (or no) corrosion starting at the edges of the dots can take place (Figure III-42).

Figure III-42: a sketch of proposed mechanism of carbon oxidation for electrochemically prepared Pt/GCHT20 model electrodes

Increasing the temperature from room temperature to 60°C led to higher amounts of oxidised carbon moieties on both GCU and GCHT20. However, the difference in content of oxidised carbon between the experiments at room temperature and 60°C is more pronounced for GCU. The porous layer is probably again the explanation for this behaviour, perhaps the influence of the applied potential on the concentration of functional groups on the GCHT20 surface is higher than that of the temperature, meaning that the surface oxidation is fast enough already at room temperature. Also the hints at Pt-enhanced carbon oxidation are present to a lesser extent on Pt/GCHT20 model
electrodes. Probably, the porous structure of GCHT20 possesses a higher number of low-coordinated carbon atoms than GCU; these low-coordinated carbons are prone to oxidise first, thus, the oxidation process is not influenced by small amounts of Pt present on Pt/GCHT20 model electrodes and the effect of Pt is too small to be observed.

The oxidation experiments on electrochemically prepared model electrodes showed that we could trace the presence of oxidised carbon species and that carbon oxidation was dependent on the substrate. No oxidation, loss or movement of Pt could be observed on the GC. The mean diameter of the particles, obtained by electrochemical Pt deposition, did not seem to change upon oxidation but the size distribution was very broad and the standard deviation value extremely high, usually almost double the value of diameter change before/after ec, so it was difficult to make any certain statements. For this reason, lithographically prepared model electrodes, possessing a well-controlled diameter and a defined arrangement, were the next aim.

### III.2 Model Electrodes (Pt/GC) Prepared by Lithography

#### III.2.1 Introduction

An alternative preparation method to electrochemical platinum deposition, discussed in the last chapter III.1, is the use of lithographic techniques. Their advantages, such as defined arrangement as well as defined size and size distribution of particles, were shortly mentioned in the introduction (I.4.3.) together with the biggest drawback: the complexity of the preparation process. The following chapters will describe the preparation of model electrodes by two lithographic techniques, extreme-ultraviolet interference lithography (EUV-IL) and electron beam (e-beam) lithography (EBL).

In course of the work, after the first results of EUV-IL exposures, structuring of the glassy carbon surface via e-beam was chosen as an alternative to the EUV-IL process. The advantages of e-beam is rapid sample processing due to easier access, less stringent vacuum requirements, a possibility to easily tune the particle size from approximately 20 to 200 nm by adjusting the size of the electron beam spot or varying the distance between the particles (the larger the distance, the smaller the particles) and no use for a specifically
Results and Discussion

designed mask. The EBL process was discussed and stepwise improved in collaboration with Dr. Vitaliy Guzenko (LMN).

Also subsequent oxidation experiments, conducted according to the procedures described in III.1. for electrochemically prepared model electrodes will be discussed.

III.2.2 Preparation

III.2.2.1 Extreme Ultraviolet Interference Lithography (EUV-IL)

Prior to the exposure and the spincoating step, the surface of the GC samples was probed by AFM TM and contact mode AFM to determine the surface roughness which is crucial for successful spincoating. The obtained images, exemplarily shown for GCU in Figure III-43, displayed an extremely flat surface (RMS = 0.5 nm) with RMS values comparable to the ones obtained for Si-wafers. GC heat-treated at 450°C in air for 10 (GCHT10), 20 (GCHT20), 30 (GCHT30) and even 60 (GCHT60) minutes were likewise quite smooth (middle column in Table III-8).

![Figure III-43: AFM TM image of GCU as received, before spin-coating. The Δz-range is 5 nm.](image)

After spincoating (for details refer to II.3.2) of a PMMA layer with a thickness of 44 or 65 nm, the GC surface was again measured with contact mode AFM, displaying an even smoother surface or lower RMS values (right column in Table III-8), as exemplarily shown for GCHT30 in Figure III-44. The “nano-roughness” observed for all GC samples did not influence the spincoating process.
Results and Discussion

Table III-8: RMS values of GCU and GCHT before and after spincoating. The values were measured by contact mode AFM.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS before spincoating / nm</th>
<th>RMS after spincoating / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>GCU</td>
<td>0.5</td>
<td>0.24</td>
</tr>
<tr>
<td>GCHT10</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>GCHT20</td>
<td>0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>GCHT30</td>
<td>0.7</td>
<td>0.45</td>
</tr>
<tr>
<td>GCHT60</td>
<td>0.8</td>
<td>0.3</td>
</tr>
</tbody>
</table>

The numbers shown in Table III-8 are mean values and were determined as following: for each sample AFM images of different sizes (100nm, 500nm, 1µm and 5µm) were recorded, RMS was measured using WSxM 5.0 Develop 3.1. software [98] and the mean value for all four images was calculated. RMS varies slightly before and after spincoating, in general the surface is smoother when covered with photoresist and if the sample had not had any prior thermal treatment.

Figure III-44: AFM contact mode image of GCHT30 as received, after spin-coating. The \( \Delta z \)-range is 5 nm.
For the XIL exposure, nine glassy carbon samples were chosen: four with the photoresist thickness of 65 nm and five with the thickness of 44 nm (see Table III-9). The samples were exposed according to the procedure described in II.3.2.

**Table III-9: description of glassy carbon samples patterned by EUV-IL**

<table>
<thead>
<tr>
<th>sample number</th>
<th>thermal pre-treatment</th>
<th>photoresist thickness / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GCU</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>GCU</td>
<td>44</td>
</tr>
<tr>
<td>3</td>
<td>GCHT10</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>GCHT20</td>
<td>44</td>
</tr>
<tr>
<td>5</td>
<td>GCHT30</td>
<td>44</td>
</tr>
<tr>
<td>6</td>
<td>GCU</td>
<td>65</td>
</tr>
<tr>
<td>7</td>
<td>GCHT10</td>
<td>65</td>
</tr>
<tr>
<td>8</td>
<td>GCHT20</td>
<td>65</td>
</tr>
<tr>
<td>9</td>
<td>GCHT30</td>
<td>65</td>
</tr>
</tbody>
</table>

In order to find optimised conditions for the lithographic process upon each spincoated GC sample 9 fields, each with a different EUV dose, were generated (Figure III-45a). Field 1 had the lowest EUV dose of 25 mJ cm$^{-2}$ and field 9 the highest (107.5 mJ cm$^{-2}$). On each field the pattern, shown enlarged in Figure III-45b, was generated. The micro- and nanostructures comprised either holes (1, 3 and 6 in Figure III-45b) created by four-beam or lines (2, 4 and 5 in Figure III-45b) created by two-beam X-ray interference. In particular, the largest cross (1 in Figure III-45b) was investigated as it contains 141 nm period structures which are of interest for the current work. The bright areas in Figure III-45b correspond to areas of direct exposure; the darker ones are those with the photoresist and/or interference patterns.
Results and Discussion

Figure III-45: a) 9 fields of an EUV exposed sample; the arrow indicates increasing exposure dose; b) light microscope image of a field with various structures indicated as following 1) 141 nm holes; 2) 100 nm lines; 3) 283 nm holes; 4) 200 nm lines; 5) 1500 nm lines and 6) 1500 nm holes created in one exposure. Taken from [135]

The platinum deposition was performed by sputtering platinum on the developed GC samples prior to the lift-off procedure. The samples were investigated prior to and after lift-off to test whether the procedure was successful. The diameter of obtained nanostructures before lift-off varied from 50 to 100 nm, depending on the dose (Figure III-46). The bright area indicates the photoresist covered by platinum and the dark round structures are holes with platinum at the bottom. As expected, the size of the holes increases with increasing EUV dose, as the employed positive photoresist is more susceptible to higher energy densities.
Results and Discussion

Figure III-46: SEM images of 141 nm period hole structures on 8 (for classification see Table III-9) with EUV dose of a) 62.2 mJ cm\(^{-2}\); b) 74.6 mJ cm\(^{-2}\); c) 89.6 mJ cm\(^{-2}\); d) 107.5 mJ cm\(^{-2}\) before lift-off.

After the lift-off, the samples were investigated once again with SEM. The completeness of the lift-off procedure was dependent on the EUV dose of the investigated field.

The 141 nm structures on the fields with lower EUV doses (d < 62.2 mJ cm\(^{-2}\)), were completely removed by the process exemplarily shown for sample 2 (for classification see Table III-9) in Figure III-47a, while for the fields with higher EUV doses the procedure was more successful. The best result has been achieved for the dose of 89.6 mJ cm\(^{-2}\) (Figure III-47b): Dark parts of the image represent the photoresist-free GC where only carbon support is left, the bright, almost white area is the photoresist covered with Pt and the gray area displays a successful lift-off with platinum nanodots. The gray area covers ca 80 % of the exposed field proving that most of the structures withstood the lift-off process under the chosen preparation conditions. The dose with the most nanodots after the lift-off was determined to be dose 8 or 89.6 mJ cm\(^{-2}\) (Figure III-47a) for both employed photoresist thicknesses and different pre-treatment conditions of the GC substrate.
Results and Discussion

Figure III-47: An SEM image of the field with 141 nm period hole structures on sample 2 (for classification see Table III-9) with EUV dose of a) 43.2 mJ cm\(^{-2}\) and b) 89.6 mJ cm\(^{-2}\) after lift-off.

Seven out of nine samples have been measured with SEM after lift-off to find the best conditions for the exposure; the results are summarised in Table III-10. Pt nanodots could be found for doses > 43.2 mJ cm\(^{-2}\), i.e. 51.8 mJ cm\(^{-2}\) to 107.5 mJ cm\(^{-2}\) (exemplarily shown for the dose of 62.2 mJ cm\(^{-2}\) in Figure III-48).

Figure III-48: An SEM image of the field with 141 nm period hole structures on sample 2 (for classification see Table III-9) with EUV dose of 62.2 mJ cm\(^{-2}\) after lift-off. Two different magnifications a) 100 k and b) 250 k.

A thinner photoresist led to better results due to a more successful lift-off procedure, there were nanodots also on the fields with lower EUV doses (compared to a thicker photoresist) and the abundance of the dots was higher (lower half of Table III-10). There was no
obvious influence of the thermal pre-treatment on the platinum adhesion (compare the rows with different length of thermal pre-treatment). The success of the lift-off step increased with higher EUV dose, however, the field with the highest EUV dose (107.5 mJ cm$^{-2}$) presented a challenge, the photoresist remained even after the lift-off process. This was probably due to “over” exposure or “over”-development of the areas, which was already observed for exposures on Si-wafers.

The SEM images have shown that the size of the nano-particles increased almost linearly with the applied EUV dose (Figure III-49), reaching from approximately 40 to 100 nm. Little difference in size was observed for two different photoresist thicknesses. After lift-off the smallest structures had the size of 40 nm and the largest of 100 +/-5 nm (Figure III-49). The only change was in the quality of the lift-off process, if a thinner photoresist was used, it was possible to find Pt nanoparticles on five doses instead of four (Table III-10).

