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Combining UHV-STM and electrochemistry for surface studies of model catalysts

PhD Thesis by
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30th of November, 2018
Abstract

Electrocatalysis is expected to play a crucial role in global society moving to an energy infrastructure largely based on renewable energy such as solar and wind power. Due to the intermittency of energy sources such as these we need an efficient way of averaging out the energy production in order for us to have access energy from renewable sources when the wind is not blowing and the sun is not shining. Electrocatalysis allows us to take the excess electricity from sources such as wind and solar power and convert it into (i) useful industrial chemicals thereby reducing the need to produce them by other means and (ii) energy rich fuels thereby lowering the demand for fossil fuels. However, if this is to become a reality we need to design catalysts that can make an impact on the large energy scales needed in a world of over 7 billion people. That means designing catalysts of active, stable and abundant materials.

Here we present an experimental method for investigating model electrocatalysts on the atomic scale, which has been developed throughout this PhD project. The method aims to further our understanding of e.g. corrosion processes and electrocatalytically active sites. This is done through being able to prepare well-defined model systems under the controlled conditions of UHV. The samples prepared in this way are subsequently transferred under vacuum to the electrochemical cell meaning that contaminants from ambient conditions are avoided. The electrochemical measurement itself is then performed in an inert atmosphere before transferring the sample back to the UHV chamber again. The UHV chamber is equipped with an STM making it possible to investigate the sample before and after the electrochemical measurements thereby facilitating the correlation of the surface sites with the electrochemical response. Furthermore, the chamber is equipped with various equipment for forming interesting surface geometries.

We present data from three different metal surfaces: Pt(111), Cu(111) and Cu(100). The Pt(111) surface’s electrochemistry is well-established and thus
serves as a good test of whether our experimental setup works or not. Thus we will showcase the setup’s capabilities by (i) investigating clean Pt(111) and (ii) investigate the corrosion process of Pt(111) in 0.1 M HClO₄ and compare the results to the literature in the field. The Cu single crystal facets are not nearly as well understood as the Pt(111) facet but let us test our setup with a different metal and different electrolyte, namely KOH. Finally, we try to replicate the Cu CVs on Cu single crystals prepared under ambient conditions through electropolishing.

The obtained Pt(111) results are in great agreement with the literature, both in terms of the shape of the CV and the observed corrosion phenomena. Through designing samples with different surface geometries we correlate an electrochemical feature at 0.12 V vs. RHE with the presence of many (111) steps on the Pt(111) surface and find an inversely proportional relationship between upper potential limit and the size of the observed adislands on the surface when corroding the surface.

For Cu(111) we find a CV between −0.2 and 0.45 V vs. RHE with just one sharply peaked redox feature due to OH adsorption and desorption. This peak corresponds roughly to an OH coverage of 0.28 ML. The results is reproduced under laboratory conditions by electropolishing a sample for 10 s at 3 V in 66 % H₃PO₄. We also show that this CV is very dependent on the lower potential limit.

The CV measured on Cu(100) contains an OH feature at −0.15 V vs. RHE corresponding to an OH coverage 0.25 ML. This CV was also dependent on the exact potential limits. In both the case of Cu(111) and Cu(100) we speculate that the OH peak’s dependence on the lower potential limit is due to a restructuring of the surface. In situ methods will have to be used to confirm this. The Cu(100) CV has so far not been reproduced under laboratory conditions, in fact it mostly looks like a polycrystalline one.

We conclude that the setup works as intended and could be very useful for understanding corrosion processes and active sites through the engineering of different surface structures using either the UHV equipment or techniques such as Pb UPD in the electrochemical cell.
Resumé

Elektrokatalyse er spået til at spille en vigtig rolle i fremtiden, hvis det globale samfund omstiller sig til en energiinfrastruktur primært baseret på bæredygtig energi såsom sol- og vindenergi. Givet den fluktuerende karakter af energikilder som disse, bliver vi nødt til at have en effektiv måde at udjævne energiproduktionen på, således at vi også har adgang til bæredygtig energi, når vinden ikke blæser, og solen ikke skinner. Elektrokatalyse gør det muligt at omdanne overskudselektriciteten fra de førnævnte kilder og omdanne den til (i) industrielt anvendelige kemikalier og dermed nedsætte behovet for at producere dem vha. andre metoder og (ii) energirige brændstoffer og dermed sænke efterspørgslen af fossile brændstoffer. Hvis dette skal blive en realitet bliver vi nødt til at designe katalysatorer, der kan gøre en forskel på en stor skala i en verden med over 7 milliarder mennesker. Det betyder at designe katalysatorer der er aktive, stabile og lavet materialer, der findes i rigelige mængder.


Vi viser data fra tre forskellige metaloverflader: Pt(111), Cu(111) og Cu(100). Pt(111)-overfladens elektrokemi er veletableret og er derfor et velegnet system at teste vores forsøgsopstilling på. Derfor viser vi forsøgsopstillingens evner ved
(i) at undersøge en ren Pt(111) overflade og (ii) Pt(111)’s korrosionsmekanismer i 0.1 M HClO₄ og sammenligner disse med resultater fra litteraturen. Cu enkrystallerne er ikke forstået i samme grad som Pt(111) men lader os teste vores forsøgsopstilling på et andet metal og i en anden elektrolyt, KOH. Slutteligt prøver vi at reproducere vores Cu CV’er målt på UHV præparerede prøver ved at måle på elektropolerede Cu enkrystaller.

Resultaterne opnået på Pt(111) er i slående lighed med dem fundet i litteraturen, både i forhold til formen af det målte CV men også i forhold til de observerede korrosionsfænomener. Ved at designe prøver med forskellige overfladestrukturer korrelerer vi en peak ved 0.12 V vs. RHE med en øget mængde af (111)-steps på overfladen. Desuden finder vi en omvendt proportional sammenhæng mellem det øvre potentiomængde og størrelsen på de observerede nanopartikler på overfladen under korrosionsforsøg.

På Cu(111) måler vi et CV mellem −0.2 og 0.45 V vs. RHE med kun en skarp peak ved 0.11 V vs. RHE. Denne peak svarer til en OH-dækningsgrad på omkring 0.28 ML. Dette resultat er reproduceret gennem at elektropolere en Cu(111) enkrystal i 66 % H₃PO₄ i 10 s ved 3 V. Vi viser desuden at dette CV er meget afhængigt af den nedre potentialgrænse.

CV’et målt på Cu(100) har en OH peak ved −0.15 V vs. RHE, der svarer til en OH-dækningsgrad på ca. 0.25 ML. Ligesom for Cu(111) er CV’et meget afhængigt af de eksakte potentialgrænser. I begge tilfælde getter vi på, at OH-peakens afhængighed af den nedre potentialgrænse hænger sammen med en restrukturering af overfladen. For at forstå dette bedre skal in situ metoder formentlig tages i brug. Det har indtil videre ikke været muligt at præparere en Cu(100) enkrystal udenfor UHV, der giver anledning til det samme CV, faktisk ligner det målte CV mest af alt et tilsvarende målt på polykrystallinsk Cu.

Vi konkluderer at vores forsøgsopstilling virker som håbet, og at den kan vise sig yderst nyttig i forbindelse med forståelsen af eksempelvis korrosionsmekanismer og aktive sites gennem at præparere prøver med interessante overfladestrukturer i UHV. Man kan ligeledes forestille sig at deponere f.eks. Pb på en prøve i den elektrokemiske celle og derefter visualisere den i UHV med STM’et.

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Preface

The thesis at hand is submitted to the Technical University of Denmark (DTU) as part of the fulfilment of the PhD degree in physics. The majority of the work presented within was carried out at the Section for Surface Physics and Catalysis (SurfCat) (formerly Center for Individual Nanoparticle Functionality (CINF)) at the Department of Physics at DTU. However, some of the data was obtained at the Korea Advanced Institute of Science and Technology (KAIST). My project was funded by a DTU grant due to the DTU-KAIST alliance. SurfCat as a whole is funded by the VILLUM FONDEN through grant 9455 and the VILLUM Center for the Science of Sustainable Fuels and Chemicals (V-Sustain). This PhD project was supervised by Professor Ib Chorkendorff and Associate Professor Sebastian Horch both of DTU Physics. The project started in December 2015 and ended in November 2018.

I would like to thank my supervisors Ib and Sebastian for giving me the opportunity to work on this PhD project over the past three years and for providing great supervision throughout that time. Especially to Sebastian for not only the fruitful discussions but also for helping out in the laboratory. Furthermore, I would like to thank my former colleagues Ifan E. L. Stephens (now at Imperial College London), Albert K. Engstfeld (now at Ulm University) and Kim D. Jensen (now at Copenhagen University) for providing good input to my project through discussions, especially on the subject of electrochemistry.

I would also like to thank Associate Professor EunAe Cho of the Energy Conversion and Storage Materials Laboratory (ECSM) at Department of Materials Science and Engineering (MSE) at KAIST for accommodating me for my external research stay from September to November 2018. It was truly interesting experiencing a different work culture such as the Korean one. On this note I would also like to thank the whole ECSM group for being very kind and welcoming (and for bringing me along for football), especially DongHoon Song who was a great help both in terms of getting started in the laboratory but also
in terms of understanding what was going on around me.

I am also thankful to Alan Landers, John Lin, Søren B. Scott and Thomas V. Hogg for some great beam times at Stanford Linear Accelerator Center (SLAC). Although intense, it was a great and unique way of working and helped along with good company in the early hours.

In general the whole research group at SurfCat has helped create a great working environment which is both inspiring and a pleasure to be in. A special thanks to Erlend Bertheussen, Martin J. Bækbo, Jakob E. Sørensen and Thomas V. Hogg for sorting out the Friday bar and to Suzanne Z. Andersen for arranging various social activities.

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Finally, I have to thank my family, my friends and flatmates for trying to understand what I have been working on during the past three years and being supportive along the way. And a very special thanks to my girlfriend, Lucy, for not only being curious about my work but especially for dealing with my mood swings during the final three months of this project and for being a fantastic person in general and a great support.

Daejeon, 30th of November 2018
Thomas Maagaard
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Chapter 1

Introduction & motivation

The work presented in this thesis was motivated by a desire to improve upon our understanding of various catalysts for e.g. the oxygen reduction reaction (ORR). Initially the idea was to use a scanning tunnelling microscope (STM) to investigate and characterise the electrochemically induced dealloying of alloys made from platinum and various transition metals or lanthanides, such as Pt–Y, as they have been shown to be efficient for the ORR\cite{1, 2, 3}. In order to do so we tried to interface a conventional ultra-high vacuum (UHV) chamber (equipped with the aforementioned STM) with an electrochemical extension to avoid contaminating our samples by carrying them through the ambient atmosphere between characterising them with the STM and the electrochemical treatment. In short, well-defined samples can be prepared and characterised under UHV conditions prior to being exposed to the electrochemical environment without a potentially contaminating transfer step. Finally, the samples can be characterised with the STM again after the electrochemical measurement. It turned out that getting this setup to work reliably and produce trustworthy results was not as simply as one could have hoped. Hence a lot of work was put into establishing the method presented here. In its current state we expect that the setup and methodology can be used to investigate active sites and corrosion processes on catalysts relevant for a range of electrochemical reactions, as will be argued later. However, before getting to the details of this project it will be placed in a broader context to further motivate the work.

Firstly, the aim of this chapter is to explain why we believe catalysis, and indeed electrocatalysis, is going to be very important in the hopefully not-too-distant future. This will be done through a brief overview of how society pro-
1.1. Societal context

If you have paid just a tiny fraction of attention to the global debate surrounding Earth’s climate and humanity’s tremendous consumption of energy you will probably know that something has to change. If we do not change our habits in terms of energy use and production the climate will most likely do it for us.
in whichever way that may turn out to be. The reason for this is that energy consumption tends to correlate well with the amount of CO\textsubscript{2} emitted into our atmosphere which in turn correlates with the global average temperature, which we will discuss shortly. The solution is of course to produce energy in a way that does not emit CO\textsubscript{2}. However, if it was as simple as that then we probably would be doing it by now.

Figure 1.1: The world’s total final energy consumption in Mtoe by fuel over time. "Coal" also includes peat and oil shale and heat, solar thermal and geothermal is included in "Other". A breakdown in the form of pie charts is shown in Fig. A.1 [4, p. 34]

Firstly, it is pertinent to ask what the global energy consumption in fact is, which sources we get the energy from and whether that impacts the amount of CO\textsubscript{2} in the atmosphere. Figure 1.1 shows the International Energy Agency’s estimate of the world’s total final consumption of energy over time in million tonnes of oil equivalent (Mtoe). In 2015 we had a consumption of 9384 Mtoe[4, p. 34]. As can be seen the energy consumption has been steadily increasing over the years, except for a few years here and there where it has actually gone down before starting its increase again. These dips are probably related to the general global economy, note for instance the sudden dip right around 2009 when we had the latest economic crash. In other words, we are increasing our
1.1. Societal context

consumption over time and there are signs that consumption is entangled with our economy, which we will get back to later in this section.

Figure 1.2: The global amount of CO\textsubscript{2} emitted from fuel combustion in Mt. This excludes emissions from non-energy use.\cite{4, p. 54}

The plot in Figure 1.1 also shows that coal and oil alone accounted for 52.1\% of our energy consumption in 2015 (also shown in Fig. A.1). So even though we have an increased focus on renewable energy (like solar and wind power) these days it is clear that we have not stopped using coal or oil at all. Furthermore, these two resources are by far responsible for most of our global CO\textsubscript{2} emissions from fuel combustion as can be seen from Figure 1.2 non-energy use of these resources has been excluded from this plot\textsuperscript{1}. Of the total consumption of coal, natural gas and oil the non-energy use amounts to 5.8\%, 11.4\% and 15.9\%, respectively, this is also shown in Figures A.2, A.4 and A.3 in Appendix A \cite{4, p. 38-40}.

The reason the emission of CO\textsubscript{2} to the atmosphere can be expected to heat the earth can be found in the way light interacts with matter. Matter can interact with light through absorbing the energy of photons and thus entering an excited state. The greenhouse effect is a great, if critical, example of how

\textsuperscript{1}”Non-energy use covers those fuels that are used as raw materials in the different sectors and are not consumed as a fuel or transformed into another fuel. Non-energy use also includes petrochemical feedstocks.” \cite{4, p. 76}
this works. Radiation from the sun enters the atmosphere and is mostly passing through to the surface of the earth[5, p. 11]. Here it is radiated back towards space but the radiation has now shifted to higher wavelengths with a large part of the spectrum being in the infrared regime. Due to some of the wavelengths of this radiation matching the frequencies of two of the vibrational modes of the CO$_2$ molecule the energy of these photons are absorbed by the molecules for some time. This means that instead of the radiation passing through our atmosphere the energy is stored in the CO$_2$ molecules' vibrational states before being emitted again. The reason these two modes absorb the infrared light is that they come with a change in the CO$_2$ molecule's dipole moment. CO$_2$ has a third vibrational mode but it is a symmetric stretching of the two C-O bonds which does not result in a change in dipole moment. This also explains why H$_2$O acts as a greenhouse gas and why e.g. N$_2$ and O$_2$ does not. As we know from thermodynamics temperature as a concept is precisely defined from energy and the distribution of it meaning that if we keep energy in the atmosphere we can expect to raise the temperature[6, p. 34-36].

**Figure 1.3: Concentration of CO$_2$ in the atmosphere over the past 800,000 years**

![CO$_2$ concentration over time](image)

Figure 1.3: Concentration of CO$_2$ in the atmosphere over the past ~ 800,000 years up to 2017.[7]

With that in mind we would certainly expect additional CO$_2$ in our atmosphere to give rise to some heating. Figure 1.3 shows the concentration of CO$_2$ in the atmosphere over 800,000 years. The past 50 - 100 years we have seen a very rapid increase of CO$_2$ in the atmosphere which has taken the concentration to unprecedented levels, at least within the time scale shown here. That
1.1. Societal context

Figure 1.4: The global average temperature from 1880 up to 2017. The data is shown as the difference between the average global temperature a given year and the average global temperature from 1901-2000.[8]

might have been OK if not for the fact this seem to increase the global average temperature, as shown in Figure 1.4, which in turn might lead to a range of undesired effects, such as rising sea levels[9], a higher frequency of anomalous weather events[10], loss of biodiversity[11] etc. Some of these events might further fuel the release of undesired gases to our atmosphere, like methane from thawing of the Siberian permafrost[12]. This year (2018) alone has seen a lot of extreme weather in the form of droughts and forest fires in regions where you do not usually see those and even discussion on whether our classification system for hurricanes is obsolete given we only see hurricanes in the top end of the scale[13]. This effect of more anomalous weather events has been predicted earlier by Hansen and co-workers[10].

The numbers for global consumption and CO$_2$ emissions shown in Figures 1.1 and 1.2 respectively, go up to 2015. In 2015 there were roughly 7.35 billion people alive[14]. Last year (2017) there were 7.55 billion of us and the United Nations’ projections see us pass 11 billion by the turn of the century. That is roughly a 50% global population increase, the bulk of which will be in Africa[15]. Add to that the fact that 38.6% of the total energy consumption takes place in the OECD countries which only account for about 17.4% of the global popula-
1.1. Societal context

Figure 1.5: Breakdown of the total energy consumption (9383.60 Mtoe) in 2015 by region.[4, p. 36]

In other words, within this century we will need to produce a lot more energy than we currently are and we will have to do so from renewable sources. If every single person in 2015 had the same energy consumption as an average person from the OECD countries the world would consume a staggering 20 900 Mtoe over the course of a year. This number is assuming the respective populations from 2015. If we extrapolate to the projected 11 billion people we get a consumption of around 31 000 Mtoe. This of course assumes a steady consumption per capita over the next ∼ 80 years. Luckily the trend of an increasing energy consumption per capita reversed around 2004 for the OECD members on average meaning we are now at a level we have not seen since around 1986[17]. Thus there are reasons to believe that the number given above overestimates the actual energy consumption we will see in 2100.

The good news is of course that we will not need those extra ∼ 20 000 Mtoe tomorrow, it will take some time for the developing world to catch up with the OECD countries. However, we probably will need something like it given enough time, unless we drastically change our consumption of energy (or the number of people we count on being). Clearly we are not going to argue that the rest of the world should not be allowed to consume as much energy as we currently are as energy consumption seems to be tied to the human development index, which aims to put a number on how good a life people generally lead in a given country. This is shown in Figure 1.6. Note how some countries with very
1.1. Societal context

Figure 1.6: Human development index of 129 countries plotted against energy consumption per capita. Based on data from [18] [19].
large populations like China and India sit relatively low on the HDI scale with room to move up.

The international society has recognised the challenge of anthropogenic climate change for a couple of decades now and 192 countries agreed to decrease the emission of six different greenhouse gasses in 1997 starting from 2005 with the Kyoto Protocol. The Kyoto Protocol aimed to look at each countries potential for mitigating climate change and set targets according to these. A second amendment (and thus commitment period) of the Kyoto Protocol was commenced in 2012, however at this point only 37 countries have set binding targets. More recently the Paris Agreement was signed by 195 UNFCCC members which commits the members to keep global warming below 2 °C\textsuperscript{20}. However, the Paris Agreement has on one hand come under critique for not being ambitious enough\textsuperscript{21} and on the other hand seen the United States withdraw from it (effective from 2020) because it was deemed ”unfair” to the US economy\textsuperscript{22}. The latest IPCC report says we in general have to go to unprecedented lengths to stay under a warming of 2 °C let alone 1.5 °C\textsuperscript{23}.

So to sum up it is clear we are consuming a lot of energy already and that we will only consume more if we follow the path we have laid out for ourselves so far. This leads to an increase in atmospheric CO\textsubscript{2} which then leads to a rise in global temperatures which threatens the very existence of not only our society and species, but most of the biosphere’s as we know it. For these reasons ways of decreasing CO\textsubscript{2} emissions has received a great deal of attention the last few decades. In the next section we shall see, among other things, how electrocatalysis might help us in a society based on renewable energy.

1.2 Renewable energy & catalysis

The conventional fossil fuels, like coal and oil, have truly been important for our society the last century. A lot of the technology we use daily has to a large degree been made possible by utilising the vast amount of energy stored in these fuels. Furthermore, it has in many cases been relatively easy to get to this natural resource and tap into its potential. Given that these fossil fuels have very high energy densities (Fig. 1.10) it is evident why it has been so attractive for us to use them. It was first later we fully started understanding the detrimental effects of basing our society on such fuels.

If we look at renewable energy sources instead the two most widespread ones (solar and wind) suffer from being intermittent. That means you will not necessarily have the energy available to you when you want to use it. A snapshot
1.2. Renewable energy & catalysis

Figure 1.7: The energy production and consumption in western Denmark between the 23rd and 30th of June 2017. Note that production of energy from wind turbines is in excess of the consumption at times during this week. [21]

of energy production in western Denmark for the period the 23rd to the 30th of June 2017 can be seen in Figure 1.7 and shows that especially wind production varies a lot. Furthermore, the fact that you get the energy out directly as electricity means you either use it instantly, when the sun is shining or the wind is blowing, or you store it by some means. Of course the latter option requires that you have an infrastructure in place for readily converting the produced energy to stored energy in whichever technology you have chosen. This often means that any excess energy is just sold off to neighbouring countries for next to nothing. Given all this it is easy to imagine that if we indeed build an infrastructure based on, say, solar and wind power, then we will end up with more of these periods of having excess energy due to the particular weather any given day. Conversely there will also be periods where we have no energy from theses sources. This is where catalysis, and especially electrocatalysis, comes into the picture.

1.2.1 Catalysis

Catalysis is the process of accelerating a given chemical reaction by improving the probability of it happening through lowering the energetic barrier of said reaction. Furthermore, the catalyst is not consumed in a catalytic reaction. This means that a catalyst’s job is to provide a surface, or site if you will, on which a
A given reaction can take place quicker than it would without the catalyst. To run the reaction as efficiently as possible the catalyst often needs the right reaction conditions for a given reaction which could mean the right temperature, the right gas composition, the right overpotential, the right electrolyte etc. However, if the conditions are ideal it should be possible to produce the desired product from the given reactants more efficiently than otherwise possible. Figure 1.8 shows the principle behind a catalytic reaction. Often times a catalyst is made from metal or metal-oxides and produced as nanoparticles to maximise the amount of surface area per unit mass of the material.

![Figure 1.8](image)

Figure 1.8: Sketch of the principle of catalysis. The addition of the catalytic surface lower the energy barrier of producing product P from reactants A and B. [25]

The binding energies between the catalyst, the reactants and reaction intermediates are what governs whether a given element or material is good at catalysing a given reaction. Basically you need the catalyst to bind the reactant to some degree to start the reaction in the first place, but you also need the catalyst to let go of the products of the reaction again. This principle was formulated by Paul Sabatier and states that there is some intermediate energy between binding the reactant too strongly and too weakly which is optimal for the reaction at hand [25, p. 261-262]. Sometimes the binding energies of reactants, intermediates and products to a given catalyst can be expressed in terms of a common binding energy thereby simplifying the theoretical considerations to take into account. The reason for this is that reactants, intermediates and products will bind to a given surface through the same atomic bond [26].
Of course this is a rather simplified picture of a catalyst as a real working catalyst is made up of a range of different sites with different binding energies. The most commonly discussed of these includes terrace sites, step sites and kink sites, these can be seen in Figure 1.9. The depicted sites are of course not the complete picture, as you can imagine several different binding sites on just a terrace; on top of a given atom, in the hollow site between e.g. four atoms, bridging between to atoms etc. The goal of the catalysis scientist or engineer is then to design a given catalyst such that you have as many of the most active sites per unit of material. Investigating which sites give rise to a given activity of a catalyst is one of the main focus areas of catalysis research. If you can understand the origin of the catalyst’s activity maybe you can design your catalyst to include a higher proportion of active sites.

Catalysts are investigated using a range of different techniques complementing each other in order to better understand how the catalysts work. A few of these techniques will be described in chapter 2.

Going back to how we imagine catalysis fits into an energy infrastructure based on renewable energy it can in principle be put quite simply: If we at times throughout the week produce an excess of electricity from our renewable sources we can imagine taking that electricity and using it to run our electrocatalytic reactions. In this way we can produce desired fuels or chemicals for later use. Doing it through electrocatalysis also means that you in principle can have small decentralised units as they can run under ambient conditions. Of course you
need the right catalysts for a given reaction.

Currently most commercial catalysis takes place at large scale industrial plants where it is economically viable to run e.g. the Haber-Bosch process producing ammonia. In fact, this process serves as a good argument for why electrocatalysis could play an important role in the future. At this point roughly 2% of the global energy consumption goes to the production of ammonia. That is a staggering amount to produce just one specific chemical. On top of that 2.5% of CO₂ emissions from fossil fuels can be accounted for by the ammonia production[27]. As mentioned, it is produced at large plants and need to be transported to where it is going to be used. Decentralising the production of ammonia would firstly make it easier to produce the ammonia on demand, and secondly cut out the transport costs. Electrocatalysis could theoretically provide the means for doing this as electrocatalytic processes can be started solely by applying a potential given the right catalyst, electrolyte etc.

![Energy-density](image)

Figure 1.10: An overview of the volumetric and gravimetric energy densities of various energy storage technologies.[28]

Finally, catalysis can also be used to produce fuels you can run your car on, for example. Of course you can also run your car on a battery but in general the energy density of conventional batteries is rather low, meaning you either transport something that weighs a lot, takes up a lot of room or both. Thus it might be a better solution to run a car on a chemical with a higher energy density like hydrogen or methanol. Furthermore, with the challenge facing us we
1.2. Renewable energy & catalysis

have to exhaust all possible venues for improving our CO$_2$ footprint. Figure 1.10 shows the energy densities of various ways of storing energy.

The above description of catalysis is simplified and it is not as straightforward in reality, but nevertheless it shows why electrocatalysis has received a great deal of attention. In this thesis we will mainly be discussing electrocatalysts used for hydrogen evolution, oxygen reduction and CO$_2$ reduction.
Chapter 2

Experimental techniques

In this chapter we will look at some of the techniques employed in this thesis. We will do so in order to understand how you can choose to investigate a catalyst and which experimental considerations might be important. In many cases we are dealing with highly surface sensitive techniques, meaning that we are probing as few atomic layers of the surface of our catalyst as possible. This is of course because the catalytic reactions take place on the surface of the catalyst, as mentioned in section 1.2.1 and so it is crucial to isolate the part of the signal originating from the surface to keep it from getting drowned in the response of the bulk of the catalyst.

Firstly, our primary technique, scanning tunnelling microscopy (STM), will be described. Secondly, we will go over a few electrochemical techniques. After this we will look at X-ray photoelectron spectroscopy (XPS). Finally, we will briefly touch upon what we can use mass spectroscopy to with regards to the research presented here.

2.1 Scanning tunnelling microscopy

STM is a method for visualising a sample by measuring the tunnel current between an (ideally) atomically thin tip and the given sample’s surface. Of course, and as with tunnelling electrons in general, you need a small enough potential barrier to allow electrons to tunnel between the sample and the STM tip. This means that you only observe a current if you bring the tip sufficiently close to the sample. In the end the tunnel current depends exponentially on the
2.1. Scanning tunnelling microscopy

distance between the sample and the tip. In our case our barrier will be defined by a vacuum gap as the STM experiments are carried out in an ultra-high vacuum (UHV) chamber. Figure 2.1 shows a sketch of the working principle of the STM. The reason for performing the experiments in UHV is that the very low pressure means our samples stay clean for longer due to having very few contaminants depositing on the sample over time. In an atmosphere with a pressure of $1.33 \times 10^{-6}$ mbar the lower time limit for covering a given surface with a monolayer of gas molecules is $\sim 1$ s, however if we go to a pressure regime of $1 \times 10^{-11}$ mbar this lower limit increases to $\sim 37$ hours leaving on ample time to perform an experiment before a sample is thoroughly contaminated.

Figure 2.1: A sketch showing the principle of an STM. When the tip is brought close enough to the sample and it is biased a tunnel current will arise which can be used to image the electronic density of states of the sample.

The STM can be operated in either a constant current mode or constant height mode. We use the former as our mode of operation which means the current is kept constant while the distance between the sample and tip is adjusted according to a feedback loop. The information on the changing height is then used to construct an image of the surface as the tip is scanned linewise over it. In order to obtain good STM images you need an atomically thin tip and atomically flat, conducting samples.

In this case we will be employing an Aarhus type STM. This particular type of STM has the tip sitting on top of a piezo tube, which also means the sample is facing downwards. By having four symmetric electrodes on the outside of the piezo tube and one continuous on the inside it is possible to control the
movement of the tip by applying potentials of opposite polarity to two opposing electrodes. One side of the tube will contract whereas the opposite side will extend giving rise to a bending of the tip to one side. By using this principle of varying potentials the tip can be scanned quickly across the surface to obtain the image.\[29, 30\]

In terms of interpretation of an STM image, one should be careful. It is easy to assume that what you see in an image is in fact just height differences observed on the surface of a given sample. This can be correct but it is not always the case. The reason for this is that an STM is probing the electron structure of the surface or, with a really good tip, the electron structure of single atoms. Depending on which elements are present on the surface of a sample some adatoms might look like depressions and or protrusions depending on the relative electronegativity of the substrate and the adatoms, as shown by e.g. \[31, 32\]. If you are dealing with e.g. monometallic samples (like we will do most of the time here) it is quite safe to assume that any perceived height difference is in fact just that and any perturbations of the surface are due to e.g. contaminants. In fact detecting minute quantities of contaminants is a real strength of the STM. Very small amounts of contaminants will often be under the detection limit of other techniques, like e.g. XPS.

The strength of the STM as a technique lies in its structural characterisation capabilities. Under the right conditions it is possible to get atomic resolution of a given sample. This makes it possible to see atomic lattices, dislocations, characteristic directions on the sample and so on. However, you will not get chemical information out of STM measurements so one has to employ other techniques to obtain that. We will get back to this fact later as it becomes quite obvious why this might be an issue.

In this thesis the STM will be used to try and correlate surface structures on our samples with the electrochemical response. In general that means we will use relatively large STM images to say something about the general cleanliness and the uniformity of a given distribution, e.g. coverage of adislands.

2.1.1 Electrochemical scanning tunnelling microscopy

To image and gain insights into electrochemically induced surface processes on a given sample a so-called electrochemical STM can be employed (EC-STM). The technique basically involves performing STM on a sample while it is submerged in an electrolyte. As one can imagine this complicates matters quite a lot. For one, an EC-STM setup is basically a four-electrode electrochemical setup meaning that the STM tip might partake in the phenomenon under
investigation. This also means that you risk ruining the tip by corroding it. Finally, fabricating a working tip becomes quite a challenge. As we saw above you want the tunnel current to go to the very tip of the STM tip to the sample. This is easily achieved in the conventional STM as the current from the sample has to go through vacuum or air. In the case of the EC-STM the STM tip is submerged in a conducting medium, namely the electrolyte. This means that the STM tip will have to be covered in something electrically insulating (and chemically stable) such that as little of the tip as possible is in contact with the electrolyte. Needless to say, that is rather challenging to achieve.

That is not to say you cannot get good data from doing EC-STM, you absolutely can, there are just reasons for why you might want to consider other options as well. In this study we are focused on correlating an electrochemical response with a model catalyst and that is more convenient to do if you can prepare said catalyst in UHV. In this way we get rid of any doubts about what happens to the sample when it is transferred from the preparation setup to the characterisation tool, i.e. the STM. It is possible to obtain useful data with an EC-STM and some relevant examples from the literature will be cited in this work. Furthermore, the EC-STM might be a valuable tool for continuing the research shown here as we will see later.

2.2 Electrochemical techniques

In the majority of cases electrochemical measurements are carried out by programming a potentiostat to set a given potential for a given system and record the current response or vice versa. The potential or current can then be set to vary in different ways; they can be swept through values, stepped from one value to another, and oscillate or one of multiple other possibilities. With just a few simple building blocks (and a high-tech piece of equipment) it is possible to imagine and perform a myriad of different electrochemical measurements.

Of course you also need some kind of setup aside from the potentiostat and the most common one is the three-electrode setup. A simple sketch of such a setup can be seen in Figure 2.2. Many other geometries of a three-electrode setup can be imagined but this encompasses the basics. In such a setup you need a working electrode (WE), a counter electrode (CE) and a reference electrode (RE). The WE is the one we are interested in studying so when we ask the potentiostat to give us a certain potential it is the one on the WE we are talking about. The RE is a non-polarisable electrode with a certain fixed potential. Usually the potential is based on the chemical potential of a redox couple. The
2.2. Electrochemical techniques

WE potential is usually given relative to that of the RE. Finally, the current runs between the WE and CE. The CE facilitates the potential requested of the WE by assuming a potential itself suitable for whatever was requested. That means you are not directly in control of the CE potential and that it is sometimes worthwhile to keep an eye on this as it may be in regions where you might see undesired effects, such as bubble formation on or dissolution of the CE. We will get back to these effects as they become relevant later in this thesis.

Cyclic voltammetry will mainly be considered in this thesis as it serves as a fingerprint of a given system, i.e. a certain element, for instance a Pt(111) single crystal will have a well-defined voltammogram. Cyclic voltammetry is the process of changing your working electrode’s potential linearly between two set values and record the current response. This is done for however many cycles are desired. The features seen in a voltammogram are subsequently at-
2.2. Electrochemical techniques

Figure 2.3: A plot showing electrochemical data from an experiment on Cu(111) in 0.1 M KOH involving both cyclic voltammetry (up to \(~\)255 s) and chronoamperometry.

...tributed to various charge transfer processes taking place on the surface of the catalyst. This includes oxidation and reduction reactions, adsorption, desorption and dissolution processes. Of course just seeing a given feature in a given voltammogram will not tell you whether it is one or the other type of process but piecing it together with complementary measurements might reveal it. Nevertheless it can still serve as the aforementioned fingerprint, or benchmark, of a system. **Figure 2.3** shows a voltammetric cycle of Cu(111) in 0.1 M KOH between –0.2 and 0.45 V vs. the reversible hydrogen electrode (RHE).

Other commonly used techniques are chronoamperometry and electrochemical impedance spectroscopy which has been used sporadically in the work presented here. The former simply involves applying a constant potential over time and tracking the current (and for example the catalytic products produced at this potential). This could for instance be used to show a deactivation of a catalyst over time. In this work we mainly use chronoamperometry to be able to immerse our samples under potential control. **Figure 2.3** shows about 20 s of chronoamperometry on a Cu(111) single crystal.

Electrochemical impedance spectroscopy involves applying a set potential and adding a small oscillating potential on top of that. In this way it is possible to measure the response due to the impedance of the system. This can give
information on the various resistances present (Faradaic resistances, membrane resistance etc.), as well as capacitances and inductances. Further information can be obtained by fitting the response of an equivalent electrical circuit to the obtained data. In this thesis impedance spectroscopy has been used to determine the ohmic drop we need to compensate for in our measurements. The ohmic drop is the potential drop due to the uncompensated electrical resistance between the WE and the RE\textsuperscript{33} p. 24-28).

It should be noted that electrochemical measurements differ quite dramatically from STM measurements in terms of the probe area. Electrochemical measurements are global probes and thus you get signal from every part of your sample in contact with the electrolyte. When you use an STM you get images on the order of square nanometres up to a few square micrometres. Nevertheless the intention here is to be able to use a combination of the STM and our electrochemical techniques to establish a good method for benchmarking well-defined samples electrochemically.

As alluded to we generally use cyclic voltammetry for our electrochemical measurements.

2.3 X-ray photoelectron spectroscopy

XPS is a widely used and rather versatile technique which provides chemical information about a sample. If used in the right way it can provide depth information as well.

![Figure 2.4: A sketch of the basic principle of XPS. An X-ray photon is emitted onto a sample. The energy of the photon is high enough to "knock" loose electrons from the atoms in the sample. These electrons are then detected.](image-url)
2.4. Mass spectroscopy

XPS works by directing a beam of X-ray photons of a well-defined energy onto the sample in question. The incident photons will then give rise to the emission of photoelectrons from the various electron orbitals present in the elements of the sample. A detector measures the kinetic energy of the photoelectrons emitted from the sample. Figure 2.4 shows a simple sketch of the principle of XPS. The kinetic energy of the photoelectrons can then be related to the binding energy of the electrons to the atoms they came from through

\[ E_{\text{bind}} = E_{\text{photon}} - E_{\text{kin}} - \phi \]

where \( \phi \) is the work function of the detector, which can be corrected for systematically. This binding energy, or rather a spectrum of binding energies, is characteristic of a given element meaning that we can use our XPS spectrum to estimate the chemical composition of a given sample. Using XPS can also provide information on the oxidation state of a given sample.

Common sources of X-ray photons are aluminium and magnesium as they can, when bombarded with high energy electrons, emit relatively well-defined X-ray photons of 1486.6 eV and 1253.6 eV respectively.

In general the probing depth of XPS is up to around 5 nm due to the mean free path of electrons escaping from the sample. It is possible to make XPS even more surface sensitive by tilting the sample with regards to the detector such that electrons have to travel comparably further in the sample in order to get to the detector.\(^2\)

In this work XPS has been used to look for a contaminant thought to be localised at the edges of a Pt(111) sample.

2.4 Mass spectroscopy

In this section two types of mass spectroscopy will be introduced. One helps us determine what is in the gas phase of our UHV chamber and what is evaporating from the sample when we heat it. The other helps us obtain information about the contents of our electrolyte.

2.4.1 Quadrupole mass analyser

A quadrupole mass analyser (QMA) employs four metal rods arranged in two pairs sitting parallel with and opposite to each other such that a positively charged pair sits e.g. above and below a centre ”channel” and the negatively charged pair sits to the left and the right of this channel. This means that
positively charged ions entering the channel will be attracted to either of the vertically arranged rods and repelled from those arranged horizontally. By applying an alternating current on top of the positive and negative direct currents it is possible to accelerate the ions back and forth between either set of rods resulting in a net spiral trajectory of the ion. Depending on the exact ratio between the direct currents and the alternating current it is possible to tune the mass to charge ratio that gets all the way through the QMA to the detector. In order for this principle to work the gas to be analysed needs to be ionised first which can be achieved by using e.g. a filament. In doing so a mass spectrum of the gas composition can be obtained. The principle of the QMA is sketched in Figure 2.5.

Figure 2.5: A sketch showing the idea behind a QMA. By applying specific AC signals on top of the already polarised rods the charged particles can be guided through according to their mass to charge ratio. Only particles of a given mass to charge ratio will pass all the way through the QMA and get detected. By systematically altering the AC signal it is possible to scan through mass to charge ratios and thus obtain a mass spectrum.

QMAa are widely used in various research areas and the UHV chamber employed in this work is equipped with one such. This allows us to measure the background of our chamber, detect leaks and, maybe more interestingly, detect
2.4. Mass spectroscopy

what evaporates from a given sample when it is heated.

2.4.2 Inductively coupled plasma mass spectroscopy

Inductively coupled plasma mass spectroscopy (ICP-MS) is a powerful technique for detecting minute quantities of e.g. metal ions in solutions all the way down the parts per trillion level. ICP-MS works by injecting a small dose of a dilute sample solution into the nebuliser where the sample is mixed with argon acting as a carrier gas. This results in an aerosol containing the sample. The aerosol is brought through the titular plasma where the high temperature of the plasma ionises the aerosol. The ions resulting from the ionisation are focused through ion lenses in order to get rid of neutral species. From here the ions are sent through e.g. a QMA which, as explained above, can analyse the ions according to their mass to charge ratio and thus produce a mass spectrum.

ICP-MS has been used sparingly throughout this project to look for both electrode dissolution and contaminants but the technique is expected to play a larger role in connection with the primary experimental method developed in this work.
Chapter 3

Setup & experimental method

This chapter aims to describe the setup and method which has been used and improved upon throughout this work. One half of the setup, the UHV chamber and its various pieces of equipment, has been in place for a number of years and only undergoes small changes and improvements sporadically whereas the electrochemical part of the setup has been through a number of iterations since December 2015. To be clear, there was a cell design, a holder for the cell and a general working principle in place, however, as we shall see, a range of improvements have been made in order for us to completely trust our electrochemical results.

This chapter will also include a description of the rotating disk electrode (RDE) setup employed at KAIST to measure the voltammogram of copper single crystals prepared under laboratory conditions as opposed to under UHV conditions.

3.1 UHV chamber

The UHV chamber is a conventional stainless steel chamber equipped with a range of different instruments. Firstly, there is the central manipulator which can be controlled in the $x$, $y$ and $z$ directions, furthermore it can rotate around the $z$-axis and the house can be tilted as well making it possible to ”point” the samples in different directions, e.g. towards the sputter gun. The $z$-direction
3.1. UHV chamber

and the two rotational directions can be controlled with a motor. The house
in the manipulator has an attached filament and thermocouple allowing us to
anneal the sample. The chamber is also equipped with a QMA, a Mini e-Beam
Evaporator (EGN4, Oxford Applied Research) for physical vapour deposition
(PVD) procedures, a quartz crystal microbalance (QCM) (TM-400 Thickness
Monitor, Maxtek) and, of course, an STM of the Aarhus type as mentioned
in section 2.1. Finally, there is a number of gas bottles attached to
piezo leak valves on the chamber making it possible to dose various gases like
O$_2$ during the sample preparation procedure. The chamber is pumped with
a magnetically suspended turbopump (Pfeiffer) most of the time, but there is
also an ion pump. The base pressure of the chamber is in the $1 \times 10^{-11}$ to
$10^{-12}$ mbar range as measured by an inverted-magnetron gauge (Agilent IMG-
300). A magnetic transfer arm (Ferrovac) is located on one side of the chamber
making it possible to take samples in and out without venting the chamber.
A 4.5” spherical vacuum cube (Kimball Physics) is located on the middle of
the transfer arm. This cube is used as a load lock and it is also here the
electrochemical measurements take place. Throughout this thesis the vacuum
cube will be referred to as the EC cube or simply the cube when the context
is obvious. The chamber and cube are shown in the picture in Figure 3.1. A
wobble stick is sitting perpendicular to the transfer arm in the main chamber
and is used to move the sample from the manipulator house to the STM.

3.1.1 Samples & sample holders

In connection with the UHV chamber we use single crystals with a hat shape
(MaTeck, Jülich). "Hat shape" means it is a circular crystal with a base that
is wider than the face of it. In our case the bases of our crystals are 8 mm in
diameter whereas the faces are 6 mm. The surface area we use to normalise our
electrochemical currents with is also derived from this 6 mm diameter.