*Table III-10: Summarised results of the lift-off process, the numbers (percentage) indicate(s) the part of Field 1 (Figure III-45b) which is covered with Pt nanodots*
The smallest nanodots were obtained for the fields with EUV dose lower than 70 mJ cm\(^{-2}\) (Figure III-49). However, only little area upon these fields withstood the lift-off process and displayed the desired arrangement of the nanodots (Table III-10). Thus, a possibility to further decrease the diameter of nanodots without lowering the EUV dose was tested. For this purpose, before sputtering of Pt an additional Cr/Ag mask was evaporated on the EUV exposed sample using a glancing-angle-deposition (GLAD) process, according to F. A. Zoller et al. [122] (for more technical details refer to II.3.2).

Afterwards, the sample was investigated via SEM to measure whether the diameter of the holes was reduced and to make sure that the vapour-deposition process was successful (Figure III-50). The figure displays the nanoholes (black and round, highlighted by white circles around them, with a diameter of approximately 44 nm); some silver-uncoated chromium (grayish) and chromium/silver mask (bright, largely oval-shaped islands). The results of SEM measurements were very satisfactory, upon the dose of 89.6 mJ cm\(^{-2}\), for instance, the size of the nanoholes could be decreased by 40 % (from approx. 100 nm to approx. 60 nm). The smallest holes which could be produced were in the range of 40-45 nm (Figure III-50a). The next step was to deposit platinum and test whether this
metal would “survive” the etching conditions and whether the obtained platinum nanodots would be free from chromium and silver residues.

After deposition of a 5 nm thin Pt layer via sputtering, the chromium/silver mask was removed by treating the sample with chromium etch solution, which removed not only chromium and silver but also the excess photoresist. The size of the resulting nanodots ranged from 40 nm (dose of 51.8 mJ cm\(^{-2}\), Figure III-50b) to 80 nm (dose of 107.5 mJ cm\(^{-2}\)). The etching process was very thorough, neither chromium nor silver were found on the sample surface. The only contamination which could be measured with XPS was traces of cerium (0.5 at %) originating from the etching solution.

To gain more quantitative information about the surface topography of the samples, contact mode AFM measurements were conducted. The obtained images, exemplarily shown for sample 4 (for classification refer to Table III-9) in Figure III-51a, confirmed the size of the nanoparticles measured via SEM; also the height of the platinum dots of approximately 5 nm could be determined (Figure III-51b).
Results and Discussion

Figure III-51: a) AFM image and b) height profile of 141 nm period dots for the dose of 74.6 mJ cm$^{-2}$ on sample 4 (for classification see Table III-9)

EUV-IL could be successfully employed to prepare well-ordered Pt structures on both untreated and heat-treated GC. The diameter could be varied by changing the exposure dose; smaller dots were obtained for lower energy densities. The first EUV-IL experiments, however, also revealed several drawbacks of the process. The accessibility of the facilities, the stringent vacuum requirements and the need for a design of a special mask made the preparation and the exposure very challenging. The lift-off procedure did not work well for most samples; certain areas on the samples were either over-exposed or under-exposed. Therefore, structuring of the glassy carbon surface via e-beam was chosen as an alternative to the EUV-IL process. An easier access, less stringent vacuum requirements, a possibility to tune the particle size by adjusting the size of the electron beam spot or varying the distance between the particles and no use for a specifically
Results and Discussion

designed mask made e-beam lithography an attractive alternative, thus, further attempts at structured electrodes were performed by means of EBL.

III.2.2.2 Electron Beam Lithography (EBL) (GCU)

Prior to the exposure, the glassy carbon samples were spin-coated with a so-called “positive” photoresist (the photoresist exposed to light is afterwards soluble to the photoresist developer). As a photoresist, the poly(methyl-methacrylic acid) (PMMA) / ethyl lactate solution with two different PMMA molecular weights of 50k and 950k was chosen. The advantage of the photoresist with lower molecular weight is a 20% higher beam sensitivity compared to the molecular weight of 950k. Also the soft-baking time (heating the sample directly after spin-coating at 175°C) was varied between 1.5 and 5 min to find the best spin-coating conditions for an even and smooth photoresist layer with a thickness of approximately 45 nm. The 15x15x1 mm$^3$ pieces of glassy carbon were first cleaned by immersing them into isopropanol, ultrasonicatorating for 5 min and drying in nitrogen flow. The procedure was repeated for acetone and afterwards again for isopropanol. The spin-coating reaction conditions were according to Table III-11.

*Table III-11: Spin-coating conditions for GCU samples*

<table>
<thead>
<tr>
<th>Sample</th>
<th>Photoresist</th>
<th>Velocity / rpm</th>
<th>Acceleration / rpms$^{-1}$</th>
<th>time / s</th>
<th>Softbake @ 175°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>950 k</td>
<td>2000</td>
<td>1000</td>
<td>60</td>
<td>2.5 min</td>
</tr>
<tr>
<td>2</td>
<td>50 k</td>
<td>4000</td>
<td>2000</td>
<td>60</td>
<td>2.5 min</td>
</tr>
<tr>
<td>3</td>
<td>950 k</td>
<td>2000</td>
<td>1000</td>
<td>60</td>
<td>1.5 min</td>
</tr>
<tr>
<td>4</td>
<td>950 k</td>
<td>2000</td>
<td>1000</td>
<td>60</td>
<td>5.0 min</td>
</tr>
<tr>
<td>5</td>
<td>50 k</td>
<td>4000</td>
<td>2000</td>
<td>60</td>
<td>1.5 min</td>
</tr>
</tbody>
</table>

After the spincoating the samples were exposed to the e-beam using Vistec EBPG 5000Plus with electron energy of 100 keV in “single shot” mode. The size of the electron beam spot was 13 nm. On each sample two 2500x2500 µm$^2$ fields, separated by 2500 µm, were created, each field comprising 5x5 smaller (250 µm each) fields (*Figure III-52*). This
geometry was chosen in order to find the best e-beam exposure dose. The dose was varied for each of the 25 250 μm-large fields, gradually increasing from 40 μC cm$^{-2}$ (field 1) to 280 μC cm$^{-2}$ (field 25).

![Diagram of field arrangement](image)

*Figure III-52: the arrangement of the fields upon GC exposed to the e-beam*

The investigation of the model electrodes after preparation revealed one major advantage of the e-beam exposure as compared to EUV-IL: the lift-off procedure went well for more than 80% of the sample surface for all 5 samples. However, there were important differences in the employed photoresist: although more sensitive to the electron beam, the PMMA photoresist with a lower molecular weight was more difficult to remove under the chosen lift-off conditions (*Figure III-53 left*). The 950k photoresist was less of a challenge (*Figure III-53 right*). The comparison between the three samples with the same 950k photoresist but different soft-baking times showed that 1.5 min were most suitable for a successful lift-off procedure.
Results and Discussion

Figure III-53: SEM image of samples 3 (a) and 5 (b) after the lift-off. For classification refer to Table III-11

The size of the nanodots upon the model electrode was controlled using different e-beam doses. As in case of the EUV-IL process, the smallest nanodots with a diameter of 27 nm were obtained for the smallest e-beam doses of 40 µC cm\(^{-2}\) (Figure III-54a) and the largest (47 nm) for the e-beam dose of 280 µC cm\(^{-2}\) (Figure III-54b).

Figure III-54: Sample 3 (for classification refer to Table III-11). The nanodots are displayed for the e-beam dose of a) 40 µC cm\(^{-2}\) and b) 280 µC cm\(^{-2}\).

Although the diameter of nanodots, obtained with lower e-beam doses, is rather small and the exposure time grows with the exposure dose, the dose of 130 µC cm\(^{-2}\), chosen for
further experiments, lay between the two extreme values. The reason for the decision was an incomplete exposure pattern for very low exposure doses as even a thin photoresist is less likely to be completely penetrated by the electron beam if very low charge densities are used. A possibility to further decrease the size of the nanodots and enhance the success of the lift-off process without having to change the e-beam dose is to use a multilayered photoresist, which was the next step taken.

Another challenge was to homogeneously pattern an area of 1 cm x 1 cm$^2$, as the e-beam is usually used for covering smaller areas and prior to this work, no one has tried to structure large area with the Vistec EBPG 5000Plus machine.

The first attempt at a 1 cm$^2$ field was only partially successful (Figure III-55). The 1 cm$^2$ surface was not covered homogeneously, but comprised “stitched” areas with a pattern displayed in Figure III-55. The reason for the inhomogeneity is rather profane, as the movement of the stage which holds the sample is controlled analogue but the movement of the beam, which is constantly adjusted to a round shape, is digital. The exposure dose, however, is controlled via repeated exposure of the same spot to the electron beam.

The problem was that the electron beam created a pattern on a certain area on the surface during its first run and then, upon the return to the supposedly same spot, missed it and patterned the photoresist in a different place. This discrepancy, however, becomes evident only for large (> 500 µm$^2$ areas), which no one has attempted to pattern before.
Results and Discussion

Figure III-55: Model electrode with 5 nm Pt layer after the lift-off process

The reason was not only of optical nature, there were no Pt dots on the darker areas, shown in the enlargement of Figure III-55b. These areas were probably completely skipped by the e-beam.

Therefore, a new attempt was made by changing the aperture of e-beam and by choosing a smaller area, which was exposed in one shot to the electron beam. These measures helped to significantly improve the quality of the produced samples (Figure III-56), although the exposure time had to be slightly increased due to “stitching” a higher number of smaller exposed areas and an effort to eliminate all traces of “stitching” by making the e-beam “steps” smaller. The diameter of the dots was then usually 28 nm. It was reproducible for the whole sample area as well as for a different GC electrode prepared and exposed under the same conditions.
Results and Discussion

Figure III-56: Model electrode with 5 nm Pt layer after the lift-off process, improved EBL conditions.

The EBL Pt/GCU electrodes were also characterised by STM and AFM in air. The STM images (Figure III-57) revealed well-resolved dots with a diameter of approximately 30 nm and a height of 6 to 7 nm. The RMS value of the GCU substrate after EBL was in the range of 1 to 1.5 nm. The bright features around or between some dots were most probably remains of the photoresist (so-called skirts) or excess platinum.

Figure III-57: STM images of Pt/GCU EBL model electrode in air: a) topographic image and b) height profile. The Δz-range is 5 nm.
The AFM images likewise showed well-defined Pt-dot-arrays (Figure III-58), the height of the Pt-dots was in the same range of 6-7 nm as measured with STM. However, the diameter of the dots measured 45-50 nm. This deviation from the values obtained from SEM and STM can be explained by the specifications of the TM AFM tip, which diameter is 20-30 nm. The size of the tip determines the lateral resolution of the surface structures, thus, features which size is smaller or equal to the tip diameter appear (slightly) larger than they really are.

Figure III-58: TM AFM of Pt/GCU EBL model electrode in air. The Δz-range is 5 nm.

The big advantage of AFM imaging of Pt/GCU as compared to STM is an easier image acquisition, as TM AFM is not sensitive to minor changes in conductivity which might occur on GC as a consequence of EBL processing steps. STM, which relies on electron tunneling, detects every little change in current and responds to it by abruptly adjusting the tip-surface distance which sometimes leads to tip crashes.

In general, EBL was successfully applied to GCU to prepare model electrodes with defined diameter and controlled arrangement. After some adjustment of the spin-coating procedure, the exposure dose, the aperture settings and the exposure conditions, dots with diameters < 35 nm and pitches of 100 (Figure III-59a-b) and 200 nm (Figure III-59c-d), homogeneously distributed on an area of 1 cm² could be reproducibly obtained (Figure III-59). The lift-off step was likewise very successful; no PMMA or Pt residues were found
on the surface. The model electrodes were then ready to be investigated in course of electrochemical experiments.