The reason for having samples with this particular shape is that it allows us
to keep the samples in the sample holders when the face of the crystal is facing
downwards, which it is doing during STM characterisation. The sample holder
is a plate of molybdenum with a thermoelement mounted on the backside and a
hole slightly larger than 6 mm drilled through it. The sample is then mounted
such that the face of the crystal is on the opposite side of the thermoelement.
A strip of tantalum foil is then keeping the crystal in place on the back side
by being spotwelded onto the sample holder on either side of the crystal. The
sample holder and sample can be seen sketched in Figure 3.2.

The hole through the sample holder is tapered such that it is wider on the
3.1. UHV chamber

Figure 3.1: The main UHV chamber with the transfer arm on the right. The EC cube is the small compartment lit up on the transfer arm. Note also the small turbopump halfway between the main chamber and the cube.

crystal face side of the sample holder. This is to avoid electrolyte accidentally coming in contact with the sample holder and capillary forces between the sample and sample holder dragging the electrolyte to the backside of the crystal. The reason being we do not want to risk corroding the sample holder, thermoelement etc. and get impurities from those onto our nice single crystals.

As single crystals go these are not as good as the bead type crystals used elsewhere. However, those would be incredibly difficult getting into an STM so we have had to make a trade-off in this regard. However, as we shall see, we still get very nice electrochemical measurements meaning there is no doubt we are actually measuring on e.g. Pt(111).

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3.2. EC cube & electrochemical setup

The EC cube is connected to the main chamber through two DN 40 CF mini UHV gate valves (VAT) in line with the transfer arm. Between the cube and the chamber a small turbo pump is placed, as marked on Figure 3.3 making it possible to pump down the cube without opening to the main chamber. The pressure of the cube is usually $\sim 10^{-8}$ mbar, but can be brought down to $\sim 10^{-9}$ mbar if we bake the cube and transfer arm. On top of the cube there is an $xyz$-manipulator with an attached house for the sample similar to the one in the main chamber. This manipulator also rotates around the z-axis. At the bottom there is another VAT valve through which the electrochemical cell is inserted when doing measurements. Aside from this there is a gas line going from the mass flow controller (MFC) to a leak valve (Swagelok) on the side of the cube. Additionally there are two mirrors mounted inside the cube making alignment
of sample and cell a little bit easier, these can be seen in Figure 3.4. Lastly, there is another VAT valve to the transfer arm so we do not have to vent and pump down the rather large volume of the arm before and after measurements, respectively. For the electrochemical measurements we use a Bio-Logic SP-200 potentiostat and the accompanying software, EC-Lab.

Prior to December 2015 work on the electrochemical side of the experiments had been undertaken by Sebastian Horch, Christian Schlaup and Albert K. Engstfeld. The cell design was very much a prototype of what was to come later, and the process of venting the EC cube and electrolyte introduction was considerably more fiddly and involved a number of extra components which could potentially be sources of contamination (or even human errors). In short preparing the electrochemical setup involved first rinsing the inlet tube with warm millipore water and then with deaerated electrolyte before connecting the tube to the cell. This is still part of the preparation of the preparation procedure, to be sure, however back then it was done by sucking liquid from a glass bottle into a gastight syringe before pressing it out again into a waste glass bottle several times. This was even done through a T-piece that had to be turned
3.2. EC cube & electrochemical setup

Figure 3.4: A measurement underway. Behind the house containing the sample you can see two roughly symmetrically placed mirrors which help with the alignment of the sample and the EC cell.

from one side to the other between each syringe action. The syringe would also be used for the introduction of electrolyte to the cell immediately before a measurement. The venting of the cube was basically done through a ziplock bag put around the venting connection of the small turbopump. Finally, we did not have an MFC in place for controlling the gas flow during measurements (which later proved to be very important indeed). While all of this made it possible to measure there was clearly still room for improvement.

While we were working on this setup A. K. Engstfeld was working on establishing a flow cell setup in connection with the XPS chamber at DTU Physics. Obviously he needed steady electrolyte flow conditions for his experiments and thus could not be satisfied with using a syringe as the way of introducing electrolyte to his cell. Instead he had a rather large glass bottle designed with a drain and a stopcock at the bottom of it. Elevating this bottle above the cell and connecting it to the inlet tubes would of course make it possible to start and stop the flow by just opening and closing the stopcock. Realising this probably could be used in our setup to get rid of the syringe we had a smaller version
of the bottle made (as we had no need for a very large volume of electrolyte). Now rinsing the system prior to a measurement was just a question of filling the bottle and opening the stopcock. Lastly, the contents of the supply bottle are easily bubbled through the custom-made bubbler. Later when we started using KOH as our electrolyte we acquired a supply bottle made of PFA (Savillex) to avoid getting dissolved glassware in our electrolyte. A sketch of the PFA supply bottle and electrochemical setup as a whole is shown in Figure 3.5. The sketch has been somewhat simplified since the real system includes a reducer fitting on either side of the stopcock to connect first the 3/8” drain with the 1/4” stopcock and then the stopcock with the 1/8” inlet tube. This amount of extra fittings is clearly not ideal in terms of potential leaks or dead volumes of oxygen. The stopcock is integrated into the glass bottle so there are no extra fittings in this case since a Luer connection fits directly onto the drain beneath the stopcock. Pictures of both supply bottles are shown in Figure B.1 in Appendix B.

Alongside this we installed an MFC we borrowed from Debasish Chakraborty. This MFC connected a bottle of either Ar or N$_2$ (6.0, AGA) to our EC cube through stainless steel pipes. While it worked fine we figured that the very high maximum flow rate (35 000 sccm) was probably a bit too much for our needs and that it came at the expense of precision. In its place we acquired an MFC from MKS of the type GM50A with a maximum flow rate of 10 000 sccm. For most laboratory application that is still a very high flow rate but we decided on that as we wanted to be able to have a flow on the order of litres per minute when opening the valve of the EC cube to the outside to insert the EC cell. That said we quickly learned that the flow needed to be considerably lower when doing our measurements as too high flow gave rise to oscillations in our currents. Conversely too low flows would make oxygen leak in faster. Most measurements are carried out with a gas flow of 2000 sccm, whereas a flow of 7000 sccm is used when inserting the cell. Lastly, we have put in a kind of deflector right in front of the gas inlet in the cube as a means to avoid the gas going directly onto the electrolyte droplet in the cell and drying it out quicker.

### 3.2.1 Cell design

The original cell design consisted of two coaxial cylinders machined from a single piece of Kel-F, with the central cylinder having just a single channel for electrolyte. Kel-F was chosen due to its great chemical resistance. The inner cylinder were a couple of millimetres higher than the outer one and had an inner diameter of 6 mm to match the diameter of the crystals used as samples. The outer cylinder measured 25 mm in diameter and served both as an overflow
3.2. EC cube & electrochemical setup

Figure 3.5: Sketch showing the electrolyte supply bottle, the EC cell and the rest of the electrochemical setup. The syringes are used to get rid of bubbles. The reducer fittings shown in Figure B.1 have been left out for simplicity.
volume and as a way to give the cell a larger body so there would be room for nuts and ferrules in the inlets and outlets. Furthermore when mounted in the cell stand it would fit precisely through the valve at the bottom of the EC cube keeping as much ambient air out as possible.

Figure 3.6: Sketch of the new cell design which was adopted to get rid of the ohmic compensation problems. Note that it is the inner diameter of the electrolyte cylinder which is 5 mm. The dummy working electrode is shown in the side view.

In principle this design worked fine and at least gave us reason to believe our project was not a hopeless endeavour and given time could produce some great results. However, when A. K. Engstfeld started working on his copper measurements and we wanted to reproduce those it simply was not possible. After much testing we arrived at the conclusion that our cell design had to be tweaked as we suspected that having the reference electrode’s “line of sight” across the electric field between the sample and the counter electrode was the issue. The observant reader might have noticed that the cell shown in Figure 3.3 does not consist of just two coaxial cylinders. In fact the central cylinder has been parted in two parallel channels. The cell is still made from a single piece
3.2. EC cube & electrochemical setup

of Kel-f but now the central cylinder features a narrow channel as outlet and "path" of the RE and a wider channel for the inlet and the CE. In this way the narrow channel almost acts as a built-in Luggin capillary. A sketch of the updated design can be seen in Figure 3.6. The total electrolyte volume of the cell, including the hemispherical droplet of electrolyte on top, comes to 0.22 mL.

Figure 3.7 shows a comparison between our results on Cu(100) in 0.1 M KOH with the old and the new cell design and one of A. K. Engstfeld’s measurements from his flow cell. We generally find our setup to have an ohmic drop of $\sim 20 \Omega$ found through electrochemical impedance spectroscopy.

![Figure 3.7: A comparison of voltammetric cycles from −0.2 - 0.5 V vs. RHE on Cu(100) in 0.1 M KOH. The cycles were obtained in A. K. Engstfeld’s flow cell, the old single-channel hanging meniscus cell and the new two-channel hanging meniscus cell. As can be seen the voltammogram from the old cell appears very ohmic compared to the two other ones.](image)

Lastly, we had a new stand for the cell made which incorporated a rod of stainless steel for the purpose of being able to mount an additional wire used as a dummy working electrode. This allowed us to immerse and emerge samples under potential control thus limiting the time spent at open circuit potential.
3.3 Experimental

This section firstly explains the preparation needed before a measurement can commence before moving on to what a typical measurement would look like.

3.3.1 Preparing the electrochemical setup

There are few things more important than cleanliness when you try to investigate phenomena on the atomic scale, that is unsurprisingly also true of doing electrochemical measurements. When doing experiments like the ones described above there are quite a lot of things which need to be very clean before being used. On a daily basis we use: the supply bottle and its bubbler, a PTFE or PFA stopcock for the supply bottle (depending on whether we use the glass or PFA supply bottle), a glass bottle for bringing warm millipore to the supply bottle, the electrochemical cell, a large pair of teflon tweezers and an extra beaker for preparing e.g. the RE. Furthermore we have designated volumetric flasks for each electrolyte used, again either made from glass or PFA.

The glass supply bottle and its accompanying bubbler is stored in a ∼ 3 M KOH (85 %, EMSURE, Merck) bath. Their PFA counterparts, including stopcock and reducer fittings, are occasionally left in 2 % HNO$_3$ (69 % EMSURE ACS reagent Ph.Eur., Merck) over night but otherwise stored in millipore water (18.2 MΩ, Merck) when not in use. The rest of the things are generally stored in millipore as well and occasionally left in a KOH bath or piranha solution (3:1 H$_2$SO$_4$ (98 % EMSURE, Merck) : H$_2$O$_2$ (30 % EMSURE Iso for analysis, Merck)) over night.

Before any given experiment the following is done:

1. If using the glass supply bottle: The supply bottle and bubbler is taken out of the KOH bath and boiled in millipore water in a clean beaker. The teflon stopcock is boiled three times in millipore in a smaller beaker

2. If using the PFA supply bottle and accessories: The supply bottle is taken out of the HNO$_3$ bath and dipped in a beaker full of warm millipore along with its reducer fittings and stopcock then rinsed thoroughly with millipore

3. The bottle for millipore and the electrochemical cell are boiled three times in millipore.

4. The beaker for the electrodes is emptied of concentrated KOH and boiled in millipore
5. After boiling, rinsing and assembling the supply bottle it is placed in its stand slightly elevated over the EC cube

6. The inlet tube is connected using the appropriate fitting and warm millipore is poured through the system by filling the supply bottle with warm millipore from the millipore bottle

7. The supply bottle is filled with the given electrolyte and a bit of it is flushed through the inlet tube to get rid of the remaining millipore

8. At this point the electrolyte is bubbled continuously with $N_2$ (5.0, AGA)

9. The cell is taken out of the millipore water with the teflon tweezers and is mounted in the stand with the counter electrode and dummy working electrode

10. Immediately before the inlet tube is connected to the EC cell the tube is once again rinsed with the now bubbled electrolyte

11. The outlet and inlet tubes are fixed in the respective ports of the cell

After all of this is done the electrochemical part of the setup is ready to be used and looks like shown in Figure 3.8. The counter electrode and dummy working electrode were only mentioned in passing above for the sake of simplicity. Below follows a more detailed description of how they are prepared.

**Electrode preparation**

Aside from cleaning and preparing the glassware and the cell the CE, RE and dummy working electrode (DWE) also need to be prepared for the measurements. These procedures will be described below.

We use a reversible hydrogen electrode (RHE) as our RE. The RE is located in a cylinder akin to a graduated cylinder but with a ground glass connector up top and an outlet on one side close to the bottom. This outlet connects to a T-piece on the outlet of the electrochemical setup through 1/8” PFA tubes (IDEX Health & Science). The ground glass connector fits with the actual RE which is a custom-made piece of glass with a platinum wire (0.5 mm diameter, 99.99 %, Chempur) fed through. A platinum foil (99.99 %, Chempur) is attached to the wire in a glass enclosure with a small opening facing downwards, narrow enough that the electrolyte will not drip out of it. Figure 3.9a shows a photo of the RE when it is out of the cylinder which holds it during experiments. Figure 3.9b...
3.3. Experimental

Figure 3.8: Two pictures of the EC cell mounted in its stand. (a) shows most of the stand with the rod for the DWE being behind the cell but with the DWE raised out of the picture. (b) shows the cell from below where the CE can be seen in the back of the picture.

shows the RE when it is in use, sitting in the cylinder which is connected to the outlet of the full electrochemical setup (Fig. 3.5).

In order for this system to work as an RE the volume containing the foil is filled with a given electrolyte with a designated syringe ("designated" in that it is only ever used for this type of electrolyte, e.g. HClO₄). Then it is put in the clean glass beaker mentioned in section 3.3.1 which is now containing the same electrolyte. A platinum wire is put into the beaker as well and a potential is applied across the two electrodes using a conventional power source until enough hydrogen is evolved on the platinum foil to cover roughly half of it. This procedure is sketched in Figure 3.10. Finally, the RE can be placed in the cylinder mentioned above. This cylinder should of course also be filled with electrolyte such that the electrolyte from the RE is in contact with the electrolyte in the cylinder.

The CE is made from a piece of platinum wire (0.5 mm, 99.99%, Chempur) which is long enough to reach almost to the edge of the parting wall in the EC cell through one of the threaded ports. The wire is first flame annealed and then glued stuck inside a piece of PFA tube of ~ 1.5 cm. The glue has to
3.3. Experimental

Figure 3.9: (a) A photo of the RE when there is no electrolyte in it. Note that just above the Pt foil the glass is sealed around the Pt wire to keep the hydrogen from escaping. (b) The RE placed in its holder which is connected to the outlet of the EC cell. In this picture the RE is ready to be used as the RE and the holder is full of electrolyte. If you look carefully the hydrogen bubble around the Pt foil can also be seen. The stopcock is in its closed position which is also the case when measuring. This only works after rotating the stopcock a few times to form an electrolyte film around it in order to get electric contact to the setup.

make the tube completely tight so electrolyte cannot leak from the cell. Then a ferrule and nut is put around the tube and a gold pin is clamped around the backside of the wire. It is through this pin we get electric contact to the CE. It is important that the glue at the top of the tube is in plane with the tube and ferrule so it is possible to screw the CE into the port of the cell properly. At this point the CE should look like the one shown in the Figure 3.11. Before the CE is put to use it is cycled in e.g. 0.1 M HClO₄ from 0 to 1.6 V vs. RHE in a setup similar to the one shown in Figure 3.10 until the voltammogram is stable. We use the RHE as RE and a platinum wire as the third electrode. The electrochemical procedure alternates between oxidising and reducing the
platinum thereby hopefully getting rid of any contaminants that might come off in the electrolyte. When not in use the CE is stored in a beaker full of millipore with a watch glass on top. The first and the last cycle of such a cleaning procedure can be seen in Figure 3.12.

If the DWE is made of platinum the cleaning procedure is the same as for the CE. But often it is just a matter of flame annealing it briefly while it is still fastened to the cell stand. When measuring on copper samples we have opted to use a copper wire as DWE instead of platinum. In order to clean that we cycle it in 0.1 M KOH from −0.5 to 1.7 V vs. RHE until a stable voltammogram is recorded. Representative cycles of this procedure can be seen in Figure 3.13. This is again done under the assumption that anything that can dissolve in KOH and potentially contaminate the sample will do so under these potentials. If nothing comes off the wire it probably will not do so either under the less extreme potential the wire will see during the experiments.
3.3. Experimental

Figure 3.11: A photo of the CE after it has just been taken out of its beaker full of millipore, hence the droplet on the ferrule.

3.3.2 Typical experiment

Below is an outline of a typical experiment:

1. The sample is prepared using cycles of sputtering, annealing, and often O$_2$ dosing for removal of e.g. carbon species

2. The sample is transferred from the manipulator to the STM

3. STM is performed to investigate whether the sample looks like what was hoped for

4. If the STM images are satisfactory the sample is transferred to the manipulator in the EC cube via the transfer arm (the cube is still under vacuum at this point). The valve to the UHV chamber and that to the transfer arm is closed as soon as the sample is sitting securely in the house

5. While the cube is vented with Ar or N$_2$ (both 6.0, AGA) through the MFC while the electrochemical cell is mounted in the cell stand along with the dummy working electrode

6. When the cube is vented and the turbo pump has spun down the valve between the turbo pump and cube is closed, the bottom valve of the cube is opened and the cell raised into the cube, roughly to the height of the mirrors

7. The supply bottle’s stopcock is opened and the electrolyte is allowed to flow over the edges of the cell a few times before a syringe is used to slowly suck electrolyte out through the outlet. If everything goes according to plan you should be able to measure a resistance between the reference
3.3. Experimental

Figure 3.12: Two cycles from 0 to 1.6 V vs. RHE showing the electrochemical cleaning procedure used on Pt wires such as the CE. The newly regenerated RE is usually used for this procedure.

- Electrode and the counter electrode as soon as the electrolyte reaches the T-piece of the outlet
- Now a droplet the size of the desired meniscus is formed on top of the cell (usually a droplet within the perimeter of the cell as opposed to sitting on the edges of it)
- The DWE is put into the electrolyte droplet and desired potential is set
- The sample is now aligned with the meniscus and immersed
- The DWE is taken out of the meniscus and the measurement can commence
- When ending the measurement a constant potential is applied and the DWE is put into the meniscus again and the sample is raised out of the electrolyte
3.3. Experimental

Figure 3.13: Two representative cycles of a cleaning procedure of the Cu wire used as DWE in 0.1 M KOH. The RE is used for this procedure as with the Pt wire cleaning.

13. The cell is taken out of the cube and any remaining electrolyte on the sample is removed with a Kimwipe and the cube is pumped back down.

14. Finally the sample can be transferred back to the main chamber and STM can be performed again to investigate what happened to the surface during the electrochemical measurement.

The above more or less fleshes out how our measurements work. Of course the actual sample preparation procedure can vary from day to day and the electrochemical measurements will use different techniques depending on what we are looking for but that will be discussed in the relevant sections. What will always be constant no matter the exact electrochemical measurement is the need for having everything clean prior to measuring.
3.4 Rotating disk electrode setup

As a small side project towards the end of this PhD project the preparation of copper single crystals under laboratory conditions (as opposed to UHV conditions) was explored. The idea was to investigate whether it actually is possible to prepare a copper single crystal outside of UHV and obtain the same voltammogram as on the UHV prepared sample. In order to do so a custom-made RDE tip was fabricated and the experiments were carried out at KAIST during the last three months of this project.

To be clear, using an RDE setup for this type of experiments is not exactly ideal. When you are doing electrochemical single crystal measurements you only want to measure signal from the main facet of the single crystal. That means you want to avoid wetting the edges of the crystals as these will not have the well-defined single crystal phase you were hoping to measure. In order to avoid wetting the edges we put a PTFE cap over our single crystals used for these measurements. That means you lose a bit of surface area, you risk squeezing the crystal a bit too much (which might be an issue when working with a relatively soft material like copper) and with the cap you end up having an edge which will undoubtedly break the flow field induced by rotation which is the strong point of RDE experiments. Ideally a conventional bead type crystal would be used in a suitable setup.

However, choosing to carry out the measurements in an RDE type setup allowed us to do three things: Firstly, it made it possible to use the copper single crystal samples we already had in our laboratory at DTU (normally used for e.g. EC-STM). As with the samples used in the UHV based STM these were from Mateck too. Secondly, it made it possible to design and produce the custom-made RDE tip in a relatively short amount of time without a lot of prior knowledge of the surrounding setup. In this case we had to know the diameter of our samples, the threads on and in a commercial RDE shaft used at KAIST and the diameter of the opening of the electrochemical cell we intended to put the RDE tip through. Finally, we decided to perform the measurements in a PTFE cell. Given that PTFE is opaque it was possible to immerse the sample without immersing it too much and thus wet the edges of the sample due to the protective cap. It should be made clear that the intention was not at this point to actually rotate the electrode. The commercial RDE shaft available at KAIST provided a convenient way to use the disk electrode already in our possession. Had we had more time when planning the trip to KAIST we might have conceived of a different way to do things.

The design we ended up with consists of a few different pieces: A PTFE
3.4. Rotating disk electrode setup

Figure 3.14: A sketch of the RDE tip used for our Cu single crystal measurements. Pictures of the RDE tip are found in Figures 3.15c-e.

sample holder which fits on the RDE shaft and can hold an 8 mm sample when it is standing upright, a PTFE cap which fits around the sample holder, a conducting spring which fits inside the sample holder and a conducting rod which fits in the thread inside the RDE shaft and serves to ”guide” the spring. All of this is sketched in Figure 3.14.