Figure III-59: SEM images of Pt/GCU model electrodes with 100 nm pitch (a-b) and 200 nm pitch (c-d). Two different magnifications, 100 k (a,c) and 250 k (b,d)
Results and Discussion

III.2.3 Oxidation Experiments (Ex-Situ)

III.2.3.1 Potentiostatic Hold

III.2.3.1.1 Room Temperature

Pt/GCU model electrodes prepared by EBL were used for oxidation experiments, which were performed by potentiostatic hold of 30 minutes at 1.9 V vs. SHE, in order to compare the induced carbon and/or Pt oxidation/corrosion to a model electrode prepared by electrochemical Pt deposition. The advantage of the electrodes prepared by EBL as opposed to the ones prepared by EUV-IL and electrochemical Pt deposition was that the EBL samples had a homogeneous pattern and, thus, all dots were equally exposed to the electrolyte. This structure homogeneity was also reflected by the SD values, which at 10-15 % were much smaller than 40-50% calculated for electrochemically prepared model electrodes.

The recorded transients showed the same course as already observed for electrochemically prepared Pt/GCU model electrodes at this potential, however, the current values were higher (Figure III-60). These increased values might be due to higher amount of Pt on the EBL samples (5-6 µg cm\(^{-2}\) compared to 2-4 µg cm\(^{-2}\) for electrochemically prepared model electrodes).
Results and Discussion

Figure III-60: Oxidation /corrosion transients recorded for electrochemically prepared (black) (deposition pulse length 2 s) and lithographically prepared (red) (pitch 100 nm) Pt/GCU model electrodes during the potentiostatic hold at 1.9 V vs. SHE at RT

The SEM images before and after the electrochemical experiment (Figure III-61) showed that the GC surface after the hold was covered with some impurities, highlighted with white ovals in Figure III-61b, however, the Pt dots have not changed their positions. Their diameter, though, slightly decreased from 32 to 30 nm. This change in diameter was again smaller than the SD value calculated for the mean diameter of the dots before and after the potential hold.
Results and Discussion

The XPS measurements confirmed that the chemical properties of the sample surface have changed after the potentiostatic hold, the amount of oxygen, for instance, has doubled from almost 10 at % to 22 at %. Also, the normalised carbon C1s spectra revealed strongly oxidised carbon at high binding energies (apart from the C-carbon peak at 284.4 eV) (Figure III-62a). The normalised platinum spectra showed that also after the hold there was mostly elemental Pt on the surface with only hints at oxidised Pt 4f\textsubscript{7/2} (II) between 73 and 74 eV (indicated by an arrow in Figure III-62b). As already mentioned, this behaviour has been expected and described in literature [54].

Figure III-61: SEM images of Pt/GCU sample, prepared by EBL, a) before and b) after potentiostatic hold at 1.9 V vs. SHE for 30 minutes. White ovals in b) highlight the impurities present on the GC surface after a potentiostatic hold.
Figure III-62: Normalised XPS spectra of Pt/GCU sample prepared by EBL before (solid black line) and after (red dashed line) the potentiostatic hold of 30 min at 1.9 V vs. SHE. a) C1s and b) Pt4f spectra.
Both, the elemental composition and the Pt4f spectra of the EBL Pt/GCU samples showed great similarities to the ones recorded for electrochemically prepared Pt/GCU samples,
Results and Discussion

treated under the same conditions, as is illustrated in Figure III-63. The normalised C1s spectra of EBL Pt/GCU model electrodes, though, revealed a higher amount of oxygen-containing carbon moieties (Figure III-63a). These increased oxidation values might be due to higher amount of Pt on the EBL samples (5-6 µg cm\(^{-2}\) compared to 2-4 µg cm\(^{-2}\) for electrochemically prepared model electrodes) or to the fact that Pt dots resulting from EBL have much smaller height (5 nm) compared to electrochemically prepared Pt particles (50-60 nm), thus, on the EBL samples the thin Pt oxide film contributes more to the Pt4f signal and can be easier detected.

It was also attempted to record STM images; however, the exposure to the electrolyte rendered the samples unsuitable for any STM measurements. The obtained images featured misaligned dots with disturbed proportions (Figure III-64b). Some of the dots were imaged partially and some were completely missing. Comparison to the SEM images, likewise recorded after the oxidation (Figure III-61b) and, later on, AFM images, showed that the pattern and the shape of the dots was still preserved, indicating that the scanning tunneling microscope had difficulties to resolve Pt on oxidised carbon. One reason for lower quality of the images after the potentiostatic hold seems to be a “hopping” of the STM tip probably due to an inhomogeneous conductivity of GC upon contact with sulphuric acid. The acid might provoke a formation of a non-conducting oxidised carbon layer, especially in the vicinity of the Pt dots, which in turns led to rapidly changing tip-surface currents (the surface is imaged using constant current mode), causing the tip to jump to a different position. Another reason for the poor image quality in the sulphuric acid might be the slightly increased surface roughness, which augments up to 2 nm. Under such conditions it is difficult to obtain a well-resolved image of the dots with a height of 5 nm. Changing the tip bias, the imaging current or the integral/proportional gain did not lead to an improvement of the image. Also, the use of a different metal for the STM tip, a change of scanner and improved acoustic insulation did not ameliorate the image quality.
Figure III-64: STM images (air) of Pt/GCU sample prepared by EBL a) before and b) after potentiostatic hold. The Δz-range is 5 nm.

**III.2.3.1.2 Elevated Temperature (60°C)**

Stronger carbon oxidation at elevated temperatures (if compared to room temperature) was observed for electrochemically prepared Pt/GCU model electrodes and discussed in chapter III.1.3.1.2.1. The same approach was applied to model electrodes prepared by EBL and subsequent Pt sputtering.

The oxidation of Pt/GCU model electrodes with two different pitches, 100 and 200 nm, prepared by EBL was performed by potentiostatic hold of 30 minutes at 1.8 V vs. SHE at 60°C. Due to the fact, that no STM measurements were possible after the sample exposure to the electrolyte, TM AFM was used to evaluate the height of the dots before and after the potentiostatic hold and monitor the changes, if present.

The recorded transients showed the same course as the ones for electrochemically prepared Pt/GCU model electrodes (exemplarily shown for the pitch of 100 nm in Figure III-65), but the observed current values were higher. Again, a higher amount of Pt might explain this behaviour, as was already mentioned for the experiments at RT.
Results and Discussion

Figure III-65: Oxidation /corrosion transients recorded for electrochemically prepared (black)(deposition pulse length 2 s) and lithographically prepared (red) (pitch 100 nm) Pt/GCU model electrodes during the potentiostatic hold at 1.8 V vs. SHE at 60°C

The SEM images before and after the electrochemical experiment (exemplarily shown in Figure III-66) revealed that the dots after the potentiostatic hold looked ragged, especially around the edges (Figure III-66b), maybe as a result of the high potential and high temperature, but their pattern was preserved. The mean diameter, though, reproducibly slightly decreased for both pitch lengths (Table III-12). However, the observed difference was smaller than the standard deviation (SD) values, implying that the change of diameter – if actually present – was extremely small and difficult to trace.
Results and Discussion

Figure III-66: SEM image of an EBL prepared Pt/GCU sample with the pitch of 100 nm a) before and b) after a potentiostatic hold at 1.8 V vs. SHE at 60°C.

Table III-12: Mean diameter values before and after hold experiments at 60°C, determined using SEM.

<table>
<thead>
<tr>
<th>Name</th>
<th>d before ec / nm</th>
<th>d after ec / nm</th>
<th>Δd</th>
</tr>
</thead>
<tbody>
<tr>
<td>SNDots_17, pitch 100 nm</td>
<td>25.1 +/- 3</td>
<td>21.9 +/- 2.9</td>
<td>3.2</td>
</tr>
<tr>
<td>SNDots_36, pitch 100 nm</td>
<td>26.7 +/- 8.3</td>
<td>23.7 +/- 6.6</td>
<td>3</td>
</tr>
<tr>
<td>SNDots_45, pitch 200 nm</td>
<td>25.6 +/- 5.6</td>
<td>23.8 +/- 5.7</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Also the TM AFM images of the electrodes recorded before and after the potentiostatic hold were compared. Figure III-67 implies that before the potentiostatic hold, the dots reproducibly had a more homogeneous appearance and a rather uniform height (Figure III-67a), while after the electrochemical treatment some dots were higher and larger than others (extremely bright, white dots in Figure III-67b). To confirm or prove wrong this impression, a detailed evaluation of the TM AFM images was conducted. For this purpose, for each horizontal or vertical dots’ row in an 2 x 2 μm² image (as shown in Figure III-67) a height profile was obtained, using the WSxM 5.0 Develop 3.1. software [98]. The height profiles were then used to evaluate the height of every single dot and to plot this height in a chart (Figure III-68). The evaluation confirmed that before the electrochemical treatment (Figure III-68a) the height of the dots was quite homogeneous in either x- (circles in
Results and Discussion

Figure III-68) or y-direction (stars in Figure III-68) and that the average value was around 2.5 to 3 nm.

Figure III-67: TM AFM of an EBL prepared Pt/GCU sample (SNDots_36) with the pitch of 100 nm a) before and b) after a potentiostatic hold at 1.8 V vs. SHE at 60°C. Δz-range is 10 nm.

After the potentiostatic hold (Figure III-68b), the height of the dots significantly varied from dot to dot. For the pitch of 100 nm, for instance, the smallest dots still had the values of approximately 1 nm, but the highest were between 15 and 20 nm (Figure III-68b). It was also rather difficult to pinpoint the average height due to the broad distribution of measured values.
Figure III-68: detailed evaluation of the dots’ height, obtained from a TM AFM image a) before and b) after the potentiostatic hold. The circles represent the data from a horizontal row, while the stars the data from a vertical row. Different colours represent different data points. Pitch 100 nm (SNDots_36).

Also the sample with the pitch of 200 nm reproducibly presented a picture similar to the model electrodes with a pitch of 100 nm. However, for these samples there were more
Results and Discussion

surface residues, obscuring the dots, after the potentiostatic hold (compare Figure III-66b and Figure III-69b or Figure III-67b and Figure III-70b). Also the average height value was slightly higher at around 4 nm (5 nm would be expected, according to the sputtering conditions), however, it was likewise quite homogeneous (Figure III-71a). This larger height value can be explained by a doubled pitch length: the bigger the distance between the dots, the exacter the measured dimensions (the TM AFM tip diameter of approximately 20-30 nm has to be considered for small(er) pitches).

Figure III-69: SEM image of an EBL prepared Pt/GCU sample (SNDots_45) with the pitch of 200 nm a) before and b) after a potentiostatic hold at 1.8 V vs. SHE at 60°C. White ovals in b) highlight some impurities on the electrode surface.
Results and Discussion

Figure III-70: TM AFM of an EBL prepared Pt/GCU sample (SNDots_45) with the pitch of 200 nm a) before and b) after a potentiostatic hold at 1.8 V vs. SHE at 60°C. Δz-range is 10 nm.

After the potentiostatic hold, also for the samples with the pitch of 200 nm (and, thus, fewer data points) the height was deviating a lot between 4 nm and almost 20 nm (Figure III-71b).
Results and Discussion

Figure III-71: detailed evaluation of the dots’ height, obtained from a TM AFM image a) before and b) after the potentiostatic hold. The circles represent the data from a horizontal row, while the stars the data from a vertical row. Different colours represent different data points. Pitch 200 nm (SNDots_45).
Results and Discussion

III.2.3.1.3 Conclusions

Oxidation experiments at room temperature and at 60°C were performed on Pt/GCU model electrodes prepared by EBL by holding the samples for 30 minutes at 1.8 V or 1.9 V (vs. SHE).

The XP spectra revealed that the oxygen content on the surface more than doubled and carbon oxidation was quite progressed for these potentials, as already observed for electrochemically prepared samples in III.1.3.1.1.1. and III.1.3.1.2.1. The oxidation process which occurs during the potentiostatic hold obviously influences the chemical properties of the samples. However, there is no evidence for any potential-induced surface movement or loss of Pt dots, as was measured by SEM.

A slight decrease of the diameter of the dots coupled to a significant increase in respective height, as well as an inhomogeneous height distribution was observed for EBL Pt/GCU model electrodes with two different pitches (100 and 200 nm), especially at 60°C. This inhomogeneity and a height increase was particularly pronounced for the samples with a smaller pitch, possibly indicating resolution difficulties of dots with a diameter of approximately 30 nm with an TM AFM tip with a similarly large tip diameter (25-30 nm).

An explanation for the inhomogeneity of the dots' height after the potentiostatic hold might be Pt and potential-induced and/or accelerated carbon corrosion. It could create “craters” around the dots, which then, in turn, would automatically seem higher (Figure III-72).
Results and Discussion

Figure III-72: Glassy carbon corrosion/oxidation to carbon dioxide starts preferably in the immediate vicinity/around the Pt dots, the carbon background in the AFM scan becomes more uneven, and there are bigger height differences. The Pt dots seem higher as the carbon around them disappears, creating “craters”. $h_a$ labels the height of the dots before ec and $h_b$ after ec.

Any STM measurements of Pt/GCU model electrodes in sulphuric acid turned out to be impossible probably due to the formation of an insulating carbon oxide layer on the GCU surface, which led to uneven conductivity and resulting “hopping” of the STM tip.
III.2.3.2 Potential Cycling

III.2.3.2.1 Elevated Temperature (60°C)

The detrimental effect of cycling between the Pt oxide formation and reduction on Pt/C systems is known from literature, e.g. [66, 93, 133, 134], and was already discussed in III.1.1. and III.1.3.2. for electrochemically prepared Pt/GC model electrodes.

The oxidation of Pt/GCU model electrodes with two different pitches, 100 and 200 nm, prepared by EBL was also performed by cycling the samples for 500 cycles between 0.5 and 1.2 vs. SHE at 60°C with a scan-rate of 100 mV s⁻¹. An example of a recorded CV is shown in Figure III-73.

![Figure III-73: Cycles 400-450 for Pt/GCU model electrode (pitch 100 nm). The sample was cycled between 0.5 V and 1.2 V vs. SHE at 60°C. The scan-rate is 100 mV s⁻¹.](image)

Again, no STM measurements were possible after the sample exposure to the electrolyte, thus, TM AFM was used to evaluate the height of the dots before and after the potentiostatic hold and monitor the changes, if present.

The SEM images before and after the electrochemical experiment (exemplarily shown in Figure III-74) revealed that the dots largely looked the same, if a little ragged (Figure...
Results and Discussion

*III-74b*) and have not changed their positions. Their diameter, though, reproducibly slightly decreased for both pitch lengths (*Table III-13*). Again, the SD value was larger than the observed difference in diameter (before/after the cycling).

![Figure III-74: SEM images of Pt/GCU EBL model electrodes (SNDots_18, pitch 100 nm) a) before and b) after cycling for 500 cycles between 0.5 and 1.2 V vs. SHE at 60°C at a scan-rate of 100 mV s⁻¹](image)

*Table III-13: Mean diameter values before and after cycling experiments at 60°C, determined using SEM*

<table>
<thead>
<tr>
<th>Name</th>
<th>d before ec / nm</th>
<th>d after ec / nm</th>
<th>Δd</th>
</tr>
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<tbody>
<tr>
<td>SNDots_13, pitch 100 nm</td>
<td>27.1 +/- 4.2</td>
<td>25.9 +/- 5.9</td>
<td>1.2</td>
</tr>
<tr>
<td>SNDots_37, pitch 200 nm</td>
<td>25 +/- 6.8</td>
<td>23.5 +/- 8</td>
<td>1.5</td>
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<tr>
<td>SNDots_44, pitch 200 nm</td>
<td>22.9 +/- 4.4</td>
<td>20.5 +/- 6.8</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Again, the TM AFM images of the electrodes recorded before and after the cycling were compared.
Results and Discussion

Figure III-75: TM AFM of an EBL prepared Pt/GCU sample (SNDots_18) with the pitch of 100 nm a) before and b) after cycling between 0.5 and 1.2 V vs. SHE at 60°C. Δz-range is 10 nm.

Also here the images imply that prior to cycling, the dots reproducibly had a more homogeneous appearance and a more uniform height (Figure III-75a), while after the electrochemical treatment some dots were higher and larger than others (bright, white dots in Figure III-75b). Again, a detailed evaluation of the TM AFM images, described in III.2.3.1.2. was conducted. The evaluation confirmed that before cycling the height of the dots was quite homogeneous in either x- (circles in Figure III-76a) or y-direction (stars in Figure III-76a) and that the average value was around 2.5 to 3 nm.

After the cycling experiment, the height of the dots for all investigated samples significantly varied from dot to dot. For the pitch of 100 nm, for instance, the smallest dots had the values of around 2 nm, but the highest were between 10 and 15 nm (Figure III-76b).
Figure III-76: detailed evaluation of the dots' height, obtained from a TM AFM image a) before and b) after the potential cycling. The circles represent the data from a horizontal row, while the stars the data from a vertical row. Pitch 100 nm (SNDots_18).

As in case of potentiostatic hold, also the sample with the pitch of 200 nm reproducibly presented picture similar to the one observed for model electrodes with the pitch of
100 nm, considering the recorded CV () and the SEM images (Figure III-78 and Figure III-79).

![Graph](image_url)

*Figure III-77: Cycles 300-350 for Pt/GCU model electrode (pitch 200 nm). The sample was cycled between 0.5 V and 1.2 V vs. SHE at 60°C. The scan-rate is 100 mV s⁻¹.*

However, for these samples there were more surface residues, obscuring the dots, after the cycling (compare Figure III-74b and Figure III-78b or Figure III-75b and Figure III-79b). Also the average height value was slightly higher at around 4.5 nm (5 nm would be expected, according to the sputtering conditions), however, it was likewise quite homogeneous (Figure III-80a). This larger value can be explained by a doubled pitch length: the bigger the distance between the dots, the exacter the measured dimensions (the TM AFM tip diameter of approximately 20-30 nm has to be considered for small(er) pitches).
Results and Discussion

Figure III-78: SEM images of Pt/GCU EBL model electrodes (SNDots_44, pitch 200 nm) a) before and b) after cycling between 0.5 and 1.2 V vs. SHE at 60°C.

Figure III-79: TM AFM of an EBL prepared Pt/GCU (SNDots_44) sample with the pitch of 200 nm a) before and b) after cycling between 0.5 and 1.2 V vs. SHE at 60°C. Δz-range is 10 nm.
Figure III-80: detailed evaluation of the dots’ height, obtained from a TM AFM image a) before and b) after the potential cycling. The circles represent the data from a horizontal row, while the stars the data from a vertical row. Pitch 200 nm (SNDots_44).
After the cycling experiment, the height of the dots for all investigated samples significantly varied from dot to dot. It was again rather difficult to pinpoint the average height due to the broad distribution of measured values. Also for the samples with the pitch of 200 nm (and, thus, fewer data points) the height was deviating a lot between 3 nm and 15 nm (Figure III-80b).

III.2.3.2.2 Conclusions

Oxidation of Pt/GCU, prepared by EBL was investigated by cycling the samples at elevated temperatures (60°C) between 0.5 and 1.2 V (vs. SHE).

A slight decrease of the diameter of the dots coupled to a significant increase in respective height, as well as an inhomogeneous height distribution was observed for EBL Pt/GCU model electrodes with two different pitches (100 and 200 nm). This inhomogeneity and a height increase was particularly pronounced for the samples with a smaller pitch, possibly indicating resolution difficulties of dots with a diameter of approximately 30 nm with an TM AFM tip with a similarly large tip diameter (25-30 nm).

One explanation would be the carbon corrosion, given in 2.2.1 and illustrated by Figure III-72. Another explanation for the height change would be partial oxidation of Pt at high anodic potentials, leading to dissolution and subsequent reduction and, thus, redeposition of platinum occurring upon cycling to 0.5 V vs. SHE (Figure III-81), as discussed e.g. by Wang et al. [66] or modeled by Zhdanov and Kasemo [136]. The processes are additionally enhanced by elevated temperature (as described, for instance, by Inzelt et al. in [69]). The decreased value of the dots’ diameter, observed by SEM, would confirm this hypothesis. It is possible that Pt is principally dissolved at the edges of the dots (giving them the ragged appearance detected by SEM, also see Figure III-74b), reducing their diameter and is later on redeposited on top of the dots, increasing their height. This process is not controlled and, thus, creates an inhomogeneity, depicted in the charts in Figure III-76b.
Figure III-81: Pt dissolution and redeposition in course of an oxidation experiment. Pt dots are first dissolved at the edges, some Pt is present in the electrolyte and the diameter of the dots decreases. Then, Pt is redeposited from the solution on top of some dots, inhomogeneously increasing their height.

The comparison of the obtained results to the effects of the potentiostatic hold (chapter III.2.3.1.2.) reveals that the inhomogeneous character of the dots’ height after the electrochemical experiment is more distinct in case of potentiostatic hold at 1.8 V vs. SHE. An explanation is most probably the extremely high value of the anodic potential.
III.3 Model Electrodes (Pt/HOPG) Prepared by EBL: \textit{in situ} STM

III.3.1 Introduction

The attempt to use GC as a substrate for the preparation of Pt/C model electrodes by means of EBL was described in III.2 and elaborated the advantages and the drawbacks of this approach. The flat, easily and evenly spincoated GC could be used for EBL without any further difficulties. Also the precarious lift-off step was a success after the introduction of the double-layer photoresist and adjustment of the exposure dose. Thus-prepared Pt/GC model electrodes seemed very well suited for scanning probe microscopy, as an area of 1 cm$^2$ on a flat support was homogeneously patterned with dots of a defined diameter and defined height, arranged in a defined manner. However, first measurements in an electrolyte, sulphuric acid, have shown that GC was poorly suited for \textit{in situ} STM investigations. As soon as the samples were in contact with sulphuric acid at 0.6 V vs. SHE, STM images could not be recorded, despite the ongoing presence of the dots on the surface as proven by SEM measurements. This fact as well as interest in HOPG as a substrate, led to the preparation of Pt dots on HOPG by means of EBL. HOPG provides basal planes as well as step-edges and can be thus considered as a good model substrate for a CB shell [116]. Although HOPG is a well-known substrate for SPM [73, 75, 127, 137-145], it was difficult to predict whether the preparation of Pt dots on HOPG will be successful, as it is known from literature that Pt is mobile on the flat HOPG surface and to our best knowledge this carbon has not yet been used as a substrate for EBL lithography.