The RDE tip is assembled by putting the sample holder in the upright position and carefully placing the sample in the slot. Afterwards the cap is screwed on the outside of the sample holder to keep the sample in place. Now the whole thing can be turned upside down and the spring can be put in through the backside. The metal rod can be screwed into the RDE shaft and the tip can be screwed onto the shaft afterwards. The spring makes contact between the shaft and the sample without applying a lot of pressure.

As mentioned above the measurements were conducted in a PTFE cell (again to avoid mixing glassware and KOH) and can be seen in Figure 3.15. The cell was the Alkaline Resistant RDE/RRDE Cell (Pine Research Instrumentation, Inc.) and features a lid that can come off completely and closes tightly again through the use of three clamps and an O-ring placed in a groove on the edge of the cell. The lid has one central opening for the RDE and four smaller openings for e.g. the CE, RE and bubbler. A platinum wire was used as CE and a Alkaline/Mercurous Oxide Reference Electrode (CH Instruments, Inc.) was used as RE. A PFA volumetric flask is used for mixing the KOH used here.

As with the PFA parts used described earlier in this chapter the PTFE
3.4. Rotating disk electrode setup

![Figure 3.15: Pictures of the PTFE cell. Both the cell (a) and the lid, seen in (b), are machined from one piece of PTFE. (c), (d) and (e) shows the RDE tip before, during and after assembly.](image)

parts were cleaned by being placed in a 2% HNO$_3$ bath (68.0-70% extra pure, Samchun Chemicals). In the case of the PTFE cell it was left full of the HNO$_3$ over the weekend with the lid on. The CE was stored in 10% H$_2$SO$_4$ (95%+ Guaranteed Reagent, Junsei Chemical Co.) and rinsed thoroughly before use. A platinum mesh attached to a platinum wire was used as well and stored and cleaned in the same way as the CE wire. This mesh was used for calibrating the reference electrode prior to experiments.

For electropolishing the copper single crystals a clean beaker and 66% H$_3$PO$_4$ was used. A copper mesh is used as cathode and the RDE tip and shaft is still used to hold the sample. A picture of the setup used for electropolishing is shown in Figure B.2 in Appendix B.

A typical experiment would progress as follows:

1. Rinse EC cell, RE, CE and Pt mesh with millipore water (18.2 MΩ, Merck)
3.4. Rotating disk electrode setup

2. Fill cell with KOH
3. Set up Pt mesh as WE through the central hole in the lid and put the CE and RE on either side of it through two of the smaller holes
4. Start bubbling with hydrogen through a PFA tube and put the clamps on the lid
5. Cycle the WE from $\sim -0.1$ to $1.6$ V vs. RHE (at this point we are just assuming an RE potential of $-0.9$ V vs. RHE)
6. When the voltammogram is stable (usually after $\sim 25$ cycles) end the cycling at $-0.1$ V vs. RHE and let the open circuit potential stabilise
7. The open circuit potential is then used as our reference potential
8. Take out and put away the Pt mesh, get rid of the KOH and rinse the cell with millipore water
9. Put in new KOH and let it saturate with Ar
10. While the KOH is bubbled the electropolishing setup is put in place
11. The two parts of the RDE tip are first rinsed with millipore water and then dried using compressed air
12. The sample is put into the sample holder and the RDE tip is assembled
13. The sample is rinsed in millipore while it is in the tip
14. The sample is then electropolished and subsequently rinsed with millipore again to get rid of the $\text{H}_3\text{PO}_4$ both on the sample and the PTFE parts
15. The EC measurement is performed
16. Finally, the sample and everything else is rinsed in millipore before being put away again

With that we have reached the end of this section and chapter outlining our primary experimental methods. In summary we have seen two different ways of measuring single crystals electrochemically, one based on being able to measure UHV prepared single crystals without exposing them to ambient conditions and characterising them with STM before and after the electrochemical measurement measurement, and one designed specifically for measuring the elusive copper single crystal voltammograms on samples prepared under laboratory conditions.
Chapter 4

Benchmarking the setup: Pt(111)

In this chapter we will look at the capabilities of the setup described in chapter 3. To do so we have chosen to measure on a Pt(111) sample. The reason for picking exactly this element and this facet of it is that it is probably one of the most studied electrochemical systems. Thus the literature will serve as a way to rationalise our results and hopefully confirm whether our system works or not. Furthermore, it is also possible to prepare a Pt(111) crystal outside of UHV by simply flame annealing it [34] which means the electrochemical cell and the rest of the setup can be tested on a tabletop outside the EC cube thereby making it possible to deconvolve issues related to the experimental setup and break it up into smaller parts. This has been used frequently throughout this project, usually to isolate sources of contaminants which might show up in the voltammogram from time to time.

Before we get to the results obtained on our Pt(111) electrodes we will briefly look at the Pt(111) voltammogram in order to introduce the terminology to be used to make it simpler to discuss the obtained results later on.

Through the results shown here we will see how we can use this setup to understand corrosion processes by not only looking at the flat, clean Pt(111) surface, but also using the UHV chamber’s PVD capabilities to form adislands, and programmed sputtering and annealing to form well-defined vacancy islands. This shows both what the setup is capable of and how one might design experiments to further one’s understanding of a given investigated system.
4.1. The Pt(111) voltammogram

Most of the measurements shown in the coming sections were carried out in 0.1 M HClO$_4$ (70 % Suprapur, Merck). We will see measurements from both the cell with the design shown in Figure 3.6 and ones obtained using the old single channel cell design. That means some of the voltammograms might appear more ohmic than what you would expect, but the processes observed on the surface should not be affected. STM images were treated in SPIP (Image Metrology), which generally just means background corrections and flattening of the images to make them presentable.

4.1 The Pt(111) voltammogram

As mentioned the electrochemistry of platinum, and indeed the Pt(111) facet, has been studied extensively historically. Climent and Feliu wrote a review paper in the beginning of this decade where they walked us through the historical data and understanding of platinum in different electrolytes[35].

In general the stable Pt(111) voltammogram (Fig. 4.2a) can be divided in three regions: The hydrogen UPD region from the onset potential of the hydrogen evolution to $\sim$ 0.4 V vs. RHE, the OH region from $\sim$ 0.6 to $\sim$ 0.85 V vs. RHE and the double layer region between those two. In the hydrogen UPD region hydrogen is adsorbed in the cathodic scan and desorbed again in the anodic scan. In the OH region water and OH groups are adsorbed in the anodic scan and desorbed again in the cathodic scan[36], this region is also sometimes referred to as the butterfly region, due to the peculiar symmetric shape of the features. The exact shape, size and position in of the sharp peak in the OH region is dependent on the chloride concentration in the electrolyte, a common contaminant in HClO$_4$[37]. It is generally accepted that the small current observed in the double layer region is due to the charging of the interfacial layer between the electrode and the electrolyte. If the potential is increased further oxygen starts adsorbing and eventually the oxygen exchange reaction happens meaning oxygen atoms swap places with the platinum atoms in the surface of the electrode. The adsorption of oxygen is proposed to start already at 1.025 V vs. RHE[38], however others have had difficulties observing it below 1.1 V[39]. In any case, the general consensus in the field is that alternating between oxidising and reducing the sample disorders the surface and causes a given sample to become more rough by exchanging platinum atoms in the surface layer with oxygen from the electrolyte. Upon reduction some of the platinum is dissolved in the electrolyte and some redeposits on the sample giving rise to a rougher surface now featuring both vacancies and adatoms[39, 40, 41].
Finally, any sharply peaked features that might be observed in the hydrogen region is thought to be due to specific adsorption sites, like e.g. step sites. This was investigated on crystals cut such that the crystal face would be one of the vicinal surfaces to e.g. Pt(111). However, it has also been proposed that features in the hydrogen UPD region could in fact be due to a displacement of $H^+$ by $OH^-$ or vice versa[42].

### 4.2 Results

In this section we will start out by taking a flat, clean Pt(111) sample through the setup one step at a time. First imaging it with the STM then try to measure the well-established Pt(111) voltammogram in perchloric acid before imaging it once more after the electrochemical treatment. Secondly, the upper potential will be changed somewhat such that we will start corroding the sample to see if the surface can be imaged with the STM afterwards. Then we will look at the stability of platinum adislands on the Pt(111) facet. These adislands will be deposited on the surface using PVD. After this we will form well-defined vacancy islands in the surface through controlled sputtering and annealing. Finally, we will combine the two, i.e. have both vacancy islands and adislands. All of this should hopefully provide a sound basis for discussing the corrosion process of Pt(111) in perchloric acid.

In the very end of this section we will look at a contamination of the Pt(111) sample which frustrated us for a while.

#### 4.2.1 Clean Pt(111) and initial corrosion

As promised we will start out with just investigating a flat Pt(111) sample. To obtain the flat and clean Pt(111) surface we usually prepare it using three cycles of argon sputtering and annealing. The first cycle consists of sputtering $\sim 10$ monolayers off while heating from room temperature to around 800 K and then the sample is annealed to 1200 K at 1 K/s and held there for 2 minutes. The subsequent cycles happen at elevated temperatures as the sputtering routine is started while the sample is still cooling down from the 1200 K, usually this happens around 800 K. If we suspect there is carbon on the sample we dose $1 \times 10^{-6}$ mbar O$_2$ on the temperature ramp between 800 and 1000 K.

Figure 4.1a shows a representative 500 nm × 500 nm STM image of a clean Pt(111) surface we routinely observe by using the above procedure. An STM image with atomic resolution of the sample is shown Figure 4.1b. From the
4.2. Results

Figure 4.1: (a) 500 nm × 500 nm STM image of a clean Pt(111) surface. (b) Atomic resolution STM image of Pt(111) surface. The unit cell of the Pt(111) lattice is superimposed on the STM image and was found using SPIP’s fast Fourier transform module.

fast Fourier transform (FFT) of the atomic scale image it is possible to get the unit cell vectors of Pt(111) which can be used as a calibration for how well we measure with the STM. The atomic scale image and the corresponding FFT is shown in Figure C.1 in Appendix C. The large scale image show large, clean terraces free of contaminants and dislocations. Smooth monoatomic steps are separating these terraces.

In Figure 4.2a an electrochemical cycle between 0.06 and 0.9 V vs. RHE is shown. In this measurement the sample was exposed to five of these cycles before being taken out of the electrolyte at 0.5 V vs. RHE in the cathodic scan. Note that the voltammogram looks like the expected Pt(111) one. As can be seen on the post-EC STM image in Figure 4.2b not much has changed on the surface. The steps are still quite smooth and the terraces look relatively clean as well, aside from something reminiscent of “film grain” which is probably due to contaminants in the electrolyte or in the gas of the EC cube. In short Figure 4.2 shows that the Pt(111) surface is quite stable under these conditions (and for this amount of time) and that we can expect to get reasonably resolved images with the STM after the electrochemical measurement. The latter of which will
4.2. Results

Figure 4.2: (a) The 5th and final cycle from 0.06 to 0.9 V vs. RHE on a clean Pt(111) sample in 0.1 M HClO$_4$. (b) A 200 nm × 200 nm STM image of the surface after being exposed to the EC environment. As can be seen the steps still seem intact and the terraces clean. Prior to the EC treatment the sample was similar to the one shown in Fig. Figure 4.1.

be even more apparent in a moment.

It was alluded to above that the time spend in the electrochemical environment might be crucial to the stability of the Pt(111) surface. So we tried to measure for 100 cycles, as opposed to just five, at 100 mV/s between 0.06 and 0.9 V vs. RHE. The data in Figure 4.3 shows this measurement. As can be seen in the 150 nm × 150 nm images before and after the electrochemical treatment the steps are no longer as smooth as what they were prior to the electrochemical measurement. That seems to suggest that there is some kind of reordering or corrosion process going on, it just happens so slowly that you have to cycle many times before you see it with the STM. As can be seen in the difference of the voltammograms shown in Figure 4.3b, the voltammogram straightens somewhat up over time and the small feature around 0.12 V vs. RHE disappears. Furthermore the current decreases which can be attributed to the evaporation of electrolyte over time.

So the question now is whether we can observe a change on the surface if we on purpose try to e.g. oxidise the sample and reduce it again. In theory we should change the crystal structure through the incorporation of oxygen in
4.2. Results

Figure 4.3: (a) STM image prior to the EC experiment showing clean terraces and smooth steps. (b) The first and the 100th cycle of the experiment from 0.06 to 0.9 V vs. RHE. The measurement was stopped at 0.5 V vs. RHE in the cathodic sweep of the 101st cycle. (c) Post-EC STM image of the now slightly corroded surface.

the surface layer as mentioned in section 4.1. Figure 4.4 shows a series of three different measurements on a clean Pt(111) sample. Each measurement consists of a number of cycles between 0.02 and 1 V vs. RHE and 0.05 and 1 V vs. RHE at different scan rates before stepping the potential from 1 V vs. RHE to the desired potential and keeping it there for 10 s. Afterwards the potential was stepped down to 1 V vs. RHE again and a few more cycles were recorded. Finally the sample was taken out of the electrolyte at 0.2 V vs. RHE. It should be mentioned that the following procedures are overly complicated, but at the time of recording the data we tried doing many things at once and were still getting used to performing the measurements. If/when they will be carried out again it will certainly be more simple.

The experiment shown in Figures 4.4a and b shows a measurement where the sample was held at 1.2 V vs. RHE for 10 s and subsequently reduced again. The sample was cycled 11 times between 0.02 and 1 V and three times between 0.05 and 1 V at 200 mV/s and three times in the latter potential window at 50 mV/s. After the 10 s of chronoamperometry the sample was cycled between 0.05 and 1 V, twice at 50 mV/s and four and half cycles at 200 mV/s with the measurement being stopped at 0.2 V vs. RHE. As can be seen close to the step edge at the upper part of the STM picture in Figure 4.4b we start forming small adislands by treating the sample like this. However, at this point they are too few and far between to do meaningful statistics on them.
4.2. Results

Figure 4.4: (a), (c) and (e) show EC data where a clean Pt(111) sample was stepped from 1 V vs. RHE to 1.2, 1.3 and 1.4 V vs. RHE for 10 s, respectively, after EC cycling (see text). (b), (d) and (f) show the corresponding 300 nm × 300 nm post-EC STM images.
4.2. Results

If we go to higher potentials like 1.3 V vs. RHE as shown in Figure 4.4c and d we start forming more of these adislands, unsurprisingly. Prior to the chronoamperometric part of the experiment the sample had been cycled between 0.02 and 1 V vs. RHE 13 times and between 0.05 and 1 V vs. RHE four times at 200 mV/s and between 0.05 and 1 V vs. RHE four times at 50 mV/s for a total of 21 cycles. After the chronoamperometric step the sample was cycled again. This time solely between 0.05 and 1 V vs. RHE, three times at 50 mV/s and three and a half times at 200 mV/s. The measurement was stopped at 0.2 V vs. RHE in the last cycle. At this point there are enough of the adislands to do a statistical analysis. To this end SPIP’s Particle and Pore Analysis tool was used. The adislands cover roughly 7% of the surface and have a mean size of 53 nm² (giving the results in area as opposed to diameter makes more sense given the shape of the islands). The full size distribution along with more STM images is shown in Figure C.2 in Appendix C. It should be noted that the current shown in Figure 4.4c is not the real current. In fact it does not show the current to any satisfactory degree. The reason for this is that the potentiostat was mistakenly set to changing the so-called current range automatically during the measurement. Sadly (and unsurprisingly) that change coincided with the high currents during the oxidation and reduction of the surface.

Finally, if we bring the potential of the sample to 1.4 V vs. RHE for 10 s we see a lot of very small adislands all over the surface. In this case the sample was first cycled 10 times between 0.02 and 1 V vs. RHE and three times between 0.05 and 1 V vs. RHE at 200 mV/s and then four times between 0.05 and 1 V vs. RHE at 50 mV/s. After holding the potential for 10 s at 1.4 V vs. RHE the sample was cycled between 0.05 and 1 V vs. RHE, three times at 50 mV/s and four and a half at 200 mV/s before stopping the measurement at 0.2 V vs. RHE. Doing the statistical analysis we found that the adislands cover ~20% of the surface and have a mean size of ~2.5 nm in diameter based on 3883 (alleged) adislands in three STM images. In this case a lot of the adislands observed are approximately spherical meaning using the diameter of them makes sense. The full size distribution can be seen in Figure 4.12c in section 4.2.4 and more STM images are shown in Figure C.3 in Appendix C.

The base voltammograms measured after the three different treatments shown above can be seen in Figure 4.5 in conventional IV-plots. As can be seen the voltammogram barely changes after holding the sample at 1.2 V vs. RHE for 10 s. The only real observable change is seen as a small peak at 0.16 V vs. RHE in the cathodic part of the hydrogen UPD region of the voltammogram. When the potential is increased further features in both the anodic and cathodic part of the hydrogen UPD region becomes apparent. For the sample
4.2. Results

Figure 4.5: The three different CVs observed between 0.05 and 1 V vs. RHE after the corrosion experiments shown in Figure 4.4. The black dashed line is the CV observed during one of these experiments prior to the corrosion of the surface shown here for comparison.
4.2. Results

held at 1.3 V vs. RHE for 10 s we see two features right next to each other, one at 0.12 V, and one at 0.16 V vs. RHE in the cathodic scan like before, whereas there is only a visible counter peak to the former feature in the anodic part. Furthermore, there is a reversible feature right on the edge of the hydrogen UPD region at 0.29 V vs. RHE. Finally, the two neighbouring peaks in the cathodic part of the hydrogen region has grown even more and become slightly more well-defined in the scan recorded after corroding the sample for 10 s at 1.4 V vs. RHE. However now the one at 0.12 V is clearly largest. Likewise the peak at 0.12 V vs. RHE in the anodic part has grown as well.

The reason for performing the measurements as in Figure 4.4 by stepping and holding the potential constant for a certain amount of time is to deconvolve the effect of the upper potential and the time spent at oxidising potentials. If the measurement was carried out simply by sweeping the potential to a given upper potential and down again a desired number of times the scan rate would play a role as well. If, say, you measure at 50 mV/s and you increase your upper potential from 1.2 V to 1.3 V vs. RHE you add 4 seconds to the time spent at potentials above 1.2 V. Thus we chose to carry out our measurements using potential steps.

![Graph](image)

Figure 4.6: An experiment similar to that shown in Fig. 4.4a and b only this time the potential was held at 1.2 V vs. RHE for 100 s. As can be seen in (b) more adislands appear but the coverage is still much lower than resulting from applying 1.3 V vs. RHE for 10 s.

To see whether the time spent at oxidising potentials actually matter we
tried holding the potential at 1.2 V for 100 s instead of just 10 s. The result of this experiment is shown in Figure 4.6. By holding the potential longer at 1.2 V vs. RHE it appears as if we form more of the adislands observed previously (Fig. 4.4b). Although you would probably expect most of the oxidation of the surface to happen in the first half a second as the current spikes sharply and quickly decreases to a constant current of around 0.6 µA/cm². Furthermore, integrating the reduction peaks in the subsequent reduction for both the measurement in Figure 4.4a and in Figure 4.6a results in the larger one being found in the first measurement. So the data does not seem conclusive.

Figure 4.7: (a) shows an EC treatment similar to that in Fig. 4.4 only without the subsequent reduction. (b) A post-EC STM image taken after this measurement. The lack of adislands here is in stark contrast to how many we saw in Figure 4.4d.

Finally, we wanted to see whether the reduction after the potential excursion was crucial to forming the adislands. For the data shown in Figure 4.7, the sample was cycled 26 times between 0.01 and 1 V vs. RHE, one time between 0.05 and 1 V vs. RHE and four times between 0.06 and 1 V vs. RHE at 200 mV/s and four times in the final potential window at 50 mV/s before the potential was stepped to 1.3 V vs. RHE and kept there for 100 s. The contact was then broken at this potential. This should, if anything, give rise to more adislands than shown in Figure 4.4d if the subsequent reduction was not important. However, as we can see, there is barely anything on the surface. It more or less looks as clean as the one shown in Figure 4.2b.
4.2 Results

4.2.2 Platinum adislands on Pt(111)

In order to check whether platinum adislands would be stable in the electrochemical environment and look anything like the ones seen from our corrosion measurements we tried depositing a small amount of platinum on the Pt(111) single crystal. In doing so we would also obtain information on whether the adislands would change the voltammogram of the Pt(111) sample.

Figure 4.8: (a) STM image of Pt adislands deposited by PVD on the Pt(111) sample. (b) The voltammogram resulting from this sample. Note the new reversible feature at 0.12 V vs. RHE. (c) The post-EC STM image. As can be seen the adislands now look slightly smaller and more triangular. (d) The size distributions of the as prepared and post EC adislands given in area. More STM images are found in Figures C.4, C.5 and C.6

The platinum adislands were deposited through a PVD procedure. By heating a platinum rod we obtained a deposition rate of 0.0076 Å/s as measured by the QCM. The goal was to deposit less than a monolayer of platinum to just end up with adislands on the otherwise flat surface. In this case we deposited ∼ 0.49 Å at ∼ 290 K (which came about by cooling the whole lab down, to our
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dismay).

Figure 4.8a shows an STM image of the adislands as a result of this deposition, as can be seen they are mostly of monoatomic height. The deposition resulted in a surface coverage of 21% and adislands with a mean area of 36 nm\(^2\). Furthermore, it does not look like the adislands are preferentially shaped. The full size distribution can be seen in Figure 4.8d. Figure 4.8b shows the voltammogram obtained on such a sample between 0.05 and 1 V vs. RHE. The full electrochemical procedure of this sample consisted of 34 cycles between 0.02 and 1 V vs. RHE and five cycles between 0.05 and 1 V vs. RHE at 200 mV/s and then seven and a half cycles in the latter potential window at 50 mV/s before the measurement was stopped at 0.2 V vs. RHE in the cathodic scan. As can be seen it almost looks like the normal Pt(111) voltammogram except for the reversible feature in the hydrogen UPD region around 0.12 V vs. RHE and a small cathodic peak at 0.17 V vs. RHE. Finally, the post-EC STM image is shown in Figure 4.8c. Although the resolution in this case is not great we still see what looks like a kind of preferential shaping of the adislands. It seems like they are becoming more triangular as compared to the adislands in Figure 4.8a.

In fact if we do the statistical analysis now something peculiar has happened. Firstly, the coverage is only about 14% now as opposed to the 21% observed prior to exposing the sample to the electrochemical environment. Furthermore, the mean size of the adislands has gone slightly up and is now 39 nm\(^2\) compared to the 36 nm\(^2\) from before. The two size distributions are compared in Figure 4.8d.

To sum up the data shown suggest we can expect platinum islands to be stable to some extent on the surface. That is to say we still see them but they appear to be shaped preferentially after the electrochemical measurement.

4.2.3 Vacancy islands in the Pt(111) surface

In an attempt to further look into whether it was step or terrace corrosion taking place on Pt(111) we decided to prepare a surface with more steps on it than a sample prepared to be flat and clean. We would do so by having a well-defined structure thereby making it easy to see whether the structure survived the electrochemical environment or not. Again, this could also yield information on the voltammetry of Pt(111).

If a Pt(111) sample is exposed to the right sputter procedure it is possible to form well-defined truncated hexagonal vacancy islands in the surface of the sample. In doing so you more or less form an "inverted" 2D Wulff construction in the surface. This can give you information about e.g. the characteristic
directions of your surface or maybe step effects. As mentioned we tried to use it to see if we could observe step corrosion as these vacancy islands have two types of steps, namely steps forming \( \{100\} \) microfacets and steps forming \( \{111\} \) microfacets.\(^{[43]}\)

The procedure used to form the vacancy islands we will discuss here consisted of two of the usual cleaning cycles with \( \mathrm{O}_2 \) but annealing for 300 s at 1200 K as opposed to the usual 120 s. Then the sample was cooled down to 850 K where about 0.4 monolayers (20 \( \mu \mathrm{A} \mathrm{s} \)) were sputtered off. Finally, the sample was annealed at 830 K for 60 s. This gave rise to a vacancy island coverage of \( \sim 12\% \). The vacancy islands had a mean diameter of 17 nm. The full size distribution can be seen in Figure 4.9.

Figure 4.9: (a) STM image of the truncated hexagonal holes formed by the sputtering procedure. (b) The voltammogram of the sample as prepared (black) and after an oxidation and reduction cycle to 1.3 V vs. RHE recorded at 200 mV/s (red). (c) 300 nm \( \times \) 300 nm post-EC STM image of the surface of the sample. (d) The diameter distributions of the vacancy islands before and after the EC treatment. More STM images are shown in Figures C.7, C.8 and C.9.

Figure 4.9 shows the vacancy islands as imaged by the STM (more shown
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in Fig. [C.7]. As can be seen they are one layer deep and in the shape of truncated hexagons as expected. Otherwise the sample looks clean as we have seen previously. The steps run along the (110) directions of the crystal, with the long ones being of the \{111\} type and the short ones being of the \{100\} type mentioned before on account of free energy considerations [44, 43]. Figure 4.9b shows the voltammogram of the Pt(111) with the sputter holes before and after a potential excursion to 1.3 V vs. RHE. The full electrochemical measurement was as follows: Firstly, 16 cycles between 0.02 and 1 V vs. RHE and seven cycles between 0.05 and 1 V vs. RHE at 200 mV/s. Then three cycles in the latter potential window at 50 mV/s and four at 200 mV/s again. After this, one cycle between 0.05 and 1.3 V vs. RHE, six cycles between 0.05 and 1 V vs. RHE again, both potential windows at 200 mV/s. Finally six and a half cycle at 50 mV/s in the latter potential window before the measurement was stopped at 0.2 V vs. RHE in the cathodic sweep. Finally, Figure 4.9c shows a representative STM image of the state of the surface after such an electrochemical treatment.

As can be seen in the STM image afterwards (more shown in Figures [C.8] and [C.9]) it does not seem like the vacancy islands lose their shape all that much, in fact they are quite intact after the exposure to the electrochemical environment. It does seem like the steps of the hexagons are not quite as straight as they were prior to the electrochemical measurement, but this could be deposition of platinum adatoms on the step rather than corrosion. Note how the step in the bottom left quarter of the image has comparably more platinum on it than the steps of the holes. This suggests that the terrace is in fact supplying the adatoms and that it is not the steps themselves corroding. If we look at the the statistics of the vacancy islands after the electrochemical measurement we find that they now cover 19% of the surface and have a mean diameter of 17 nm. The size distributions of the as prepared vacancy islands and the vacancy islands after the electrochemical procedure is shown in Figure 4.9d. This sounds somewhat strange, that the mean diameter is more or less the same as before but the coverage is quite a bit higher. However, this might not be as strange as it sounds, and in fact it tells us something about our way of measuring, we will get back to all of this shortly in section 4.3.

4.2.4 Combining adislands and vacancy islands

To conclude this series of experiments we thought it would be interesting to mimic the surface of a corroded sample with our UHV preparation. That is forming both small vacancy islands and adislands on the surface. As we saw in the preceding section it appears as if the corrosion happens on the terraces of
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the sample thus we would expect to see tiny vacancies in the terraces. Thus our idea was to first clean and flatten the sample as usual, then sputter the sample very lightly to form tiny vacancies in the surface and finally deposit a little pit of platinum as in section 4.2.2 to form very small adislands, although this time we want them to be smaller.

![STM images](image)

Figure 4.10: (a) Shows a 300 nm × 300 nm STM image of the surface after the sputter plus PVD procedure. (b) Shows a 30 nm × 30 nm STM image of the same sample. In this image you can make out the tiny sputter holes in between the adislands.

After cleaning the surface like normally we sputtered ∼ 1 µA s at 334 K after which we deposited ∼ 0.34 Å platinum at 297 °C. This resulted in adislands with a mean diameter of 3.1 nm covering roughly 16.5 % of the surface. The size distribution is shown in Figure C.10 along with more STM images. Figure 4.10 shows two STM images of the surface, one with a size of 300 nm × 300 nm where you can see the evenly distributed adislands and one with a size of 30 nm × 30 nm where you can make out the tiny sputter holes in between the adislands.

The full electrochemical treatment consisted of 33 cycles in total in the following order: 23 cycles between 0.02 and 1 V vs. RHE and four cycles between 0.05 and 1 V vs. RHE at 200 mV/s. Finally, the latter potential window was measured six times at 50 mV/s before the measurement was stopped in the cathodic scan of the seventh cycle at 0.2 V vs. RHE. The black voltammogram
Figure 4.11: A comparison of a CV from the sample prepared with a combination of Ar sputtering and PVD (black) and one obtained after corroding the surface (red). The corrosion process was the same as the one in Fig. 4.4e and f, i.e. a potential excursion to 1.4 V vs. RHE for 10 s.

As can be seen the voltammograms of the two systems are closely resembling each other. The electrochemically corroded sample shows more smeared out OH adsorption and desorption features. Furthermore the voltammogram obtained here is rather broad from 0.9 to 1 V vs. RHE which is a hallmark of corroded Pt(111) samples (as we also see in Fig. 4.5). In both measurements we had some oxygen in the EC cube as can be seen from the general downshift of the two voltammograms. Compared to a normal Pt(111) voltammogram (e.g. Fig. 4.2a) we see three new features in the hydrogen region of the cathodic scan, two of them with counter peaks in the anodic scan. When we just had adislands we only really saw the reversible feature at 0.12 V vs. RHE, with just a small bump at 0.17 V vs. RHE. In the case of the vacancy islands we only really saw anything new after the potential excursion to 1.3 V vs. RHE in the feature at 0.16 V.
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Figure 4.12: (a) Post-EC STM image of the sample prepared using light Ar sputtering and PVD. (b) The STM image of a clean Pt(111) sample exposed to potential cycling and an excursion to 1.4 V vs. RHE for 10 s (see Fig. 4.4e-f). (c) The size distributions of the adislands on the two different samples. More STM images of the UHV prepared sample after the EC treatment is shown in Fig. C.11.
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In Figure 4.12 post-EC STM images of the sample from this measurement and the sample shown in Figures 4.4e and f are put next to each other for comparison. Figure 4.12a shows the sample prepared in UHV using argon sputtering and PVD after it had been exposed to the electrochemical treatment explained above. If you compare it to the sample that was held at 1.4 V vs. RHE for 10 s shown in Figure 4.12b the adislands look somewhat larger. It appears as if the islands formed through the PVD procedure are larger than those you get initially from corrosion. In fact, the statistical analysis of the adislands on this UHV prepared sample after the electrochemical measurement detailed above gives a surface coverage of 20.6% and adislands with a mean diameter of 3.7 nm, which means it is a somewhat higher coverage and slightly larger adislands than before the electrochemical treatment. For the sample corroded at 1.4 V vs. RHE the coverage was 19.5% and the mean diameter was 2.5 nm. The statistics of the two samples can be found in Figures C.11 and C.3 in Appendix C, respectively, the two distributions of diameters are co-plotted in Figure 4.12c to show the reasonable agreement between the two.

4.2.5 Possible molybdenum oxide contamination

As a side note we will take a little bit of time to look at a possible molybdenum oxide contamination. While trying to perfect our Pt(111) voltammogram we often encountered a redox feature in the double layer region of the voltammogram. More precisely around 0.44 V vs. RHE. Naturally we wanted to get rid of this as it meant our method was not working as intended. In fact, if you look very closely at the red voltammogram in Figure 4.5 it seems like there is a small bump right before and right after the hydrogen UPD region in the cathodic and anodic scan, respectively.

We had noticed the anomalous feature in the voltammogram tended to show up when the electrolyte went all the way to the edge of the crystal. In order to test this hypothesis we designed an experiment where we would prepare a flat and clean Pt(111) sample (as shown in Fig. 4.1) and gradually increase the radius of the meniscus touching it while cycling between 0.05 and 1 V vs. RHE. The meniscus was increased just by turning the stopcock on the supply bottle very carefully while monitoring the meniscus through the window in the EC cube.

Figure 4.13 shows a measurement where the meniscus looked as in Figure 4.13a and where we started out by cycling the sample 20 times between 0.01 and 1 V vs. RHE at 200 mV/s. Then it was cycled between 0.05 and 1 V vs. RHE at 200 mV/s 27 times and at 50 mV/s 12 times. The scan rate was
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Figure 4.13: (d) Shows three different CVs each one corresponding to the sub-figures with the same label (a), (b) and (c). As expected the current increases as more and more electrolyte is dosed to the cell. Furthermore, the peak at 0.44 V vs. RHE only shows up when the electrolyte covers the whole crystal.
then set to 200 mV/s again and the meniscus was increased to the size shown in Figure 4.13. As can be seen the current only slight increases in the voltammogram but no new features show up. After 19 cycles more the meniscus was increased again to the size shown in Figure 4.13. At this point the meniscus covers the entire crystal, more or less, and the current has increased a fair bit again. But as can be seen a redox feature at 0.44 V vs. RHE has appeared now.

The voltammogram alone does not reveal the source of this extra peak, now we just have an idea of which part of the crystal gives rise to it. We could not reproduce this feature in the voltammogram by measuring outside of the EC cube on the tabletop, but otherwise using the same setup, on a Pt(111) crystal prepared by RF heating in a gas stream of 5% hydrogen in argon. This suggested the problem came from the UHV chamber in some way. Our best guess was that the molybdenum sample holder somehow contributed to this. Furthermore, this is not completely unheard of either as Reichelt et al. has observed it on a silver sample in a molybdenum sample holder not unlike ours.

Figure 4.14: (a) An admittedly poor quality picture of the Pt(111) as seen by the camera in the XPS setup. We measured several points on either side but only a few of them are shown in (b) which shows the XPS measurement of the Mo 3d region and the Pt 4f region. A AlKα with a spot size of 50 µm was used. 20 scans were measured for each shown spectrum.

To investigate whether we had molybdenum on the our Pt(111) crystal, or at least on the edges of it, we performed an XPS measurement on it looking specifically for the Mo 3d and the Pt 4f peaks close to the edges of the sample. We did so by setting up a line scan starting on the sample holder and ending
fairly centrally on the sample itself. It was set up to measure the XPS signal both on the very edge and close to it on either side, i.e. on the slanted part of the sample holder and slightly away from the edge on the sample. A AlK$_\alpha$ source was used for these measurements.

Figure 4.14 shows a picture of the Pt(111) crystal taken with the camera in the XPS setup. This picture shows the edge of the crystal. The sample holder is above this edge and the sample itself is below it. The XPS spectra shown in Figure 4.14 shows that the Mo 3d signal is still present $\sim 346\mu m$ from the edge of the sample on the crystal face. However, the point $\sim 692\mu m$ from the edge did not show any molybdenum, hence it was omitted from the plot to avoid cluttering it too much. The obtained XPS spectra seem to be shifted a few electronvolts with respect to the tabulated values\[46, 47\]. Finally, the molybdenum peaks shift to higher binding energies on the edge of the crystal compared to on the sample holder suggesting it is molybdenum oxide.

4.3 Discussion

To finish up this chapter concerning our experiments on Pt(111) we will look at and discuss the results presented here in relation to those found in the literature. The results will also be used to argue our setup’s relevancy and what the methodology used here might offer to the field.

The first point we wanted to address with our measurements on Pt(111) was whether our electrochemical setup could be trusted. If that was not the case the whole setup’s point of being able to prepare well-defined samples and correlate their surface structure with their electrochemical response would fall to the ground. However, as we showed in Figure 4.2a in section 4.2.1 our Pt(111) voltammograms in 0.1 M HClO$_4$ looked more or less exactly like those reported in the literature\[35]\.

That being said we also showed in subsection 4.2.5 that it appears as if the edges of our Pt(111) might contain an molybdenum oxide contamination. At this point we believe that the molybdenum sample holder is oxidised when we occasionally clean the Pt(111) sample by leaking in oxygen at elevated temperatures ($\sim 800$-$1000$K) as mentioned in the beginning of section 4.2.1). Molybdenum trioxide is known to evaporate below $1000$K\[48\], whereas metallic molybdenum will not evaporate until temperatures above $2000$K\[49\]. As we are only cleaning the face of the crystal with argon sputtering the side could act as a molybdenum reservoir, so to speak. In an attempt to alleviate this issue we have tried carburising our sample holders to make them much harder (this in-
cidentally also makes them slightly easier to slip in and out of the manipulator
houses). However, we have not carried out a detailed study of whether this
helps, we do know that it makes it considerably more challenging to spot weld
the foil on the back of the sample onto the sample holder.

We also looked at the corrosion of Pt(111) and whether we could see the
change on the surface of the sample after oxidising it and reducing it again. We
noticed that a slight change of the steps was already observed after 100 cycles
in the relatively narrow potential window from 0.06 to 0.9 V vs. RHE. After
this we decided to corrode the surface by stepping the potential up to 1.2, 1.3
and 1.4 V vs. RHE for 10 s before stepping it back down again to 1 V vs. RHE.
We observed the formation of adislands on the terraces of the crystal. For the
experiment where we stepped the potential to 1.2 V vs. RHE we only saw a
small amount making any statistical analysis a bit nonsensical. For the two
other experiments we noticed and increase in adisland coverage with increasing
potential (7 and 20 %, respectively). Interestingly the adislands formed after
going to 1.3 V vs. RHE and subsequently reducing it looked a lot like the
dendritic growth of platinum on Pt(111) usually observed in UHV depositions
below room temperature\cite{50}. Furthermore, these islands were rather large with
a mean area of 53 nm$^2$. The experiment to 1.4 V vs. RHE showed almost circular
adislands with a mean diameter of 2.5 nm. The size of the observed adislands
are in good agreement with results in the literature, where several studies have
found adislands in the 2 to 5 nm range after electrochemical roughening, albeit
in various concentrations of H$_2$SO$_4$\cite{51, 52, 53}. A more recent study in 0.1 M
HClO$_4$ found adislands of around 8.9 nm after the electrochemical roughening
procedure\cite{54}. However, there seems to be consensus on increasing the upper
potential level resulting in smaller adislands (which we also saw here)\cite{55, 41}.
In the study by Jacobse et al. an upper potential limit of 1.35 V vs. RHE
was used as opposed to the 1.4 V v. RHE used in this work. It could be that
had we looked at the adislands after going to 1.3 V vs. RHE several times and
not just the one time for 10 s we would have found a similar size distribution.

In order to better understand the corrosion process we designed a series of
experiments where we changed the surface structure in various ways. Firstly,
we deposited platinum adislands on the sample. We found a surface coverage of
21 % of adislands with a mean area of 36 nm$^2$. The voltammogram only really
4.3. Discussion

showed one new feature at 0.12 V vs. RHE, and maybe a hint of one at 0.16 V vs. RHE (cathodic). After the electrochemical treatment we still had plenty of adislands on the surface although now they only covered roughly 14% of it and were apparently 39 nm$^2$ on average, however the size distributions from before and after the electrochemical treatment were in reasonable agreement with each other. Finally, they became more triangular during the electrochemical measurement, a shape we did not really observe for the potential step experiment to 1.3 V vs. RHE. However, this can probably be explained by the large difference in time spent in the electrolyte. The electrochemically induced adislands were cycled just 6.5 times after the formation of adislands, whereas the PVD deposited adislands were cycled a total of 46.5 times. It should be noted that the triangular shape observed here is again known from epitaxial growth in UHV, both experimentally\[56,57\] and theoretically\[58\]. Initially the ”direction” (and thus step type) of the triangles were thought to be a temperature effect but it later turned out to be an adsorbate effect\[59\]. This and the fact we saw dendritic adislands from our electrochemical corrosion (Fig. 4.4d) suggests the processes in islands formation in UHV and in the electrochemical environment are not too dissimilar. Finally, the fact we only really see one new feature in the voltammogram also tells us a corroded surface is not just adislands on an otherwise flat sample. This makes a lot of sense since the adislands have to come from somewhere when they appear during a corrosion measurement, that means the surface will also contain holes where the platinum atoms used to be.

After this we formed hexagonal vacancy islands in the surface to see whether the steps would change significantly as we corroded the sample. This means an increased amount of \{111\} and \{100\} steps. We started out having vacancy islands covering 12% of the surface with a mean diameter of 17 nm. After cycling once to 1.3 V vs. RHE we could see both adislands and vacancy islands on the surface of the sample. The vacancy islands now cover 19% of the surface while their mean diameter has not changed. Furthermore, the whole size distribution seems to be almost identical to the one found prior to the electrochemical treatment (Fig. 4.9d).

At this point it is pertinent to keep in mind exactly what you or any researcher is looking for when using STM for imaging a sample. When the sample was prepared the objective was to get a good overview of the surface and the distribution of the vacancy islands for statistical purposes, this in general means large scale images. After the electrochemical treatment we wanted to see whether the steps have changed in an obvious way. Thus most of the images are on a fairly small scale and focused on areas with vacancy islands. As we can see in Figure C.4a, the density of vacancy islands is unsurprisingly much
higher on the terraces. The large scale images taken prior to the electrochemical measurement are much more likely to include areas with a lot of steps close to each other thereby lowering the density of vacancy islands and thus the calculated coverage. Given that the vacancy islands have not changed in size at all it would be remarkable if they actually covered more of the surface. Lastly, in general when using SPIP to calculate coverage like this, the software tend to recognise more things as either particles or pores on the surface. This is due to the lower resolution and the ”glitches” introduced by having had electrolyte on the sample. That means you are likely to overestimate coverage (this could also explain parts of the results found in the case of deposited adislands).

In terms of the voltammetry we only saw a small change in the cathodic sweep of the hydrogen UPD region where a feature appeared around 0.16 V vs. RHE after the corrosive sweep. Given the shape of the vacancy islands was more or less unchanged it does not seem likely that corrosion of platinum happens from steps preferentially. On the other hand we cannot say that it only happens from terraces. In any case the corosions process described in section 4.1 and suggested by various researchers seems to be supported by the results shown here[39, 40, 41].

The last surface we prepared was one featuring both tiny sputter holes and small adislands. The adislands roughly covered 16.5% of the surface with a mean diameter of 3.1 nm. This gave rise to a voltammogram closely resembling that of the sample that had simply been corroded by applying a potential of 1.4 V vs. RHE for 10 s. Considering the great agreement between the size distributions of the adislands (Fig. 4.12c) this might not be that surprising. Again we see features at 0.12 and 0.16 V vs. RHE with the latter only being present in the cathodic sweep. There is also a suggestion of a feature at 0.29 V vs. RHE. In terms of the shape of the adislands, they also appeared somewhat more triangular after the electrochemical treatment.