In the following, Pt/HOPG model electrodes with three different pitches, 70, 100 and 200 nm, prepared by EBL, will be presented and observations of \textit{in situ} STM during electrochemical oxidation will be discussed.

III.3.2 Preparation

The EBL process on HOPG was more challenging if compared to GC. One of the biggest hindrances was the wavy nature of the HOPG substrate on microscopic level. It led to uneven spreading of the photoresist as well as to difficulties during pattern generation. The wavy surface caused height differences on the substrate which in turn led to errors during the e-beam scan. The laser correction system was not always capable of adjusting the e-beam to the height changes. Thus, some areas on HOPG were “under” exposed, bearing
no dots at all while other areas were still covered by photoresist after lift-off due to an exposure dose which was too low to penetrate the two layers of PMMA (Figure III-82). Attempts to adjust the spincoating process and the exposure to the wavy substrate did not lead to any improvement.

Figure III-82: SEM images of areas with an incomplete lift-off on a Pt/HOPG EBL sample (pitch 100 nm). The bright white areas indicate Pt/PMMA residues. Two magnifications a) 25 k and b) 50 k.

However, on most of the structured samples, areas showing almost intact pattern of Pt dots could be observed with SEM and, subsequently, investigated with STM. The created patterns were stable for a long time (> 4 h) during STM scans in air (Figure III-83).

During and after STM measurements of Pt/HOPG in air another interesting feature of the model electrodes, prepared by EBL, became evident. The dots’ pattern remained stable even if the same area was scanned numerous times for several hours (4-5 h) (Figure III-83). This observation is very interesting as it is known that the Pt dots of this size are rather mobile on a smooth untreated HOPG surface in air [146, 147].
Figure III-83: STM images of Pt/HOPG EBL model electrode in air a) after lift-off, b) after 1 h of scanning, c) after 2 h of scanning and d) after 3 h of scanning. Δz-range is 5 nm.

Even after storage for > 10 days the pattern was still present on the surface (Figure III-84c,d).
Figure III-84: STM images of Pt/HOPG EBL model electrode in air a) and b) after lift-off, c) and d) after storage in air for 10 days. Δz-range is 10 nm for a-c and 5 nm for d.

The profiles confirmed the diameter value of approximately 30 nm for the created dots and showed an apparent height of 2.5 nm (Figure III-85a,b). However, also height values of up to 5 nm were observed for other Pt/HOPG model electrodes (Figure III-85d). Further magnifications (Figure III-85c) revealed that the dots can be described as an agglomeration of smaller clusters of 5-10 nm in size (Figure III-85d). This grainy structure is probably formed in course of the sputtering process.
Figure III-85: STM images of Pt/HOPG EBL model electrode in air: a), c) topographic images and b), d) corresponding height profiles. The Δz-range is 5 nm.

Further measurements showed that on some areas of model electrodes the pattern was not complete, some dots were missing, the height of the dots varied from dot to dot by 1-2 nm and even holes were part of the pattern (missing dots and holes are indicated by white ovals in Figure III-86).
Figure III-86: STM images of Pt/HOPG EBL model electrode in air, the white ovals indicate a) dots missing in a pattern or, upon higher magnification, b) a hole instead of a dot. Δz-range is 4 nm.

The diameter of the defects found on the HOPG surface in air as part of the dot pattern, was approximately 20 nm (Figure III-87b-d) and the surface roughness about one nm. However, it can be stated that the shape is slightly irregular and the depth varies from one point to the next (compare b, c and d in Figure III-87).
The presence of defects on otherwise “perfect”, well-defined HOPG basal plane led to the assumption that this immobilisation of the dots is most probably due to defects on the HOPG surface (Figure III-87a). These defects obviously originated in the preparation process, such as e-beam damage or sputtering damage. The e-beam damage is not unlikely, as it is known from literature, that radiation can cause severe damage to carbon substrates [148]. Also sputtering might be responsible, as the sputtered Pt atoms hit the substrate with the speed of 2 km s⁻¹ (4 eV). So-called “implantation”, slight metal cluster embedding into the surface, and local damage of the surface is known to occur at high impact energies [149]. Even for small clusters like Ag₅₀₀Co₅₀₀, equal to 113 nm³ (1000 atoms x 4/3 x π x (0.3 nm)³) the degree of implantation was 30% at the kinetic energy of 1
Results and Discussion
eV [150]. Such high-energy cluster-surface interactions are schematically shown in Figure III-88a as opposed to cluster soft landing (Figure III-88b) [149]. In our case, the sputtered clusters (which constituted Pt dots and were resolved by STM at higher magnifications as shown in Figure III-85c) were even larger at 675 nm$^3$ (15 nm x 15 nm x 3 nm) and the kinetic energy was around 4 eV.

Figure III-88: Schematic of a) cluster-surface high-energy impact and b) cluster soft landing. Taken from [149]

The hypothesis whether the defects actually served as “anchors” for Pt dots and whether origin of the holes was due to e-beam damage or Pt sputtering was further evaluated.

To test whether the EBL process was responsible for the hole-formation, a freshly cleaved HOPG was spin-coated, exposed to the EBL and lifted in acetone. Then, scanning probe microscopies were employed to look for holes. However, neither SEM nor STM (air) nor TM AFM revealed any traces of holes (Figure III-89a, b). On the images, the HOPG steps but also remains of PMMA could be resolved, but the surface itself was completely void of any holes.

Omitting the spin-coating step and exposing a freshly cleaved HOPG surface by EBL also revealed the absence of holes, as measured by SEM, STM (air) and AFM.
To avoid possible sputtering damage, Pt was vapour-deposited in a Balzers BAK 600 (Oerlikon Balzers, Liechtenstein) evaporator. After the lift-off step, the SEM image of the surface (*Figure III-90*) showed a high amount of Pt dots, which arrangement, however, was not according to the pattern written by the e-beam. Some of the dots were still part of a square pattern with a pitch of 200 nm, but most were loosely distributed on the HOPG surface or clustered into long strings, probably decorating the steps and the edges of the HOPG substrate, thus assuming the energetically more favoured position (*Figure III-90*) [146].
Results and Discussion

Figure III-90: SEM images of a Pt/HOPG model electrode, upon which Pt has been deposited via vapour deposition

The STM and TM AFM measurements confirmed that the evaporated dots had a higher mobility compared to the sputtered dots (Figure III-91). STM scans revealed that in case of vapour-deposited Pt it became increasingly difficult to locate the dots and to obtain a stable, well-resolved image of the dots (Figure III-91a). STM imaging was difficult, probably due to the extremely loose bonding (and, subsequently, poor electrical contact) of the Pt dots to the HOPG. Although it was possible to depict the dots with TM AFM, which is less invasive than the CM AFM, the images were blurred and the dots surrounded by bright stripes, as shown in Figure III-91b.
Results and Discussion

Figure III-91: a) STM and b) TM AFM image of a Pt/HOPG model electrode, upon which Pt has been deposited via vapour deposition. The $\Delta z$-range is 5 nm

All the above-mentioned data strongly suggests, that the defects/holes were the reason for the stable STM images in air and were most likely created in the process of sputtering.

Application of EBL and sputtering to HOPG has led to successful patterning of the HOPG surface with well-defined arrays of Pt dots. The pattern was extremely stable throughout the STM measurements in air and in course of several days, suggesting an a-priori reason for immobilisation of the dots. Further insight into the preparation process was gained and strong hints at defects, created in course of the sputtering step, were obtained. These defects in turn served as “anchors” for otherwise mobile Pt on HOPG (Figure III-92). Also height deviations of the dots suggest a certain “embedding” of Pt particles in the upper graphene layers of HOPG, as sketched in Figure III-92.
Results and Discussion

Figure III-92: A sketch of immobilisation of a Pt dot on an HOPG surface due to its “embedding” upon sputtering. Adapted from [149]

The effect of oxidising electrode potentials on Pt dots with three different pitches of 70, 100 and 200 nm on HOPG was investigated by in situ STM during two different sets of experiments. One set included increasing the sample potential stepwise (in 0.1 V steps) to higher anodic values (starting from 0.7) up to 1.9 V and holding the respective potential during the image acquisition (5 to 6 minutes). Another was cycling the sample between 0.6 V vs. SHE and increasing anodic potentials up to 1.9 V vs. SHE. Every 10 cycles (0.6 – 1.x V, x = 0-9) an image was acquired at 0.6 V vs. SHE. The experiments and the obtained results will be discussed in the following chapter.

III.3.3 Oxidation Experiments

III.3.3.1 Stepwise Potential Increase

The oxidation of Pt/HOPG model electrodes was performed in 0.5 M sulphuric acid by the means of stepwise potential increase (potentiostatic hold) or potential cycling. The current responses recorded during the 100 mV scans to a higher potential grew, as shown in Figure III-93 for a sample with a pitch of 200 nm. This IV curve shows that the current flowing on the electrode surface upon immersion is close to zero (-0.5 μA), slowly rises between 1.3 and 1.7 V (start of oxygen evolution) and, finally, rapidly increases for the last two measured points of 1.8 and 1.9 V. The peak at the latter potentials is most probably due to mixed contributions of catalytic water electrolysis (oxygen evolution [54]) and carbon corrosion, the oxygen evolution and formation of monolayers of oxidised Pt (initial
Results and Discussion

Pt oxidation in sulphuric acid usually starts around 0.8 V vs. SHE [151]), which are subsequently reduced during the backscan.

![IV curve for an EBL Pt/HOPG model electrode, pitch 200 nm](image)

**Figure III-93: IV curve for an EBL Pt/HOPG model electrode, pitch 200 nm**

Upon potential-controlled immersion into the electrolyte at 0.7 V vs. SHE, the recorded sample current was around -0.5 µA and the pattern remained unchanged despite several scans of the same area for 1 h (**Figure III-94a**), the acquisition of one image was approximately 8 min. The apparent height of the dots was determined to be 3 nm (**Figure III-94b**). Some locations upon the HOPG surface (indicated with dotted ovals in **Figure III-94a**) displayed probable defects already upon immersion into the electrolyte. Apart from the dot pattern (pitch 200 nm) and steps and edges on HOPG, the image in **Figure III-94a** features several white stripes, indicated with arrows, these are artefacts, depending on the direction of the scan. In this case, the scan direction is from the right to the left.
Results and Discussion

Figure III-94: a) EC-STM image and b) height profile of a Pt/HOPG model electrode in 0.5 M sulphuric acid. The white circles indicate some locations on HOPG which are riddled with defects already upon electrolyte immersion. Tip potential is 0.4 V vs. SHE, tip bias: -0.3 V, sample potential: 0.7 V vs. SHE. The arrow in the upper right corner indicates the up- or downward direction of the scan. The $\Delta z$-range is 5 nm.

At a potential of 1.0 V, the dots appeared unchanged, also their height was preserved Figure III-95.