Peaks in the hydrogen UPD region, like those described above, have been observed in the literature before. Gómez-Marín and Feliu found peaks at 0.13 and 0.28 V vs. RHE and owed them to \{110\} and \{100\} type defects, respectively[60]. van der Niet et al. reported features at 0.125 and 0.27 V vs. RHE again owing them to (110) and (100) steps, respectively. However, they also noticed a pH dependence of these peaks suggesting the features were in fact related to both adsorption of hydrogen and OH meaning the observed current could possibly be assigned to a displacement of hydrogen in favour of OH in the anodic sweep and vice versa[42]. The peak we observe at 0.16 V vs. RHE which to begin with is more prominent than the one at 0.12 V vs. RHE has to the best of our knowledge not been discussed in the literature before.
4.3. Discussion

In our measurements we observed the feature at 0.12 V vs. RHE clearly when measuring on the small adislands plus sputter holes, the larger adislands and the sample where the potential was stepped to 1.4 V vs. RHE for 10 s. If we assume our triangular adislands mainly consist of \{111\} steps (Fig. C.12), we would have the same type of sites as found on the (554) surface measured by Gómez-Marín and Felíu [60], also illustrated by Björling et al. [61]. In other words, this suggests that the electrochemical environment promotes adislands with a majority of \{111\} steps. However, as we do not have atomic resolution of the steps, or another complimentary measurement it cannot be confirmed completely.

The peak at 0.29 V vs. RHE is only really observed here when we have corroded the sample above 1.3 V vs. RHE or on purpose formed small sputter holes. The large vacancy islands did not give rise to a feature in this part of the hydrogen UPD region. From the data shown here it is difficult to conclude what could give rise to this particular feature, but it seems to be related to the formation of small holes in the sample surface. It could be that if we had formed smaller vacancy islands of the same shape thereby having a higher density of both (111) and (100) steps, that we would see a larger feature here. According to the observed adislands it seems like the (111) step is clearly preferred meaning the (100) might only be quasistable on a Pt(111) surface under electrochemical conditions. Thus it is only formed by eating having it from the start (as with the (544) surface in Gómez-Marín and Felíu’s work [60]) or through the sites formed during corrosion procedures.

Finally, the feature at 0.16 V vs. RHE is only present for a certain amount of time during corrosive cycling. After a continuous cycling the feature disappears again as seen in Figure C.13 in Appendix C. This suggest it is just a quasi stable surface state which we can achieve given we can change the surface slowly on the atomic scale. However, it is inconclusive at this point and further studies will have to be carried out in order to understand this.

In summary, we have used a Pt(111) sample to test the capabilities of our newly built setup and found that it can produce convincing results in very good agreement with the literature. We saw that we through our corrosion of Pt(111) could not only measure the same voltammograms as those found in the literature but also get a good enough resolution with the STM after the electrochemical measurement to observe adislands of the same size as those reported by others. We showed we were capable of preparing samples in UHV and observe a change in the measured voltammogram as well. Throughout this we also noted that some of our results suggest epitaxial growth of platinum adislands in UHV and under electrochemical conditions seem to favour the same shape.
of adislands meaning the growth mechanisms are not that different, however
given adsorbates play a role in UHV it is too early to tell whether e.g. the
anion in the electrolyte does so too. Finally, it was highlighted how comple-
mentary techniques, such as XPS, can be used to better understand our results
from the combined UHV and electrochemical setup by looking for a potential
molybdenum oxide contamination.
Chapter 5

Towards understanding copper as an electrocatalyst

Since Hori’s\cite{62, 63} pioneering work on catalysts for the electroreduction of CO$_2$ to useful fuels and chemicals copper has received a lot of attention. The reason for this is that copper as the only pure metal can reduce CO or CO$_2$ to a range of valuable products such as methane, ethylene, acetaldehyde, ethanol, propionaldehyde and propanol with reasonable Faradaic efficiencies\cite{64, 65}. As many other metals copper also produces hydrogen but this is a reaction researchers would like to impede. This broad product distribution is interesting from a scientific perspective but in industrial applications you ideally just want the desired product and nothing else so you will not have to waste time and resources on separating products after the catalytic reaction. Therefore researchers have spend a lot of time trying to understand why copper produces the products it does, which sites on the copper catalyst is responsible for this production and of course whether it is possible to design a catalyst taking advantage of any findings.

There are several reasons for why this is not as straightforward as one could have hoped. Firstly, the reduction of CO$_2$ in itself is rather complicated. With the range of different products you can expect to produce you can also expect to deal with a myriad of different reaction pathways\cite{63, 64, 66, 67, 68}. Thus it is very difficult to deal with from a theoretical standpoint as there are so many combinations and possibilities to consider. And that is before we even get to discussing active sites on the catalyst. Secondly, copper itself is a difficult ma-
5.1. The electrochemistry of copper single crystals

terial to work with experimentally meaning there in general are a lot of results in the literature that do not quite fit together, some of these will be introduced in section 5.1. Even something as relatively well-defined as single crystals have not been agreed upon yet. Where platinum, as we saw in chapter 4, is a great example of a material where you know what you can expect of e.g. your voltamogram, copper simply is not. One of the issues in terms of experiments is copper’s oxyphilic nature. Copper oxidises readily and thus it is rather challenging to prepare outside of UHV like how you can with platinum. People have tried a lot of different combinations of e.g. mechanical polishing and electropolishing but it does not give voltammograms quite like those seen from UHV prepared samples. We will get back to this later in this chapter. Finally, it does not seem like copper is actually very stable at all during electrochemical cycling which further compounds the challenges. In fact, a few EC-STM studies have looked into the restructuring of copper during electrochemical cycling and found that both polycrystalline and single crystalline samples restructure [69, 70, 71, 72].

In this chapter there will be a brief overview of some of the literature related to the electrochemistry of copper single crystals, especially Cu(111) and Cu(100). This will show why model studies like the ones presented here are necessary. After this we will get to the results obtained throughout this PhD project. Finally, said results will be discussed, again with a view to place them in the context of the literature.

5.1 The electrochemistry of copper single crystals

Our work on copper single crystals started when A. K. Engstfeld was looking into the copper literature (mainly related to the electrochemical reduction of CO and CO₂). He noticed apparent discrepancies in the data reported. When you report your results on a platinum-based catalyst you will often include the base voltammogram of your catalyst and compare it with that of the pure platinum catalyst or a platinum single crystal when measuring on model systems. This way of reporting does not seem to have carried over to the electrochemical copper literature. Everyone knows what a Pt(111) voltammogram should look like but the few studies which actually report voltammograms from copper single crystals cannot seem to agree completely. Given that a voltammogram can serve as a fingerprint of a given system it would be a useful tool to add to the toolbox of diagnostic methods.
5.1. The electrochemistry of copper single crystals

As alluded to above, and to be clear, there have been studies on copper single crystals, also with regards to the electrochemical reduction of CO or CO$_2$. Often it is just difficult for other research groups to reproduce results. Either because there is no way to tell whether a single crystal prepared using a certain procedure behaves in the same way electrochemically as one prepared using another procedure\cite{73} p. 192-193, or because the study was carried out in an electrolyte with few other corroborating measurements meaning there are very few comparable data points\cite{74, 75, 76, 77, 78}. To the best of our knowledge only one study on the reduction of CO$_2$ contains a voltammogram of the investigated copper single crystals in 0.1 M KOH\cite{79, SI}.

If we include the literature that does not necessarily have to do with electroreduction of CO or CO$_2$, or indeed electrocatalysis in general, there are a number of studies investigating the electrochemical and structural properties of copper single crystals in both KOH and NaOH. However, many of these do not agree with each other on the voltammetry\cite{80, 81, 82, 70, 83, 79}, or simply only show very wide potential windows meaning the large current associated with the oxidation or reduction of the copper sample completely overshadows the finer details unique to a given copper facet\cite{84, 85, 86, 69, 87}. As we shall see later in this chapter the voltammogram of Cu(111) and Cu(100) is very dependent on the exact lower and upper potential limits, which further complicates the matter. Furthermore, a copper single crystal cycled electrochemically between the hydrogen evolution and oxygen evolution potential will give rise to voltammograms roughly looking like that of a polycrystalline sample (Fig. 3.13).

In general a low coverage of OH$^-$ is thought to be observed as the reversible feature around $-0.15$ V vs. RHE and around 0.1 V vs. RHE on Cu(100) and Cu(111), respectively\cite{86, 88, 70, 83}. After going through a region reminiscent of the double layer region on Pt(111) the anodic oxidation starts around 0.45 V vs. RHE. As the potential is increased further the copper sample goes through various oxidation processes. From forming Cu(OH)$_2$ over Cu$_2$O and CuO to Cu$_2$O$_3$\cite{69, 70}. The voltammetric features observed in the mentioned potential window seems to be very dependent on the exact preparation procedure of the copper electrode, as we showed recently\cite{89}, so we will pay special attention to that in the upcoming results.

Given the lack of any real consensus in the literature we decided to see what copper single crystal voltammograms would look like if we prepared the sample under the very well-defined UHV conditions as we did with Pt(111).
5.2 Results

The initial measurements on copper were on Cu(100) samples. As this was the surface A.K. Engstfeld had started working on in connection with his setup combining XPS and an electrochemical flow cell as mentioned in section 3.2. He started out looking the literature on this copper facet and found discrepancies. His idea was to get clean XPS spectra of the copper sample and measure the voltammogram after a clean transfer to the flow cell, much like what our setup can do but using XPS instead of STM. Naturally our setup could provide complementary measurements meaning we could correlate clean samples from both STM and XPS with a voltammogram. Some of these results can be seen in [89]. Later on we spent a considerable amount of time looking into Cu(111). We did this because we assumed it would be more tolerant to oxygen due to its close-packed structure meaning it would be somewhat more simple carrying out the measurements.

In this section we will firstly look at Cu(111) as it is the surface we have spend the most time on. During this we will also look at the importance of being able to immerse the sample under potential control. Afterwards we will look at some results on Cu(100) before discussing what the setup used here brings to the table. Lastly, a couple of the measurements on copper single crystals prepared outside of UHV at KAIST will be shown as well. The latter part is to investigate whether we can in fact get the same voltammogram by preparing the samples under laboratory conditions and not in UHV.

The measurements presented here have been carried out in 0.1 M KOH (99.995 Suprapur, Merck, unless otherwise stated). A lot of studies found in the literature have been carried out in 0.1 M NaOH but KOH and NaOH seem to give rise to the same voltammogram as far as we know [89].

5.2.1 Cu(111)

The preparation procedure used to prepare clean, flat Cu(111) samples is fairly similar to that of preparing Pt(111) samples. However, in this case we only heat the sample to 1000 K during the annealing and only sputter the sample while it is cold. At times we also let in a tiny bit of oxygen through the piezo valves to help get rid of e.g. carbon species from the surface. Some times this can be seen in the STM images of the as prepared samples through either very straight step edges or dark spots on the terraces.

After exposing the sample to the aforementioned procedure we routinely obtain surfaces like the one shown in Figure 5.1. As can be seen the surface
5.2. Results

Figure 5.1: A 500 nm × 500 nm STM image of a Cu(111) sample prepared in the UHV chamber. Aside from being very clean and flat in general, the sample also contains a number of dislocations.

is relatively flat and clean and consists of large terraces separated by smooth steps. A couple of dislocations can be seen as well.

After characterising the sample with the STM we performed the electrochemical measurement. Figure 5.2a shows the voltammogram obtained from a flat and clean Cu(111) sample in 0.1 M deaerated KOH when cycling from −0.2 to 0.45 V vs. RHE. As mentioned in section 5.1 this potential window was chosen as it acts as a kind of fingerprint of the sample due to the fact the electrochemical features in this region depend a lot on the preparation procedure. The full electrochemical procedure consisted of immersing the sample at 0.33 V vs. RHE under potential control, followed by four cycles between −0.2 and 0.45 V vs. RHE before the measurement was stopped in the cathodic scan of the fifth cycle at 0.33 V vs. RHE and the sample was taken out under potential control. As can be seen the voltammogram features just one reversible redox feature around 0.11 V vs. RHE. The charge associated with this feature is roughly 80 µC/cm² or about 0.28 monolayers of adsorbed OH assuming a planar density of 1.767 × 10¹⁵ atoms/cm². At the upper potential we are right at the edge of oxidising the sample, which fits with the Pourbaix diagram shown in Figure D.1 whilst we start seeing hydrogen evolution if the potential gets much
5.2. Results

Figure 5.2: (a) The first and the fourth cycles of CV between $-0.2$ and $0.45$ V vs. RHE on Cu(111) after immersing the sample at $0.33$ V vs. RHE under potential control. (b) The post-EC STM image after taking the sample out again at $0.33$ V vs. RHE under potential control. We see rather large terraces but many of the steps are not very smooth.

more negative. As we shall see shortly, the exact potential limits matter a great deal to the features observed in this potential window.

Figure 5.2b shows a $500 \text{ nm} \times 500 \text{ nm}$ STM image obtained after this rather short electrochemical measurement. As can be seen we still observe quite large terraces but a lot of the steps are no longer as smooth as we observed on the as prepared sample. In other words the sample survives a measurement of this duration and under these parameters but if we compare it to the Pt(111) after a short electrochemical measurement (Fig. 4.2) then it is not nearly as nice. In general the STM image shown here is a good one, too. It should be mentioned that performing STM after an electrochemical measurement in KOH is not as simple as had the measurement taken place in HClO$_4$. When KOH is heated or pumped down it crystallises as opposed to HClO$_4$, which just evaporates. That means that depending on how well you managed to remove as much KOH as possible with the Kimwipe prior to pumping the EC cube down again has an influence on how well you will be able to do STM afterwards. And in reality it could be something as random as where the STM tip happens to ”land” on the sample, whether it is right on top of leftover KOH or not.
5.2. Results

Figure 5.3: Cu(111) CVs with varying lower potential limit. As can be seen even before the onset of the HER the anodic peak at 0.11 V vs. RHE starts shifting to higher potentials and decreases. As can be seen in the magenta CV, which was measured after the HER potentials, the process seems reversible with a caveat (see text for details).

Had we gone to more negative potentials we would get nearer to hydrogen evolution and that actually turns out to be important for the voltammogram. As soon as we bring the sample to hydrogen evolution potentials the voltammogram changes reversibly. Figure 5.3 shows the voltammogram after going to more negative potentials. As can be seen the redox feature in the anodic scan quickly shifts to higher potentials and decreases and its counterpart in the cathodic scan decreases as well. The full electrochemical procedure up to the magenta voltammogram consisted of eight cycles in the usual region, four at 100 mV/s and then four at 50 mV/s, two cycles down to −0.4 V vs. RHE, two cycles to −0.5 V vs. RHE, one cycle to −0.6 V vs. RHE, three cycles to −0.7 V vs. RHE and finally four cycles in the usual region again. The magenta voltammogram was measured after the potential excursions and it shows the feature at 0.11 V vs. RHE growing back again. However, it also shows an anomalous peak at 0.32 V vs. RHE. We believe the reversibility of the OH feature depends on
whether this anomalous peak is there or not.

![Graph of Cu(111), 0.1 M KOH, 50 mV/s](image)

Figure 5.4: A CV of Cu(111) prepared in UHV showing how quickly the anomalous feature at 0.32 V vs. RHE can show up.

As alluded to above it seemed like the voltammogram shown in Figure 5.2a was not stable for a very long time. The feature we see appearing in Figure 5.3 shows up regardless of whether the samples is cycled to HER potentials or not as shown in Figure 5.4. Currently our best guess is that the feature is related to a contamination of the surface. This will be discussed further in section 5.3.

Agreeing on a voltammogram

When we first started measuring the voltammogram of Cu(111) we would observe two distinct voltammograms. One much like the one shown in Figure 5.2a, but with one or two extra features in the cathodic scan negative of the main redox feature, and one much like the one reported by Schouten et al. [83]. Naturally we wanted to investigate what gave rise to these two voltammograms and which one we thought would be closest to a voltammogram of an ideal Cu(111) electrode. Initially when we noticed this we were working on implementing the fourth electrode necessary for immersing samples under potential control.
5.2. Results

Every time we immersed our sample under potential control we observed the former and we observed the latter when immersing without potential control. Evidently we were dealing with an effect of letting the sample oxidise a bit too much at open circuit potential before starting our measurement. However, as we will see shortly that was not actually the case.

During our tests of the potential control add-on to the system we had systematically introduced an error in our measurements. We would mix 1 L of 0.1 M KOH and use it on two subsequent days before mixing the next litre. At the same time we alternated between measuring with and without potential control meaning we only used potential control when the electrolyte was freshly prepared and vice versa. When we realised this we immediately measured the other way around. Doing so revealed it was actually the wait between mixing the electrolyte and using it that caused the voltammogram to change.

![Figure 5.5: (a) Voltammograms showing the effect of having dissolved glassware in the electrolyte when measuring Cu(111) between $-0.2$ and $0.45$ V vs. RHE. (b) Two ICP-MS measurements on 0.1 M KOH taken directly from the PFA and glass flasks respectively.](image)

At this point it occurred to us that mixing our KOH in a volumetric flask made from glass might not be that great an idea given that it is well-known that KOH dissolves glass\[90]\, and silicon has been observed to deposit on copper during electrochemical measurements\[65]. As explained in section 3.2 we normally use a PFA supply bottle when measuring in KOH. We acquired said supply bottle (along with a volumetric flask etc.) when we noticed the above effect in our measurements.
5.2. Results

Figure 5.5 shows three different voltammograms, one where the electrolyte was mixed in a PFA flask and the PFA supply bottle was used, one where the electrolyte was mixed in a glass flask and used immediately (the supply bottle was the glass one as well), and finally one where the KOH was left in the glass flask overnight. As can be seen the addition of the (presumably) small amount of glass in the freshly prepared electrolyte from the glass flask already gives rise to lower current in the redox feature at 0.11 V. Furthermore, two new, small features appear negative of this expected peak. If we let the KOH stand in the glass flask over night we get the blue voltammogram shown in Figure 5.5. Now there is a very clear separation between the anodic and cathodic feature and the current in general is much lower than observed otherwise. ICP-MS measurements on electrolyte samples taken directly from the PFA flask and from the glass flask containing the day old KOH is compared in Figure 5.5. As expected the electrolyte sample from the glass flask contains large quantities of the four different elements measured (B, Al, Si and Pb) compared to the electrolyte sample from the PFA flask. The elements measured in the ICP-MS measurements were chosen according to the study by Mayrhofer et al. The exact values shown here are by no means suited to be used in a quantitative analysis but gives a qualitative picture of the situation.

Lastly, we also noticed something strange in our STM images. Figure 5.6 shows two STM images of the exact same area of our Cu(111) sample. However, the images were taken using two different bias voltages. As can be seen when scanning with a higher potential something that was almost invisible at lower potentials appears at the step edges. This could potentially be part of what causes the voltammogram change when the electrolyte has been allowed to stand in a glass flask for a day. Furthermore, this was taken after a cleaning protocol of argon sputtering and annealing so it appears as if it can be very challenging, or at least time consuming, getting the crystal back to its initial state.

Importance of potential control

When we first started working on copper measurements we noticed that the open circuit potential of our copper electrodes were located in an oxidising region (> 0.5 V vs. RHE). Due to this we started coming up with ideas on how to incorporate a fourth electrode in our rather spatially confined setup. The final solution ended up being the one shown in Figure 3.6. We want to avoid oxidising our samples too much before controlling the potential of them as we are worried the subsequent reduction might ruin the surface we prepared. Especially if we have prepared samples with sensitive surface structures such as
5.2. Results

Figure 5.6: The same 300 nm × 300 nm area imaged by STM twice but with different tunnelling parameters. For (a) we used a potential of $V_t = 1.097\,\text{V}$ (for roughly two thirds of the picture) and current of $I_t = 1.090\,\text{nA}$ and for (b) we used $V_t = 3.688\,\text{V}$ and $I_t = 1.110\,\text{nA}$. Using the very high bias voltage as in (b) reveals something at the step edges that was very vague with the lower bias voltage.

For the data shown in Table 5.1 we prepared our Cu(111) as we usually would and reduced it after spending more or less time at open circuit potential. As can be seen the more time the sample spends at open circuit potential the larger the reduction charge due to the reduction of the ”native” oxide is. Of course it’s a very small sample size but it gives an idea of why potential control might be a good idea.

If the reduction of the oxide leads to a roughening of the surface as is the case for Pt(111) as shown in chapter 4 we might be OK and still able to obtain the voltammogram of the ideal surface with our relatively large single crystal samples. Nanoparticles on the other hand (like those used in industrial catalysis) might suffer. Hence the need for potential control.
5.2. Results

Table 5.1: The charge associated with the initial reduction observed in the either the first cycle of CV or in the CA when immersing the sample under potential control. "∼ 0" refers to a sample immersed under potential control. A planar density for Cu(111) of $1.767 \times 10^{15}$ atoms/cm$^2$ has been used to calculate the charge per atom.

<table>
<thead>
<tr>
<th>$Q_{red}$ [$\mu$C/cm$^2$]</th>
<th>Electrons/surface atom</th>
<th>$t_{OCV}$ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-202</td>
<td>0.713</td>
<td>1.43</td>
</tr>
<tr>
<td>-226</td>
<td>0.798</td>
<td>∼ 0</td>
</tr>
<tr>
<td>-275</td>
<td>0.973</td>
<td>1.77</td>
</tr>
<tr>
<td>-390</td>
<td>1.37</td>
<td>5.82</td>
</tr>
</tbody>
</table>

Rotating disk electrode measurements

As mentioned previously we also tried to reproduce our voltammograms of UHV prepared Cu(111) by preparing a sample under laboratory conditions at KAIST and using the RDE setup described in section 3.4. A lot of the copper single crystal studies found in the literature use a mechanical polishing and/or electropolishing procedure to prepare the crystals. Thus they became our starting point in terms of preparation procedures. The measurements shown here were carried out in 0.1 M KOH (85% extra pure, Junsei Chemical Co.).

The Cu(111) sample was electropolished for 10 s at 3 V in 66% H$_3$PO$_4$ (85% extra pure, Samchun Chemicals) in the setup shown in Figure B.2. Then the sample and RDE tip was rinsed in millipore water and put back on the RDE shaft. The sample was cycled between $-0.2$ and 0.45 V vs. RHE. Cycle number 10 of this measurement is shown in Figure 5.7. The reason for showing cycle 10 as opposed to one of the first ones as we did with the UHV prepared sample (Fig. 5.2a) is that the EC cell here is not nearly as leak tight as the setup used in connection with the UHV chamber. That means we have residual oxygen in the cell in the beginning of a measurement. You also still see the general down shift of the voltammogram as compared to its UHV counterpart. Furthermore, the sample itself is no doubt more oxidised meaning the first few cycles see the voltammogram still stabilising just for this reason. In any case the features observed in the voltammogram quite clearly resembles those found when measuring on the UHV prepared sample. The double layer region in general looks a bit wider in this case and the onset of the oxidation seems to be slightly earlier than seen on the UHV prepared sample.
5.2. Results

Figure 5.7: (a) A picture of the Cu(111) sample sitting in the RDE tip. You can just make out macroscopic roughness. (b) The voltammogram obtained on the Cu(111) prepared by electropolishing in 66% H$_3$PO$_4$ for 10 s.

Again, as we saw earlier (Fig. 5.3), the voltammogram is quite dependent on the exact potential window as can be seen in Figure 5.8. When setting the lower turning potential more negative the feature at 0.11 V vs. RHE starts shifting to higher potentials and decreases as well. When going all the way down to −0.9 V vs. RHE the feature is almost gone. The full electrochemical procedure consisted of 10 cycles between −0.2 and 0.45 V, and then three cycles to each of −0.5, −0.7 and −0.9 V vs. RHE (still with the same upper potential limit) and finally 10 cycles between −0.2 and 0.45 V vs. RHE all at 50 mV/s. The final cycles showed that the change in the voltammogram was more or less completely reversible, meaning that the feature at 0.11 V vs. returned to almost the same level as it started.

Lastly, we did not observe the same instability of the voltammogram as we did for the UHV prepared sample (Fig. 5.4). Figure D.3 in Appendix D shows a measurement from the RDE setup where the sample was cycled 100 times. Although the anodic OH feature decreases we do not see a new feature at 0.32 V vs. RHE. However, we do see a small bump close to −0.1 V vs. RHE. We can force a peak to appear at 0.32 V vs. RHE if a crucial step of the experimental procedure is omitted. If the electrolyte was not changed after calibrating the RE the voltammogram would look quite different. The result of this can be seen in Figure 5.9 compared with a voltammogram from a UHV prepared sample. We hypothesise that the electrolyte contain an electrochemically significant amount
Figure 5.8: CVs obtained on Cu(111) in 0.1 M KOH between −0.9 and 0.45 V. The inset shows the "fingerprint" region of the CV. As can be seen the anodic feature at 0.11 V vs. RHE shifts to higher potentials and all but disappears.
5.2. Results

Figure 5.9: The black CV was measured in the RDE setup using the same electrolyte as the Pt mesh was cycled in when calibrating the RE. The red CV was measured in the EC cube on a UHV prepared sample. The HER activity of this sample is shown in Fig. D.2

of platinum after cycling the platinum mesh between \(-0.1\) and \(1.6\) V vs. RHE. This might induce the change observed in the voltammogram. Furthermore, the HER activity was seen to be much higher when the electrolyte was not changed between calibrating the RE and measuring the voltammogram, this is shown in Figure D.2 in Appendix D. We will get back to this discussion in section 5.3.

5.2.2 Cu(100)

As mentioned in the beginning of this chapter we started on the Cu(100) surface. It was actually on this surface we found out that the original design for the electrochemical cell simply made it impossible to correct for the ohmic drop in the cell. Nevertheless this was the first facet we tried establishing a base voltammogram of. As such it was also here we encountered the different issues related to working with a material such as copper and an electrolyte which is difficult to get rid of in KOH. Therefore we will also briefly touch upon a measurement where we tried to get rid of the KOH using millipore water before
5.2. Results

putting the sample back into the UHV chamber. But firstly we will look at the base voltammogram measured on a clean Cu(100) surface.

![ STM images of Cu(100) surface ]

Figure 5.10: (a) A 700 nm × 700 nm STM image showing the clean Cu(100) surface. (b) A 10 nm × 10 nm STM image of a Cu(100) sample showing the cubic unit cell. The unit cell vectors were found to be 2.55 Å and 2.52 Å.

The sputtering and annealing procedure used here closely resembles the one we used for Cu(111) where we anneal as we would Pt(111) but refrain from heating to above 1000 K. Figure 5.10 shows both a large scale STM image and one with atomic resolution of the Cu(100) sample. As can be seen in the 700 nm × 700 nm one the surface is atomically flat and features smooth clean terraces and steps. In the 10 nm × 10 nm we see the unit cell of the surface lattice found to have unit cell vectors of 2.55 Å and 2.52 Å.

Cycling the sample between −0.2 and 0.5 V vs. RHE gives rise to the voltammogram shown in Figure 5.11. This time we raised the upper potential limit by 0.05 V as we otherwise will not observe the large oxidation feature, which could be characteristic of the facet. Many different copper facets show quite similar features in the potential region around 0.45 V vs. RHE meaning that it might be difficult to discern one from the other had we stopped at this potential. The feature is at 0.49 V vs. RHE in the anodic scan and at 0.47 V vs. RHE in the cathodic scan. Furthermore, we observe the reversible redox feature at −0.15 V. The charge associated with the redox feature is 60.3 µC/cm² which
5.2. Results

Figure 5.11: The first two cycles from $-0.2$ to $0.5$ V vs. RHE on a UHV prepared Cu(100) single crystal.

amounts to roughly 0.25 monolayers of adsorbed OH assuming a planar density of $1.531 \times 10^{15}$ atoms/cm$^2$.

As we saw with the Cu(111) sample the potential limits are quite important to the features observed in the potential region we have decided to show here. This is also the case for the Cu(100) sample. Figure 5.12 shows two plots featuring voltammograms where either the lower limit or the upper potential limit has been changed. As seen in Figure 5.12, if we lower the potential limit to move into hydrogen evolution potentials we quickly see a splitting and a shift of the anodic feature at $-0.15$ V vs. RHE. Instead of being just one peak it splits into two shoulders and shifts to higher potentials. The main peak is just slightly positive of its starting position at 0.1 V vs. RHE, whereas the shoulders are located at $-0.03$ and 0.13 V vs. RHE. Again, and as on Cu(111), this change is almost completely reversible. Figure 5.12 shows what happens to the voltammogram if we change the upper potential limit slightly. As can be seen the cathodic feature at 0.46 V vs. RHE seems to split up into two peaks when we increase the turning potential to 0.52 V vs. RHE. If we continue increasing the potential to 0.53 V vs. RHE we end up with a single reduction...
5.2. Results

Figure 5.12: (a) CVs showing that the redox feature at $-0.15$ V vs. RHE shifts and splits up in several shoulders when the Cu(100) sample is brought to HER potentials. The shoulders are at $-0.03$ and $0.13$ V vs. RHE. The sixth cycle’s turning potential was $-0.5$ V vs. RHE but showed a very small shift and was thus omitted from this plot. Cycle 5 and 8 are basically on top of each other. (b) CVs showing the reduction feature at $0.46$ V vs. RHE first splits up into two peaks and then shifts entirely to $0.44$ V vs. RHE by changing the upper potential limit from $0.5$ to $0.53$ V vs. RHE. The potential limits are noted next to the cycle number.
5.2. Results

feature again, but located at 0.44 V vs. RHE. This seems to be reversible.

Removing remaining KOH from the sample

As mentioned in the beginning of this section we tried getting rid of the leftover KOH on the sample in different ways to avoid not being able to perform the post-EC STM characterisation. Among other things we tried getting rid of it by diluting it with millipore water. The argument being that we might have more areas free of dried KOH and thus would be statistically more likely to make contact between our STM tip and sample in an area where scanning would be possible. We did this by swapping our supply bottle with one full of deaerated millipore water. Then we would break the meniscus and replace the electrolyte in the cell with the millipore. After this we would form a droplet of millipore and bring into contact with the remaining KOH on the sample, subsequently break the contact again and let the millipore run over into the overflow volume of the cell. We repeated this a several times. However, as shown in Figure 5.13 the surface is completely unrecognisable after this treatment. It basically consists of a lot islands or particles, probably made from oxidised copper and residual KOH. The silver lining after such a ”cleaning” procedure was that it seemed to become easier to restore the original Cu(100) surface using sputtering and annealing than if we had left all the KOH on the surface.

Another reason for showing this particular STM image is also that a lot of preparation procedures uses combinations of mechanical polishing and electropolishing with a final step of rinsing the sample with millipore water to get rid of the remaining acid used for electropolishing. Figure 5.13 shows what such a copper sample might look like afterwards as compared to the surface of the UHV prepared Cu(100) sample shown in Figure 5.10.

Rotating disk electrode measurements

As with Cu(111) we tried reproducing our results from UHV prepared samples in the RDE setup at KAIST. It turned out that it was not quite as simple as electropolishing in H₃PO₄ at 3 V for 10 s to reproduce the UHV results.

Figure 5.14 shows two representative measurements of a Cu(100) sample electropolished in two different ways. One was electropolished for 300 s at 1.8 V, the other was electropolished for 10 s at 3 V like we did with the Cu(111) sample shown previously. As can be seen the two procedures results in very different voltammograms. The one electropolished at 1.8 V shows a very vague redox couple at 0.1 V vs. RHE and several different asymmetric features above 0.3 V vs.
5.3 Discussion

Figure 5.13: A 500 nm × 500 nm STM image showing the state of the Cu(100) surface after "cleaning" it with millipore water.

RHE. The sample electropolished at 3 V has a thoroughly uneventful voltammogram.

The measurements shown in Figure 5.14 were in fact carried out right after each other meaning the sample was first electropolished at 1.8 V then measured electrochemically, and then electropolished at 3 V before being measured electrochemically a final time. The resulting voltammograms are more or less independent of in which order this is done.

For the sake of comparison we carried out some measurements in the RDE setup on a polycrystalline copper sample cut from a 8 mm copper rod. Electropolishing that sample at 1.8 V for 300 s gives rise to a voltammogram not unlike the one measured on Cu(100) when using the same preparation procedure. In fact, the polycrystalline sample’s voltammogram has more pronounced features than the Cu(100). The results is shown in Figure D.4.

5.3 Discussion

Copper is, as opposed to platinum, still fairly poorly understood. Not least due to the fact it is a difficult material to work with experimentally as mentioned
5.3. Discussion

![Figure 5.14: CVs showing the results of two different electropolishing procedures as marked in the plot. The dashed line is the UHV prepared sample also shown in Fig. 5.11.](image)

in the beginning of this chapter. This in turn makes it more challenging for theorists to work with as well as it is difficult to know what conditions to impose on a given model. We also saw here how something as relatively simple as measuring a voltammogram turned out to be very dependent on the exact potential boundaries.

It should be mentioned that the data shown in this chapter is very recent and thus somewhat preliminary in its nature. Especially the RDE measurements were carried out right up to the submission date for this thesis so there are still plenty of work to be done in terms of understanding the electrochemistry of copper.

5.3.1 Cu(111)

We started out looking at Cu(111) to hopefully establish a base voltammogram. To this end we took inspiration from some of the potential windows shown in the literature and thus measured between $-0.2$ and $0.45$ V vs. RHE. Through
5.3. Discussion

the UHV preparation consisting of argon sputtering and annealing we could consistently measure a voltammogram featuring one sharp redox peak at 0.11 V vs. RHE (Fig. 5.2a). The charge associated with this peak was found to be 80 µC/cm² or a partial OH coverage of 0.28 monolayers. Very few reports on this coverage exist in the literature but those that do report a lower coverage of OH of ∼ 0.2 monolayers. However, it stands to reason we would report different values when the data these values are based on seemingly came about from electrochemically different samples.

The voltammogram we arrived at is not found elsewhere in the literature but we corroborated the validity of it by reproducing it in a separate setup by preparing a Cu(111) through the use of electropolishing in 66% H₃PO₄ for 10 s at 3 V like described by Schouten et al. Furthermore, we used KOH from a different supplier than we did for the voltammograms measured in connection with the UHV setup.

The voltammogram measured in the RDE setup had slightly wider double layer regions on either side of the main redox feature (which also appears a bit less well-defined) and what appeared to be an earlier onset of the oxidative feature at 0.44 V vs. RHE. Given the sample prepared by electropolishing is visibly a little bit rough this could explain the wider double layer regions and possibly the somewhat wider redox feature as you would expect a rough electrode to have a higher surface area and a wider distribution of surface sites. The early onset might be a consequence of using an RE with potential with a tendency to drift a few millivolts over the course of an experiment, or it could be due to the PTFE cell not being anywhere near leak tight with this fairly quickly designed RDE tip. In any case repeating these measurements under more controlled conditions and with the lessons obtained throughout this project will no doubt be fruitful.

We observed a huge change in the OH feature when going to HER potentials. The redox feature would shift to higher potentials around 0.2 V vs. RHE and decrease to the point of being difficult to recognise as a feature still. It could be a restructuring of the surface giving rise to this as we have recently observed 50 nm polycrystalline copper thin films to restructure during potential sweeps to CO and CO₂ reducing potentials. However, we observed that in a CO saturated electrolyte and not in one saturated with argon. It would be highly interesting to investigate this effect using an EC-STM now that we have a better idea of what to expect of the voltammogram of Cu(111).

At this point we have not carried out a detailed STM study of what happens on the Cu(111) sample during electrochemical cycling. Up until now the KOH remaining on the sample makes it very challenging and time consuming to do this as it seems to be matter of luck whether or not it is possible to get worthwhile
5.3. Discussion

STM images after the electrochemical treatment. Our initial results suggest the surface changes even after very few cycles (Fig. 5.2). Given what is already known from the literature, this is not surprising [86, 69]. Thus we need to either find an alkaline which we can remove in the same way as we do with perchloric acid, i.e. it needs to be volatile, or simply find a good way to remove the remaining KOH. However, having a better understanding of the electrochemistry of the Cu(111) sample is a good starting point for further studies, nonetheless. Again, EC-STM might be needed to understand the copper surfaces.

Over the course of these experiments we noted an increasing feature around 0.32 V vs. RHE, and especially in the measurements on the UHV prepared sample. At this point we suspect a platinum contamination as our CE is a platinum wire and occasionally goes to potentials over 1.9 V vs. RHE, as shown in [Figure D.5 in Appendix D]. We know both from the literature [92, 93] and from the experiments shown in chapter 4 that platinum dissolves at such high potentials. Thus, in the current setup, it is in principle just a matter of diffusion of platinum through the electrolyte to the sample before it shows up in the voltammogram. Suspecting platinum was also rationalised through a prominent feature appearing at 0.32 V vs. RHE in the voltammograms from the RDE setup which only appeared when the electrolyte had not been changed after cycling the platinum mesh in it. However, we only saw an anodic peak in the RDE setup as opposed to both an anodic and cathodic from the UHV setup. Finally, this seemed to correlate with an increase in HER activity as well, which platinum is very active for. It is also interesting to note how this suspected platinum contamination seemed to mainly decrease the anodic OH feature and not the cathodic one. This can specifically be seen when comparing the disappearance of the OH feature when going to HER potentials on the UHV sample (Fig. 5.3) and on the RDE sample (Fig. 5.8). In the case of the UHV sample the cathodic feature is still there when going to HER potentials whereas it has disappeared for the RDE sample, and we suspect the UHV sample to have deposited platinum on it. It could be that platinum on Cu(111) gives rise to a reduction feature coinciding with the usual OH feature on Cu(111). However, the data here is not enough to conclude it is in fact platinum on the sample, we would need an XPS or ion scattering spectroscopy (ISS) measurement to confirm this, depending on the amount of platinum on the sample.

We also noted a strong influence of having dissolved glassware in the electrolyte due to KOH’s tendency to corrode glass. We did so through correlating our voltammograms with ICP-MS measurements on electrolyte samples taken directly from the volumetric flasks they were mixed in. In terms of the voltammetry we could already see the beginning of this effect by using electrolyte that
had been mixed just before commencing a measurement. An exact quantification of the concentration of glassware in the electrolyte was not performed but the voltammograms are very reproducible when using volumetric flasks made of glass as opposed to PFA. In relation to these experiments we also observed something at the step edges of our crystal which only really stood out when performing STM at high bias voltages. Again, we would need an ISS measurement to establish what it in fact is.

5.3.2 Cu(100)

For Cu(100) it proved to be more challenging to reproduce the voltammograms obtained on the UHV prepared sample with the sample prepared under laboratory conditions. We also reported this recently[89].

The voltammogram found on the UHV prepared sample features a redox couple at $-0.15 \text{ V vs. RHE}$. The total charge of this feature comes to 60.3 $\mu\text{C/cm}^2$ or 0.25 monolayers of adsorbed OH. As with Cu(111) we seem to arrive at a value slightly higher than the ones found in the literature. Kunze et al. report a coverage of 0.12 ± 0.04 OH per copper atom[70] and Schouten et al. report an OH coverage of 0.2 monolayers for Cu(100) as well as Cu(111)[83]. In terms of the shape of the voltammogram ours is not too different from the one reported by Schouten et al. Firstly, we agree on the position of the OH feature. However, our potential window went to 0.5 V as opposed to 0.45 V vs. RHE, and unfortunately it is exactly within the last 50 mV we see a big difference. However, their oxidation feature seem to show up before the one we showed here. The feature at 0.49 V vs. RHE is quasi-stable as we reported recently. It is yet to be understood why this is the case although we speculate it could be related to residual oxygen in the electrolyte[89].

The Cu(100) sample also showed a change in the OH feature when the potential was swept to HER potentials (Fig. 5.12). Again we speculate this could be due to a restructuring induced by the electrochemical cycling. However, in order to fully understand this phenomenon in situ methods like e.g. EC-STM, low energy electron diffraction or grazing incidence X-ray diffraction (like we did for polycrystalline copper[91]) will have to be employed.

As can be seen from our measurements in the RDE setup it is not straightforward preparing a Cu(100) single crystal under laboratory conditions. If we used the same electropolishing procedure as for the Cu(111) sample (10 s at 3 V) we end up with a voltammogram without any discernible features. However, electropolishing our sample at 1.8 V for 300 s we arrive at a voltammogram not too different from the one reported by Huang et al. although they used an
5.3. Discussion

electropolishing acid consisting of both H$_3$PO$_4$ and H$_2$SO$_4$ [79, SI]. As opposed to the UHV prepared Cu(100) sample we observe the OH feature around 0.1 V vs. RHE like with the Cu(111) sample. Furthermore, the Cu(100) voltammogram shares a lot of features with the one measured on a polycrystalline sample after the same preparation procedure, as seen in Figure D.4. This suggest we have other facets than just the Cu(100) present. Data published by Kim et al. suggest a polycrystalline copper sample will undergo a reconstruction to having more Cu(100) facets when exposed to potentials around $-0.13$ V vs. RHE which might explain why the voltammogram of our polycrystalline sample shares some features with the Cu(100) voltammogram [71]. The fact the Cu(100) surface is more open than the Cu(111) might be it restructures more after an oxidation and reduction cycle meaning that it inherently is very difficult to prepare outside of UHV conditions as it will inevitably oxidise. Recently we reported that polishing the Cu(100) sample mechanically before electropolishing it might produce voltammetry closer to that of the UHV prepared sample [89]. Thus that might be a good starting point for future attempts at reproducing the voltammogram of the UHV prepared sample.

5.3.3 Summary

In short, we have seen a proposed voltammogram for Cu(111) in 0.1 M deaerated KOH. This voltammogram was measured both on a UHV prepared sample and one prepared through electropolishing in 66 % H$_3$PO$_4$ for 10 s. The OH adsorption/desorption feature was found to represent a coverage slightly higher than that reported in the literature. Furthermore, we showed that having dissolved glassware in the electrolyte has a clear effect on the shape of the Cu(111) voltammogram.

We report a voltammogram on UHV prepared Cu(100) as well, however it was at this point not possible to reproduce it under laboratory conditions. One of the voltammograms measured on the Cu(100) shares more features with a polycrystalline sample prepared in the same way than a Cu(100) sample prepared under UHV conditions. We speculate this is due to copper’s oxyphilic nature and the Cu(100) surface not being as closely packed as the Cu(111) surface therefore resulting in a sample roughened to a higher degree than the Cu(111) sample.

We note that the voltammograms measured on both Cu(111) and the UHV prepared Cu(100) are highly dependent on the lower potential limit. The reason for this is at present not fully understood, but we speculate it is due to a restructuring under HER potentials. In order to develop our understanding of
this *in situ* techniques will have to be employed.
Chapter 6

Conclusion and outlook

In this thesis we have looked at developing an experimental technique and methodology for investigating the structure of model systems and relate that to their electrochemical response, especially that obtained from cyclic voltammetry. We did so with a special focus on electrocatalysts, namely platinum in the form of Pt(111) and two different copper facets, Cu(111) and Cu(100). Our method can briefly be summarised as preparing a well-defined sample under UHV conditions, characterising it with STM, before measuring the electrochemical properties of it. Finally, the aim was to be able to use the STM on the sample again after the electrochemical measurement to track the structural changes due to the electrochemical treatment.