At 1.3 V vs. SHE (Figure III-96a) the dots still looked largely unchanged. In the lower part of Figure III-96a, indicated by a square, carbon corrosion became more pronounced, it looked like parts of the HOPG surface were being ripped out. Another explanation for the extremely bright spots could be accumulation of Pt in this area.
Results and Discussion

Figure III-95: a) EC-STM image and b) height profile of a Pt/HOPG model electrode in 0.5 M sulphuric acid. The solid-lined circle indicates a dot with a decreased height, the dotted-lined ovals areas, which start to oxidise. Tip potential is 0.4 V vs. SHE, tip bias: - 0.6 V, sample potential: 1.0 V vs. SHE. The arrow in the upper right corner indicates the up- or downward direction of the scan. The Δz-range is 5 nm.

Figure III-96: a) EC-STM image and b) height profile of a Pt/HOPG model electrode in 0.5 M sulphuric acid. The solid-lined circle indicated a dot with a decreasing height, the square the area with a pronounced loss of HOPG layers. Tip potential is 0.4 V vs. SHE, tip bias: - 0.9 V, sample potential: 1.3 V vs. SHE. The arrow in the upper right corner indicates the up- or downward direction of the scan. The Δz-range is 5 nm.
Further potential increase to 1.6 V vs. SHE led to complete disappearance of the dots (Figure III-97). The area underneath the dots either possessed the same height as the support or displayed the appearance of first holes. More HOPG pieces were missing on the lower part of the image (highlighted with a solid-lined square in Figure III-97a).

Figure III-97: a) EC-STM image and b) height profile of a Pt/HOPG model electrode in 0.5 M sulphuric acid. The dotted-lined ovals show areas with missing HOPG, the solid-lined square indicates the area with a pronounced loss of HOPG layers. Tip potential is 0.4 V vs. SHE, tip bias: -1.2 V, sample potential: 1.6 V vs. SHE. The arrow in the upper right corner indicates the up- or downward direction of the scan. The Δz-range is 5 nm.

Finally, at 1.9 V vs. SHE, all dots were missing and a hole pattern corresponding to the original dot pattern was present on the HOPG surface (Figure III-98). Likewise, some parts of HOPG, which already looked slightly ragged at 1.0 V vs. SHE (dotted-lined ovals in Figure III-95a), completely disappeared, indicating carbon corrosion of the basal planes. Some extremely bright spots on the image in Figure III-98a indicate further areas with ongoing carbon corrosion and/or loss (the areas might appear bright due to an increased height (meaning Pt accumulation) or to poorer conductivity, which in case of HOPG would mean HOPG flakes/pieces still loosely bound to the sample but almost detached from it).
Results and Discussion

Figure III-98: a) EC-STM image and b) height profile of a Pt/HOPG model electrode in 0.5 M sulphuric acid. The dotted-lined ovals indicate the areas where whole HOPG pieces were detached. The arrow in the upper right corner indicates the up- or downward direction of the scan. Tip potential is 0.4 V vs. SHE, tip bias: -1.5 V, sample potential: 1.9 V vs. SHE. The $\Delta z$-range is 5 nm.

Scanning the potential back to 0.7 V vs. SHE and recording an image at this potential (Figure III-99) confirmed that Pt dots on HOPG were “replaced” by the holes. This fact also proved that the images recorded at high tip biases showed the actual processes on the surface and the holes were not artefacts created by an extreme change of bias. Some parts of upper HOPG layers around/close to the dots were missing; the remaining (or newly formed) edges appeared quite bright, possibly indicating further loose HOPG material or accumulated Pt.
Results and Discussion

Figure III-99: a) EC-STM image and b) height profile of a Pt/HOPG model electrode in 0.5 M sulphuric acid. Tip potential is 0.4 V vs. SHE, tip bias: -0.3 V, sample potential: 0.7 V vs. SHE (return). The arrow in the upper right corner indicates the up- or downward direction of the scan. The $\Delta z$-range is 5 nm.

Also experiments with model electrodes with a pitch of 100 led to similar results (as can be exemplarily seen for a sample with a pitch of 100 nm in Figure III-100): the pattern is stable up to 1.4 V (Figure III-100a-b), some Pt dots start to disappear at anodic potentials $>1.5$ V vs. SHE (highlighted by circles in Figure III-100c-d), a hole pattern is left on the substrate after its exposure to 1.9 V (Figure III-100f) and the basal planes of HOPG seem to be damaged (compare Figure III-100a-b and Figure III-100c-f).
Results and Discussion

(a)

(b)

(c)

(d)
Results and Discussion

Figure III-100: EC-STM image of a Pt/HOPG model electrode (pitch 100 nm) in 0.5 M sulphuric acid at a) 0.9 V, b) 1.4 V, c) 1.5 V, d) 1.6 V, e) 1.7 V, f) 0.7 V vs. SHE upon return. Tip potential is 0.4 V vs. SHE, tip bias: - 0.5 V, - 1.0 V, - 1.1 V, - 1.2 V, - 1.3 V and -0.3 V, respectively. The Δz-range is 7 nm for a-e and 5 nm for f. The arrows in the upper right corner indicate the up- or downward direction of the scan. The scan direction is from the right to the left. The circles are used to highlight the disappearance of the dots. The arrows in f indicate carbon corrosion.

Additionally, it should be stated that the observed Pt loss and carbon corrosion are by no means reduced to the scanned area. The hole pattern and ragged HOPG edges could be found on different parts of model electrodes by expanding the scanned area after the experiment or scanning a different area (Figure III-101).
Results and Discussion

Figure III-101: EC-STM image of a Pt/HOPG model electrode (pitch 200 nm) in 0.5 M sulphuric acid at 0.7 V vs. SHE upon return. a) the field of view during the electrochemical experiment and b) an extended view, the field of view during the electrochemical experiment is indicated with a dotted-lined square. The arrow in the upper right corner indicates the up- or downward direction of the scan.

The summary of the experiments performed by stepwise potential increase is presented in Figure III-102. Herein, the potential is plotted against the abundance of dots on the surface (Figure III-102a) or against the height (Figure III-102b). Negative height values indicate the presence of the holes and their respective depth. The plots show that the height of some dots, irrespectively of the initial value, starts to decrease already at potentials > 1.0 V vs. SHE and that dots with different heights but also both dots and holes can be found in the potential window of 1.0 – 1.5 V vs. SHE. The dots start to disappear at > 1.4 V vs. SHE. The start of oxidation and corrosion of HOPG, especially at the edges, is observed at > 1.5 V vs. SHE. Both processes progress with increasing anodic potentials, leading to complete disappearance of the formerly observed dot pattern and well-defined step edges of HOPG.
Results and Discussion

Figure III-102: a) amount of particles (in %) still present on the sample at a given potential and b) the height/depth of the structures (dots/holes) at a given potential, the solid black line separates the dots (positive height values) from the holes (negative height values).

The comparison of the plots to the corresponding CVs reveals that the slight current increases for potentials > 1.4 V vs. SHE roughly correspond to the values at which the dots start to disappear and the holes to appear. The current further grows with rising
anodic potentials, probably indicating the onset and the progress of carbon corrosion at potentials $> 1.6$ V vs. SHE. Thus, besides, oxygen evolution, the values are also due to carbon corrosion. The high current values during the back-scan indicate that Pt is still present on the model electrode, probably accumulated at HOPG edges or in areas with insufficient lift-off.

III.3.3.2 Potential Cycling

For better comparison with stepwise potential increase also for this set of experiments the model electrodes with pitches of 70, 100 and 200 nm were employed. The scan-rate was set to $20$ mV s$^{-1}$ and the sample cycled for 10 cycles between $0.6$ V and increasing anodic potentials $1.x$, where $x$-values were $0-9$. The images were recorded at $0.6$ V vs. SHE, avoiding any bias-related artefacts. The recorded CVs (Figure III-103) showed that the currents grew larger with increasing anodic potential, as is exemplarily shown for a Pt/HOPG model electrode with a pitch of 200 nm in Figure III-103 and was already observed for electrochemically prepared Pt/GCU model electrodes in Figure III-35.

Figure III-103: CVs recorded for a Pt/HOPG EBL electrode (pitch 200 nm) in $0.5$ M sulphuric acid
After the first cycles (up to 1.3 V vs. SHE) no big changes could be observed. *Figure III-104* shows a representative STM image for a sample with a pitch of 100 nm, recorded at the beginning of the experiment and after cycles between 0.6 and 1.2 V vs. SHE. Most of the dots were still on the surface; their height of 3.5 +/- 0.5 nm was still preserved.

Further cycling led to the appearance of first holes at upper vertex potentials of 1.5 V vs. SHE as shown in *Figure III-105*. The dots were still present on the surface; however, the number of holes was growing fast so that after additional cycles up to 1.6 V vs. SHE (10 min), there was a complete hole pattern (*Figure III-106*).
Figure III-104: EC-STM image (a, c) and profiles (b, d) of a Pt/HOPG model electrode (pitch 100 nm) in 0.5 M sulphuric acid a), b) before cycling and c), d) after cycling between 0.6 and 1.2 V vs. SHE. Tip potential is 0.4 V vs. SHE, tip bias: - 0.2 V, sample potential: 0.6 V vs. SHE. The arrow in the upper right corner indicates the up- or downward direction of the scan. The Δz-range is 5 nm
Results and Discussion

Figure III-105: a) EC-STM image and b) height profile of a Pt/HOPG model electrode (pitch 100 nm) in 0.5 M sulphuric acid after cycling till upper vertex potential of 1.5 V vs. SHE. For further clarity the corresponding dots in Figures a) and b) are assigned numbers from 1 to 2. Tip potential is 0.4 V vs. SHE, tip bias: -0.2 V, sample potential: 0.6 V vs. SHE. The arrow in the upper right corner indicates the up- or downward direction of the scan. The $\Delta z$-range is 5 nm

Figure III-106: a), c) EC-STM image and b) height profile of a Pt/HOPG model electrode (pitch 100 nm) in 0.5 M sulphuric acid after cycling till upper vertex potential of 1.6 V vs. SHE. Tip potential is 0.4 V vs. SHE, tip bias: -0.2 V, sample potential: 0.6 V vs. SHE. The arrow in the upper right corner indicates the up- or downward direction of the scan. The $\Delta z$-range is 5 nm
Results and Discussion

Also experiments with model electrodes with a pitch of 200 or 70 nm led to similar results (as can be exemplarily seen for a sample with a pitch of 70 nm in Figure III-107), the pattern is stable up to a potential of 1.4 V (Figure III-107a). After cycling up to 1.5 V vs. SHE some Pt dots start to disappear (Figure III-107b-c) and a hole pattern starts to appear, which is seen on the substrate after its exposure to potentials > 1.6 V (Figure III-107d-e) and very well-resolved holes are recorded upon the back-scan to 0.7 V vs. SHE (Figure III-107f). Some HOPG edges in Figure III-107d,e look ragged, indicating carbon corrosion.
Results and Discussion

Figure III-107: EC-STM images of a Pt/HOPG model electrode (pitch 70 nm) in 0.5 M sulphuric acid after cycling to the upper limit of a) 1.2 V, b) 1.4 V, c) 1.6 V, d) 1.8 V, e) 1.9 V and f) upon the end of the cycling experiment. Tip potential is 0.4 V vs. SHE, tip bias: -0.3 V. The Δz-range is 7 nm. The arrows in the upper right corner indicate the up- or downward direction of the scan. The scan direction is from the right to the left.

Figure III-108 displays the summary of the experiments performed by potential cycling. Herein, the potential values are plotted against the abundance of dots on the surface (Figure III-108a) or against the height (Figure III-108b). Like in Figure III-102, the negative height values indicate the presence of the holes and their respective depth and the solid line in Figure III-108b separates the dots (positive height values) from the holes (negative height values).
Results and Discussion

Figure III-108: a) amount of particles (in %) still present on the sample at a given potential and b) the height/depth of the structures (dots/holes) at a given potential, the solid black line separates the dots (positive height values) from the holes (negative height values).

The plots show that the first cycles up to 1.3 V vs. SHE do not lead to any significant change of the number or height of the dots and that dots with different heights but also
Results and Discussion

both dots and holes can be found after cycling to the upper potential vertex of 1.3 – 1.4 V vs. SHE. However, in all cases the dots completely disappear above 1.5 V vs. SHE. Also, hints at corrosion and degradation of HOPG with increasing anodic potentials were found during cycling, however, further measurements are required to make any definitive statements.

Additionally, it could again be stated that the observed Pt loss was by no means reduced to the scanned area. The hole pattern could be found on different parts of model electrodes by expanding the scanned area after the experiment or scanning a different area.

III.3.3.3 Oxidation of HOPG without Pt

In order to trace the influence of Pt on the corrosion behaviour of HOPG, the in situ oxidation experiments were repeated on HOPG model electrodes without Pt.

The IV-curve recorded for the stepwise potential increase (Figure III-109) showed the same course as for the EBL Pt/HOPG model electrodes (Figure III-93), i.e. that the current flowing on the electrode surface upon immersion is close to zero (20 pA), slowly rises between 1.3 and 1.7 V and, finally, rapidly increases for the last two measured points of 1.7-1.9 V (Figure III-109). The peak at the latter potentials is most probably due to the carbon corrosion current and oxygen evolution. The obtained current values, however, were much smaller, reaching the maximum of 5 µA for pure HOPG (Figure III-109) and 70 µA for Pt/HOPG model electrodes (Figure III-93).
Results and Discussion

Figure III-109: IV curve for an HOPG model electrode

The STM images revealed that no changes on the HOPG surface were observed at potentials below 1.7 V vs. SHE (Figure III-110a-c), the corrosion onset took place at the edges of basal planes at 1.7 V vs. SHE (Figure III-110d) and further progressed with increasing potentials (Figure III-110e,f). In contrast to the model electrodes containing platinum, the corrosion on pure HOPG samples seemed to be restricted to the edges of the basal planes, no loss of HOPG pieces or peeling was found. No formation of pits, holes or blisters was observed even at highest applied potentials of 1.8-1.9 V vs. SHE. Also, no intercalation of sulfate at the applied potentials took place, the height of the steps remained the same throughout the experiment (in case of the sample presented in Figure III-110 it was 1 nm). This behaviour was expected, several authors like [152, 153] (to name some of them) observed sulfate intercalation in HOPG setting in at potentials > 2.0 V vs. SHE and at concentrations of sulphuric acid > 2 M.
Results and Discussion

III.3.4 Conclusions

The STM measurements on Pt/HOPG EBL model electrodes have shown that thus-prepared samples can be stored for up to 10 days under ambient conditions and still possess the prepared dot pattern which is stable for 4-5 h during STM measurements in air. This immobilisation of the dots seems to result from the preparation of the model electrodes, in particular the sputtering step.

The in situ STM experiments have revealed that the dot pattern prepared by EBL remains stable not only in air but also in an electrolyte at a constant potential of E < 1.0 V vs. SHE. Increasing the potential to higher anodic values leads to irreversible disappearance of platinum dots, appearance of a hole pattern corresponding to the original dots pattern as well as corrosion/degradation and partial peeling of the HOPG support.

The in situ STM experiments on pure HOPG have displayed that the HOPG corrosion starts at 1.7 V vs. SHE and is restricted to the edges of the basal planes; there are no

Figure III-110: EC STM images of HOPG in 0.5 M sulphuric acid at the potential of a) 1.2 V, b) 1.5 V, c) 1.7 V, d) 1.8 V, e) 1.9 V vs. SHE and f) 0.7 V vs. SHE upon return. Tip potential is 0.4 V vs. SHE, tip bias: - 0.8 V, - 1.1 V, - 1.3 V, - 1.4 V, – 1.5 V and -0.2 V, respectively. The Δz-range is 7 nm. The arrows in the upper right corner indicate the up- or downward direction of the scan. The scan direction is from the left to the right. The arrows in e and f indicate HOPG corrosion
Results and Discussion

traces of peeling. This behaviour and comparison to Pt/HOPG model electrodes suggest that the presence of Pt enhances carbon corrosion.

There are several possibilities as to what happens to Pt dots on the HOPG surface, a prerequisite for all of them is interplay between the mobility of Pt on the HOPG surface, the (Pt-induced) carbon corrosion/oxidation, oxygen evolution reaction, the presence of a liquid electrolyte, oxidation of Pt and, in case of cycling, reduction of the formed Pt oxide. One probable mechanism is portrayed in Figure III-111. The good anchoring of Pt dots to HOPG and their apparent immobility during the scans in air as well as in an electrolyte at a constant potential of E < 1.0 V vs. SHE hints at the presence of defects, created in course of the electrode preparation (also see sketch in Figure III-92). These defects, later on visible as a hole pattern, are, however, also pre-destined to oxidise/corrode first, once the sample is exposed to harsher conditions, such as high anodic potentials. The presence of Pt most probably accelerates the oxidation process even further by accelerating the adjustment of thermodynamic equilibrium (see also chapter I.4.1.) until the anchoring of the dots to the surface is sufficiently loosened due to the corrosion of surrounding HOPG and the dots are carried (or “washed”) away by the electrolyte. Further whereabouts of the dots are not completely clear; platinum might remain suspended in the electrolyte or be moved to the surrounding steps and edges of HOPG, which indeed appear extremely bright after the electrochemical experiment.
Figure III-111: schematic drawing of a mechanism according to which the Pt dot pattern on the HOPG surface disappears and a hole pattern appears upon application of anodic potentials above 1.3 V vs. SHE. The defects on the HOPG surface are created in course of the sample preparation and serve as anchors for the Pt dots. Upon potential application, carbon corrosion/oxidation starts first at or around the above-mentioned defects; the process is accelerated by the presence of Pt. The adhesion of Pt to HOPG is weakened and the dots are washed away by the electrolyte.

Another possibility would be “burial” of Pt dots in the formed holes, as pictured in Figure III-112. This hypothesis would be supported by the observed carbon corrosion which further continues after the disappearance of the dot pattern. However, SEM images of the Pt/HOPG model electrodes after the in situ STM imaging did not confirm the presence of the dots, the HOPG surface was bare of the pattern. Also detailed STM images of the
holes (see also Figure III-107f) did not show display any Pt at the bottom. SEM-EDX measurements are on-going in order to clarify this particular point.

**Figure III-112:** schematic drawing of a mechanism according to which the Pt dot pattern on the HOPG surface disappears and a hole pattern appears upon application of anodic potentials above 1.3 V vs. SHE. The defects on the HOPG surface are created in course of the sample preparation and serve as anchors for the Pt dots. Upon potential application, carbon corrosion/oxidation starts first at or around the above-mentioned defects; the process is accelerated by the presence of Pt. The carbon corrosion which takes place directly around the dots creates holes, Pt dots sink to the bottom of the holes and continue to catalyse formation of carbon oxides.

The pitch of the model electrodes seems to have no effect on the potential value of the onset of the degradation processes; the “communication” among the dots could not be observed or measured, most probably because the structures are too big and still too far
Results and Discussion

apart. The degradation/corrosion of carbon seems to be enhanced by the presence of Pt and starts at the edges. Also the holes, most probably originally created in course of the preparation process as defects, seem to grow in size and with increasing anodic potentials, indicating carbon oxidation/corrosion.
IV General Discussion and Conclusions

The purpose of this work was to provide fundamental insight into Pt loss processes, carbon and Pt-induced carbon corrosion as observed and discussed for PEFC electro-catalysts. Scanning probe microscopy and X-ray photoelectron spectroscopy were applied to trace electrochemically induced changes in surface structure and chemical composition. This research goal demanded a simplified system, so-called model electrodes. Glassy carbon (GC) and highly oriented pyrolytic graphite (HOPG) were chosen as substrates, due to their chemical and physical properties but also to their likeness to carbon black (CB) which is usually used as support in PEFC electro-catalysts. The non-graphitic, non-graftihised structure of GC, for instance, may be compared to the “core” of CB while the highly ordered graphitic HOPG has similarities to the “shell” of CB.

Two different approaches for preparation of Pt/C model electrodes, namely using the electrochemical and the lithographic routes were followed in course of the work. Both approaches had certain advantages and drawbacks which further manifested in course of the project. Particle size and particle size distribution as well as the surface coverage were found to relate to the surface properties of GC modified by heat-treatment. A decrease in particle diameter and an increased Pt coverage was observed after thermal pre-treatment of GC for various deposition pulse lengths. GCU samples displayed a wider range of particle diameters than GCHT. This difference in the deposition behaviour resulted from the formation of a porous layer on the GC surface during the heat-treatment. However, the diameter of obtained Pt particles on GCHT still deviated by 30-40 %. Also, there was not preferred arrangement of the particles on the surface. As expected, these properties complicated the evaluation of Pt amount on the surface as well as the characterization of the particles before and search for any changes after the electrochemical oxidation experiments. Despite the above-mentioned drawbacks, the electrochemically prepared Pt/GC model electrodes were still suitable for first oxidation experiments; the goal was to transfer the obtained knowledge, such as e.g. the potentials, to the lithographically prepared system.
Compared to the adjustment of the electrochemical Pt deposition to our needs, the optimisation of the lithographic approach was more challenging. The reason was the lack of information about carbon as a suitable substrate for lithography. First, GC and later on, HOPG had to be characterised in terms of their compatibility with all the requirements of first EUV-XIL and, later on, EBL. Both employed lithography techniques are multi-step processes, thus, it was important to adjust and then to optimise every step with respect to the Pt/C system. First results of EUV-exposures showed the big advantages of lithography as compared to electrochemical deposition, all dots were arranged in a defined pattern and their diameters deviated only by 5-7 % (SD). However, also the drawbacks became clear: once a certain amount of GC samples was placed on the sample holder for the XIL-beamline, it was very difficult to meet the vacuum requirements for the exposure. Other major obstacles were the incomplete lift-off and the need of a new mask design. The available exposure mask contained not only the desired pattern but also e.g. areas for direct exposure, which consequently contained “bulk” Pt, which in turn was a hindrance for the planned oxidation experiments on Pt dots. Most of the disadvantages of EUV-XIL could be dismissed by replacing this lithography technique with EBL. The use of two-layered PMMA helped to solve the lift-off difficulties on GC and no mask was required for the electron beam writer. Additionally, the vacuum requirements were less stringent. However, also EBL had to be optimised for the Pt/C system, the challenges like i.e. homogeneous structuring of large areas (1 cm\(^2\)) was discussed in detail in III.2.2. or described by Guzenko et al. in [123]. The result of optimised EBL and sputtered Pt processes was reproducible patterning of GC with an almost complete (> 97 %) lift-off. The only big disadvantage of EBL compared to electrochemical Pt deposition, which could not be avoided, was the complicated, time-consuming preparation, resulting from a large number of steps required for the completion of an EBL/sputtering process.

The use of HOPG as a carbon substrate has shown other interesting properties of EBL combined with Pt deposition via sputtering such as generation of a dot pattern on HOPG, which is stable over a long time during scans in air or in sulphuric acid at potentials below 1.0 V vs. SHE. However, also the short-comings and challenges of this substrate were revealed. The lift-off process on Pt/HOPG samples was extremely irreproducible, yielding samples with either an almost complete or a completely failed lift-off. It showed that HOPG was a less suitable carbon for lithography due to its macroscopically wavy surface.
General Discussion and Conclusions

However, despite the incomplete lift-off, it turned out that only Pt/HOPG samples were suitable for STM imaging in situ in an electrolyte, due to the excellent conductivity and high electrochemical stability of HOPG even in 0.5 M sulphuric acid.

After the preparation of model electrodes, the latter were employed for electrochemical oxidation experiments, which were conducted in 0.5 M sulphuric acid by either holding the sample at potentials, ranging from 1.2 to 1.9 V vs. SHE or cycling the sample between the Pt oxide formation (1.2-1.9 V vs. SHE) and Pt oxide reduction at 0.6 V vs. SHE. The high anodic potentials and sulphuric acid were required in order to be able to imitate the conditions of either OCV (potential hold) or start/stop (potential cycling) in a real PEFC. For a PEFC, the start-up of a cell is usually accomplished by purging the air-filled compartment with hydrogen (vice versa for the shutdown), leading to a formation of a hydrogen-air front which divides the compartment in two parts and to polarisation of the electrodes, so that values substantially higher than 1.0 V vs. SHE, e.g. 1.5 V vs. SHE, are possible [20, 22, 23]. The anodic potentials of 1.6 to 1.9 V vs. SHE, at which some of the model electrodes were degraded in this work, cannot be reached in a real PEFC; however, they were chosen to compensate the difference in temperature. A real PEFC operates at 80°C, a temperature at which stable measurements within a liquid electrolyte are questionable. Therefore, during this project all measurements were performed either at room temperature or at 60°C. The lower potential of 0.6 V vs. SHE for cycling experiments was chosen according to the recommendation of Nicolas Linse who observed that selecting this potential as the lower limit led to enhanced carbon corrosion, if compared to e.g. 0.9 V vs. SHE [20]. The given explanation was that the oxidation state of Pt strongly influences carbon corrosion: elemental Pt enhances the combustion of carbon to carbon dioxide while Pt oxide is rather inert in this respect.

Tracing the chemical properties with XPS before and after oxidation of electrochemically prepared Pt/GCU and Pt/GCHT20 model electrodes has shown that the formation of carbon oxides on GCU and GCHT20 progresses with increasing anodic potentials, independently on the oxidising treatment (potentiostatic hold or potential cycling) and temperature. The presence of Pt seems to enhance the carbon oxidation, at least for the GC substrate. The onset of strong Pt-enhanced carbon oxidation is at 1.7 V vs. SHE for GCU and 1.65 V vs. SHE for GCHT20 at RT and 1.6 V vs. SHE for both substrates at 60°C. Potential cycling leads to higher amounts of oxidised carbon on the substrate.
surface if compared to potentiostatic hold. These findings confirm numerous reports from literature, e.g. of Wang et al. [66], Lin et al. [133] or Fernandes et al. [134], who observed higher carbon corrosion and oxidation rates for cycling if compared to a potential hold. Also temperature has an influence on the oxidation behaviour of GCU and GCHT, more oxidised carbon was detected by XPS for the electrochemical experiments at 60°C. This data is likewise consistent with literature, it was repeatedly reported that higher temperatures lead to stronger carbon corrosion, as described by Wickman et al. [55] or Cherstiouk et al. [92], to name some of the publications. The evaluation of Pt4f signals for the same model electrodes showed no significant changes in the oxidation state of Pt, a behaviour explained by publications of Peuckert et al. [54] by formation of only one to two Pt-oxide monolayers on the surface of bulk platinum at potentials < 2.0 V vs. SHE [54]. Some model electrodes with GCU as carbon support displayed partial charging, visible from the shift of Pt4f-doublet to higher binding energies. This partial charging most probably resulted from an insufficient contact between Pt particles and the substrate. No partial charging has ever been observed for the Pt/GCHT20 model electrodes.

Detailed evaluation of SEM images of Pt/GCU and Pt/GCHT20 recorded before and after the oxidation revealed that the mean diameter of the particles has neither increased nor decreased, the difference of the mean diameter before and after the oxidation was smaller than the standard deviation of the mean diameter. Also the mean number of Pt particles on the surface has changed only within the error margin.

Potential hold and potential cycling had an oxidative effect also on Pt/GCU samples prepared by EBL. Here, in situ visualisation of degradation processes by means of EC-STM was attempted; however, GCU emerged as an unfit substrate for STM measurements in an electrolyte. Therefore, ex situ techniques, i.e. SEM, TM AFM and XPS, were applied. The XPS results were consistent with the ones obtained for electrochemically prepared Pt/GCU model electrodes: C1s spectra showed that carbon was stronger oxidised with increasing potential and increasing temperature while Pt4f signals did not change. Also the SEM findings were in agreement, neither loss of Pt nor any potential-induced movement of the dots was observed on EBL Pt/GCU, the difference of the mean diameter before and after oxidation was again smaller than the standard deviation of the mean diameter. The TM AFM measurements revealed that the dots’ height increases after both potential hold and potential cycling at 60°C which was ascribed to
enhanced carbon corrosion around the dots (in case of potential hold) and to enhanced C corrosion and/or dissolution and redeposition of Pt on top of the dots (in case of cycling). The results of neither technique suggested any influence of the pitch on the oxidation behaviour of the model electrodes.

In situ visualisation of Pt- and C-degradation was finally realised by measuring EBL Pt/HOPG model electrodes with EC-STM. Stepwise oxidation and corrosion of HOPG, starting at edges and steps, graduate disappearance of Pt dots and their replacement by holes, as well as growing diameter of the holes were traced in 0.5 M sulphuric acid upon application of potentials between 0.6 and 1.9 V vs. SHE. The appearance and propagation of holes was first attributed solely to potential-induced and Pt-enhanced carbon corrosion, further investigations, however, showed that carbon corrosion in the electrolyte started at pre-formed defects, induced by the sputtering step and the reason for the stability of the Pt dot pattern in air and in an electrolyte at potentials < 1.0 V vs. SHE. Also Pt/HOPG model electrodes were susceptible to the differences between stepwise potential increase and potential cycling, in case of cycling the visible carbon corrosion and loss of Pt started at lower anodic potentials (difference of 100 mV).

The preparation of the model electrodes but also the electrochemical oxidation experiments revealed distinct differences between the two carbon supports, GC and HOPG, in terms of, e.g. surface properties, Pt adhesion, suitability for lithography or for SPM measurements as well as oxidation/corrosion behaviour.

The EBL, for instance, never worked as well for HOPG as for GC, despite significantly smaller surface roughness of HOPG. However, any in situ STM measurements on GC were not possible due to conductivity issues; in this case HOPG better served our purpose. Also the behaviour of Pt dots depended on the substrate. Neither Pt loss nor formation of clusters nor any movement could be monitored on glassy carbon, yet potentials above 1.6 V vs. SHE were sufficient to induce complete disappearance of the pattern on HOPG. Detachment/peeling of carbon material could be observed in situ on HOPG while on GC we could measure formation of pits around the Pt dots, which would explain the increased height of the dots after the electrochemical treatment, but detected no missing material or flaking of the substrate.
Loss of Pt, either via detachment or via dissolution could be visualised on HOPG but was never detected on either GCU or GCHT20. Statements about (Pt-induced) carbon corrosion can also be made; \textit{in situ} STM measurements indicated that the onset of carbon corrosion is shifted by 100-200 mV to lower potentials in presence of platinum. Finally, the intermediates of (Pt-enhanced) carbon oxidation on both GCU and GCHT could be traced by recording XP spectra, indicating an influence of Pt presence on oxidation of GCU.
V Outlook

The continuation of several experimental approaches initiated in the present work is recommended. In particular, further *in situ* EC-STM measurements on Pt/HOPG model electrodes prepared by EBL are of interest, as e.g. the influence of the dot size on the dissolution behaviour of Pt has not been investigated.

Other topics of interest, resulting from the present project and requiring further attention can be:

- *In situ* EC-AFM measurements of Pt- and C-corrosion on Pt/GCU or Pt/GCHT20 prepared by EBL. No *in situ* EC-STM investigations were possible on this substrate due to decreased substrate conductivity upon contact with sulphuric acid, this issue can be resolved by using AFM

- Further studies of substrate influence on the degradation behaviour of the model electrodes (test other flat carbon substrates)

- “Hole research”, i.e. efforts to control the defect dimensions during the sputtering step and observe their influence on carbon corrosion

- Coupling of *in situ* STM/AFM to GC-MS in order to detect carbon dioxide emissions as a function of potential, reaction conditions or carbon substrate

Research into above-mentioned topics, combined with the knowledge gained during the present project will help to improve the understanding of processes taking place at the metal-support-electrolyte interphase and gain more detailed insight into degradation processes of platinum and carbon.
Bibliography


## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFC</td>
<td>Alkaline Fuel Cell</td>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<td>BSE</td>
<td>Back-scattered Electrons</td>
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<td>CE</td>
<td>Counter Electrode</td>
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<td>CV</td>
<td>Cyclovoltammogram</td>
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<td>DC</td>
<td>Direct Current</td>
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<tr>
<td>EBL</td>
<td>Electron Beam Lithography</td>
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<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
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<tr>
<td>EUV</td>
<td>Extreme Ultraviolet</td>
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<td>EUV-IL</td>
<td>Extreme Ultraviolet Interference Lithography</td>
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<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
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<td>FWHM</td>
<td>Full Width at Half Maximum</td>
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<tr>
<td>GC</td>
<td>Glassy Carbon</td>
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<tr>
<td>GCHT</td>
<td>Heat-treated Glassy Carbon</td>
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<td>Untreated Glassy Carbon</td>
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<td>GDL</td>
<td>Gas Diffusion Layer</td>
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<td>GLAD</td>
<td>Glancing Angle Deposition</td>
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<tr>
<td>HOPG</td>
<td>Highly Oriented Pyrolytic Graphite</td>
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<tr>
<td>ICE</td>
<td>Internal Combustion Engine</td>
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<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma Mass Spectrometry</td>
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<tr>
<td>ICP-OES</td>
<td>Inductively Coupled Plasma Optical Emission Spectroscopy</td>
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<td>IL</td>
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<tr>
<td>IPA</td>
<td>isopropanol</td>
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<td>Abbreviation</td>
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<tr>
<td>LECBD</td>
<td>Low Energy Cluster Beam Deposition</td>
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<td>MCFC</td>
<td>Molten Carbonate Fuel Cell</td>
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<tr>
<td>MEA</td>
<td>Membrane Electrode Assembly</td>
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<td>MSE</td>
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<td>MIBK</td>
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<td>OECD</td>
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<td>Poly(methyl-metacrylic acid)</td>
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<td>UHQ</td>
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<td>UV</td>
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<td>WE</td>
<td>Working Electrode</td>
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<td>Abbreviation</td>
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<tr>
<td>XIL</td>
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List of Publications


List of Selected Presentations