Before looking at the developed experimental method, we placed catalysis research in general in the context of climate change and renewable energy. Here we saw why we believe electrocatalysis will play a big role in the future if we are to implement an energy infrastructure largely based on intermittent energy sources, like solar and wind power. We also took a brief look at the theory behind some of the experimental techniques employed here.

The whole setup used was then explained in detail in order to make it possible for the reader to appreciate the considerations to take into account when designing an experimental setup aiming to combine two areas as different as UHV and electrochemistry. Here we delved into how the electrochemical cell was designed to allow for it to be inserted into the EC cube and simultaneously provide good electrochemical properties, such as the ability to compensate for ohmic drops. Furthermore, in order to try and corroborate some of our results obtained in the UHV setup we designed an RDE tip capable of holding
8 mm crystal samples thus making it possible to measure single crystal samples prepared under laboratory conditions. The point of this was not to rotate the electrode during measurements at this time (however the design employed here might serve as a prototype for the future), but rather to be able to reliably contact our disk shaped samples electrically and immerse them in electrolyte without exposing the edges of the single crystals to said electrolyte. A commercial RDE shaft and our custom-made RDE tip provided a good way of doing this. We used this setup to measure a Cu(111), a Cu(100) and a polycrystalline copper sample.

In order to test the trustworthiness of the setup shown here we started out measuring on Pt(111) due to it being the focus of many studies. For this reason we had access to a lot of data serving as a good baseline for our own measurements. If we could not reproduce Pt(111) data from the literature we would have trouble understanding data on less well-known systems as a fear of e.g. contaminants would always be on our mind. However, as we saw we were able to adequately reproduce the well-known Pt(111) voltammogram and with the post-electrochemical characterisation we were also able to reproduce results on the corrosion processes of Pt(111). For these reasons we believe our setup is very suitable for carrying out electrochemical measurements. Of course we are limited to samples that are compatible with our sample holders and UHV infrastructure at this point. However, there is no reason why e.g. the electrochemical cell cannot be adapted to other types of setups. Currently we are in the process of publishing a paper describing the workings of the cell and the setup as a whole.

Having established that we trust our setup we moved on to test it on Cu(111) and Cu(100) in 0.1 M KOH. As opposed to our measurements on Pt(111) in 0.1 M HClO₄ it proved to be quite challenging to image the sample with STM after measuring in 0.1 M KOH. Nevertheless, we could prepare clean copper single crystals and measure the voltammograms in order to try to establish what copper single crystal voltammograms look like, as there is no consensus in the literature. The strength of this approach is that we can image the sample prior to immersing it in the electrolyte and thus be very confident of having a crystal which is, in fact, clean and atomically flat. Furthermore, we did not have to expose the sample to other electrolytes as you would have to do in order to prepare it through electropolishing as generally done in the literature.

A lot of the measurements shown on copper samples are very recent and thus are still a work in progress. The plan is now to map out the three low index facets, Cu(111), Cu(110) and Cu(100) and establish exactly what to expect of their respective voltammetries. From there it makes sense to move onto the vic-
inal surfaces and carry out experiments like the ones on platinum found in the literature. The knowledge of the voltammograms of the low index facet should help with pinpointing certain site features in the voltammograms of the vicinal surfaces. Furthermore, we imagine this can be used to carry out selective blocking of e.g. step sites by, for example, lead UPD. The lead UPD would simply be performed in an electrochemical cell like the one shown in Figure 3.6, subsequently the sample would be transferred to the UHV chamber and the STM and it would be possible to image the sites blocked by this procedure. This should be possible given lead UPD is carried out in acid. Likewise, one can imagine that PVD could be used to block steps or deposit adislands or another element than the sample which would then subsequently be tested electrochemically and then imaged by the STM again. This would be akin to the exemplary MoS$_2$ study highlighting the HER activity of edge sites of MoS$_2$ nanoparticles deposited on Au(111).

While some of the things mentioned above could in principle be done at present there are still various improvements to make on the setup. It would be great to have a good way of measuring reaction products for instance, if we are serious about blocking certain active sites. One way to measure gaseous products would be to attach a thin pipe to the EC cube and bring it to the QMA we already have on the UHV chamber as a kind of leak valve. It would still be difficult to quantify the products properly but at least it could be used to investigate trends. This knowledge could then be used in complementary measurements where quantification of products would be easier. Likewise, we have performed a little bit of ICP-MS but we need to come up with a good way of extracting the right part of the electrolyte after a measurement, i.e. the droplet left on the crystal. This might be possible through the use of a thin capillary of some kind from which the sample can be injected into the ICP-MS machine for example.

In short, we have developed a trustworthy technique for imaging model catalysts before and after electrochemical measurements. We have also showed we can prepare samples in UHV with interesting surface structures which we can then investigate the electrochemical response of without exposing them to ambient conditions first. Finally we imagine the setup can also be used to prepare samples electrochemically which can then be imaged with the STM thereby making the setup work in both directions, so to speak. The end goal is of course to help further our understanding of catalysts used for reactions relevant for the production of chemicals and fuels from renewable sources. This could for instance be for the ORR and OER of fuel cells and electrolyzers or for the reduction of CO and CO$_2$ to valuable chemicals.
Appendix A

Energy statistics

This part of the appendix will feature a bit more of the data discussed in section 1.1 for the convenience of the reader.

Figure A.1: Pie charts showing the breakdown of the total final energy consumption shown over time in Fig. 1.1 in 1973 and 2015, respectively. "Coal" also includes peat and oil shale and heat, solar thermal and geothermal is included in "Other" [4, p. 34]
1973 and 2015 shares of world coal consumption

Figure A.2: Breakdown of the world’s coal consumption. [4] p. 38
1973 and 2015 shares of world oil consumption

Figure A.3: Breakdown of the world’s oil consumption. [4] p. 39
Figure A.4: Breakdown of the world’s natural gas consumption. [4, p. 40]
Appendix B

Experimental

Figure B.1: (a) The glass supply bottle used for electrolyte when measuring in acid. Note that the stopcock is built into the bottle making it very easy to assemble. (b) The PFA supply bottle also sketched in Fig. 3.5. Sadly this system has a number of reduction fittings making it easier to get bubbles in the system.
Figure B.2: A picture of the setup used for electropolishing the Cu single crystals used in the RDE setup. A Cu mesh was used as cathode and the Cu single crystal is sitting in the RDE tip.
Appendix C

Supplementary Pt(111) data

This part of the appendix will contain some obtained along with that shown in [chapter 4]. The reason for having it here is that while it is still important it does not tell the story as concisely as the data actually shown in the main body of this thesis. Furthermore, using STM invariably produces a lot of visual data which takes up a lot of room if put into the main text so in order to not make [chapter 4] too much of a picture book with text and accompanying figures residing far from each other. A lot of the data shown here was used to do statistics on e.g. the adislands shown in the main text.
Figure C.1: (a) The STM image also shown in Figure 4.1b. (b) The fast Fourier transform of said STM image with the two unit cell vectors shown. This was used to estimate a unit cell of 0.270 Å and 0.263 Å and with an angle of 121.2°.
Figure C.2: (a)-(d) shows the STM images used to determine the size distribution of adislands after the experiment shown in Fig. 4.4c and d. (e) The size distribution as area.
Figure C.3: (a)-(b) The STM images used to determine the size distribution of the adislands found on the surface after the experiment shown in Fig. 4.4e and f. The full size distribution is shown in Fig. 4.12.
Figure C.4: (a)-(c) The STM images used to obtain the size distribution for the adislands deposited using PVD. The size distribution is shown in Fig. 4.8c.
Figure C.5: (a)-(d) The first four STM images used to find the size distribution of the adislands deposited with PVD after the EC treatment. The size distribution is shown in Fig. 4.8.
Figure C.6: (a)-(d) The final four STM images used to find the size distribution of the adislands deposited with PVD after the EC treatment. The size distribution is shown in Fig. 4.8c.
Figure C.7: (a)-(c) STM images of the vacancy islands in the Pt(111) surface. The size distribution is shown in Fig. 4.9.1.
Figure C.8: (a)-(e) The first five STM images used to find the size distribution of the vacancy islands after the EC treatment. The size distribution is shown in Fig. 4.9d.
Figure C.9: (a)-(e) The final four STM images used to find the size distribution of the vacancy islands after the EC treatment. The size distribution is shown in Fig. 4.9d.
Figure C.10: (a)-(e) Five STM images used to determine the size distribution of the small adislands on the Pt(111) sample. (f) The size distribution of the adislands.
Figure C.11: (a)-(e) The five STM images used to find the size distribution of the adislands after the EC treatment for the sample that was both sputtered lightly and deposited adislands on. The size distribution is shown in Fig. 4.12c.
Figure C.12: A model showing the Pt(554) surface featuring \{111\} steps.

Figure C.13: CVs showing how the features in the H-UPD region come and go over time.
Appendix D

Supplementary copper data

Figure D.1: Pourbaix diagram of Cu.[101]
Figure D.2: Two CVs showing the HER activity of Cu(111) in 0.1 M KOH using either new electrolyte (black) after calibrating the RE, or the same electrolyte as the RE was calibrated in (red).
Figure D.3: The 10th and the 100th cycle of a measurement on Cu(111) electropolished for 10 s in the RDE setup.

Figure D.4: A comparison of the CVs of a polycrystalline Cu sample and a Cu(100) single crystal. Both of them were electropolished for 300 s at 1.8 V in 66% H$_3$PO$_4$. 
Figure D.5: The potential of the Pt CE used during the measurement on Cu(111) shown in Fig. 5.4. As can be seen it is well above the potential oxidising the Pt surface as discussed in Ch. 4.
Appendix E

Appended papers

E.1 Paper I

Novel and versatile setup for investigating model catalysts by extending a UHV-STM with electrochemistry

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Notes: Submitted, November 2018, cited as [24] in this thesis
Novel and versatile setup for investigating model catalysts by extending a UHV-STM with electrochemistry

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In this paper we present a setup for conducting electrochemical measurements on ultra-high vacuum (UHV) prepared single-crystalline electrodes without exposing the samples to atmospheric air. Nano-scale structural information of such an electrode is obtained using a scanning tunneling microscope (STM) in UHV prior to the electrochemical measurements, thus allowing to correlate the electrode’s initial structure and electrochemical properties. Similarly, after transfer back into UHV, STM can be used to visualize structural changes of the electrode caused by its interaction with the electrochemical environment, thus allowing for investigation of e.g. corrosion processes. We showcase the capabilities of the setup by some prototypical measurements on Pt(111) and Cu(111). Finally we discuss the current limits of our setup including the removal of remaining electrolyte and the before-after nature of our sample characterization.

Keywords: STM, electrochemistry, UHV, catalysis, hanging meniscus, surface structure, single crystal electrodes

I. INTRODUCTION

Electrocatalysis is envisioned to play an important role in the transition towards a sustainable-energy economy because it allows for converting excess electricity from e.g. solar and wind power to useful chemicals. In order to do so efficiently, we need to design catalysts that are not only active but also selective for the desired product and stable under reaction conditions. To design these catalysts rationally, we need to understand the relationship between the catalyst’s nano-scale structure and its catalytic properties. Ultimately, we would like to know the atomic-scale nature of both the active sites involved in the desired reaction, as well as the sites that might be critical to the catalyst’s stability or active for competing reactions, thus undermining its selectivity. Such information is typically obtained by high-resolution microscopy.

In this paper, we present a novel and versatile extension to an existing ultra high vacuum (UHV) based high-resolution scanning tunneling microscope (STM) setup enabling imaging of the surface of a model catalyst prepared in UHV both before and after it is exposed to the relevant electrochemical environment. A crucial point in this is to ensure that the sample is not exposed to ambient air, especially oxygen, both during transfer between UHV and the electrochemical (EC) cell and during the EC measurement itself. At the same time, the setup should allow for a rapid measurement cycle of one to two measurements per day including full sample preparation and analysis. We were able to meet this demand without compromising the quality and versatility of the EC cell.

Our motivation for setting up a new system stems from our previous experience with in-situ electrochemical STM (EC-STM)1. While using the EC-STM, we realized that there are numerous advantages obtainable by combining a UHV based STM with an external EC setup instead, i.e., by replacing the in-situ imaging by pre- and post-EC imaging. Decoupling these two steps makes imaging in general much more simple than it turned out to be in the EC-STM with its complicated four electrode setup. Combining UHV and EC also opens for exciting new options for sample preparation and analysis that are only possible in such a combined setup. As an example, the equipment of the UHV chamber allows us to not only prepare clean crystals but also to deposit adislards of various metals or form well-defined sputter holes in the surface to investigate e.g. step effects. On the other hand, the resulting structures of electrochemical techniques such as under potential deposition (UPD) can be investigated with the STM shortly after the deposition and without going through ambient conditions.

II. SETUP CONFIGURATION

A. UHV system

1. Main chamber

The main UHV chamber is a conventional one made of stainless steel. It is equipped with an Aarhus type STM2, an argon sputter gun, a stage that allows for heating of the sample, a quartz crystal microbalance (QCM), a metal evaporator for physical vapour deposition (PVD), a mass spectrometer, leak valves for letting in e.g. O2, and an Auger electron spectroscopy system. The chamber is mainly pumped by a magnetically suspended turbopump (Pfeiffer) with a reasonably low noise level so it can be left running during STM imaging and EC measurements. Additionally, an ion pump is available and we routinely reach a base pressure of $1 \times 10^{-11}$ mbar as measured using an inverted-magnetron gauge (Agilent IMG-
2. Add-on system for electrochemistry

A home-built add-on system consisting of a magnetic transfer arm (Ferrovac) with a 4.5” spherical cube vacuum chamber (Kimball Physics) placed midway on it is connected to the main chamber (c.f. Figure 1 and Figures S1 and S2 in the supporting information). Using the transfer arm, the sample can be moved from the main UHV chamber into the cube under UHV conditions. A 3-axis manipulator attached to the cube is used to move a sample container similar to the one in the main UHV chamber. This container receives the sample from the transfer arm. Before electrochemical measurements the cube is sealed off from the main UHV chamber and is solely pumped by a small turbo pump (Pfeiffer). When the sample is in the container in the cube, the cube is vented to proceed with the measurement. To this end, a gas line is connected directly to the cube to facilitate the introduction of inert gases to sustain a mild overpressure during the measurements, thus preventing back-flow of oxygen through the opening through which the EC cell is introduced. The typical base pressure of the entire add-on system is $\sim 10^{-8}$ mbar when pumped by the small turbo pump only. In principle, the system can be further baked over night to remove remaining water condensed on the walls, resulting in a base pressure below $10^{-9}$ mbar. In practice, however, we prefer a rapid measuring cycle and aim for one experiment per day and thus do not bake the system on a daily basis.

B. Electrochemical setup

Considerable effort has been put into designing an electrochemical cell that allows for obtaining trustworthy electrochemical measurements despite of the tight spatial constraints of it. The major restriction here is that the entire cell setup has to pass through a VAT valve at the bottom of the cube (to be discussed further down) and the cell is therefore limited in diameter to 25 mm. In order to minimize contamination of the samples, we opted for an open hanging meniscus type cell, i.e. without any O-ring touching the surface. The cell body is home-made in Kel-F. Its overall form is cylindrical (c.f. Figure 2 and Figure S4) with three threaded ports in the bottom at an angle of 30° with respect to the cell’s normal. These three ports are 120° apart and lead into two different channels in a smaller cylinder coaxial with the main body of the cell and extending above it. Note that the whole cell is machined from a single piece of Kel-F. It is within the inner diameter of this protruding inner cylinder that the actual meniscus is formed. The total volume of a half spherical meniscus plus the electrolyte columns in the two channels underneath amounts to roughly 0.22 mL. The volume around the small cylinder acts as an overflow volume for the electrolyte.

The wide channel in the inner cylinder contains the electrolyte inlet and the counter electrode, the latter of which will be described shortly. The narrow channel acts as the outlet down which the reference electrode is also located. The reason for doing so is that we in this way almost have a built-in Luggin capillary. Earlier iterations of this cell design led us to realize that this two-channel design is much better with regards to ohmic drop compensation than the typical single-channel design (see e.g.³ and citations therein). Typical ohmic drop values obtained by electrochemical impedance spectroscopy are on the order of 20 .. 30 $\Omega$.

Before measurements, the cell is mounted in a stand which also contains a conducting rod which holds a (fourth) dummy working electrode. This rod can be contacted and manipulated from outside the cube. This extra electrode allows us to immerse our samples under potential control.

The cell is introduced into the cube via a DN 40 CF mini UHV gate valve (VAT) valve sitting at the bottom of the cube. This valve is necessary to be able to pump the cube down to UHV and bake it. It introduces, however, the above mentioned spatial restrictions to the cell design. Prior to introducing the cell in the cube, the valve is opened under overpressure of inert gas and a teflon pipe is inserted as guide for the cell stand. The outer diameter of the fixation ring for the cell (visible in Figure S4) fits tightly into this teflon pipe and thus basically fills the opening of the valve. Combined with the overpressure in the cube, oxygen can thus efficiently be kept out of the system.

Freshly prepared electrolyte is fed to the cell from a supply bottle through PFA tubes (IDEX Health & Science). The supply bottle is kept elevated slightly above the operation height of the cell so electrolyte enters the system solely by way of hydrostatic pressure. The supply bottle has a stopcock sitting in the tube immediately below the drain such that the flow of electrolyte can be controlled just by turning the stopcock (cf. Figure S3).

Electrochemical measurements are performed using a Bio-Logic SP-200 Potentiostat in floating mode. The Potentiostat is equipped with a low-current probe amplifier. Because of our wish of rapid sample turnover, we keep all turbopumps at the UHV chamber running both while performing STM and EC measurements. The Potentiostat’s floating mode is necessary to reject electronic noise from the turbopumps. For similar reasons, we run the WE on floating ground that is identical to the UHV chamber. Bio-Logic’s software EC-Lab is used to acquire the EC data.
1. Electrodes

Reference electrode

Very often in such tiny cells, the reference electrode is realized by a pseudo-reference, e.g. a Pt wire sitting in the cell itself. Such pseudo-reference electrodes need, however, to be calibrated for each type of electrolyte and we thus decided to use a reversible hydrogen electrode (RHE) instead. Due to the spatial constraints, the RE is located outside the cube and connected to the cell via the outlet tube through a three-way valve (c.f. Figure S7). It is routinely regenerated to avoid potential drifts.

The electrode is a custom-made piece of glassware in which a platinum wire (0.5 mm diameter, 99.99 % Chempur) is melted through the glass from the outside into a small volume (c.f. Figure S5). A platinum foil (99.99 % Chempur) is attached to the wire in this volume. The volume is shaped in such a way that the opening is narrow enough to avoid that electrolyte will drip out of it even when facing downward. Prior to experiments, the electrolyte in the volume also containing the platinum foil is replaced by fresh electrolyte before experiments is evolved on the foil in a beaker using a conventional power supply and a platinum wire as the anode. The electrolyte is always the same as the one used in the actual experiment.

Counter electrode

The counter electrode is made from a flame annealed platinum wire (0.5 mm diameter, 99.99 % Chempur) glued into a piece of PFA tube such that the length of wire sticking into the wide channel is roughly long enough to reach the edge of the "wall" separating the two channels in the cell (c.f. Figure S6). On the outside of the cell, 1 - 2 cm of the wire sticks out to allow for electrical contact. By putting a nut and ferrule around the tube containing the Pt wire the CE can be connected to one of the threaded ports of the cell described above. For initial electrochemical cleaning, the counter electrode is placed in a beaker with the same electrolyte used later for measurements and cycled from 0 .. 1.6 V vs. RHE until the CV is stable. Another platinum wire is used as counter electrode in this case. When not in use, the counter electrode is stored in millipore water.

Dummy working electrode

The tip of a dummy working electrode can be rotated into the meniscus via a rotateable rod in the cell stand and is generally made of high-purity wire of the same metal as the sample (c.f. Figure S6). When a platinum wire is used, it is flame annealed prior to the experiment whereas copper wires are cycled from −0.5 .. 1.7 V vs. RHE in a beaker in the same electrolyte used later for measurements until the CV is stable. The reasoning behind this potential window is that any contaminants on the wire which will dissolve in the given electrolyte should do so in this potential window and thus not in the much narrower one used when immersing the sample under potential control.

The Cu wire is emersed from the electrolyte at −0.5 V vs. RHE and immediately mounted into the cell and transferred into the cube. Nevertheless, some oxidation of the wire can not be avoided. It shows up as an initial reduction peak after the wire is entered into the electrolyte and during the potential sweep from open circuit to the desired potential for subsequent immersion of the crystal. The reduction of the wire proceeds typically much faster than the time it takes to align the crystal over the meniscus. The wire is therefore considered to be reduced by the time, we immerse the crystal.
II. EXPERIMENTAL

A. Sample preparation

Sample preparation consists of cycles of argon sputtering and annealing. If just a flat clean sample is desired, STM characterisation is performed as soon as the sample has cooled down after the last cycle. If more complicated structures like surface alloys, sputter holes or adlayers are needed, these can be formed on the now clean surface using the available UHV based equipment. For the systems shown here (clean metal single crystals) only sputtering and annealing were applied.

Typically the sample is prepared roughly an hour before the electrochemical setup is ready such that its structure can be visualised by STM just before the electrochemical measurement.

B. Preparation of electrochemical setup

Prior to mounting the cell in the stand and putting the electrolyte supply bottle in place they are cleaned. The cell is boiled three times in millipore water before being used in the experiment. Usually it is stored in millipore water as well when not in use, however it will occasionally be cleaned in piranha solution (3:1 H₂SO₄ (98 % EMSURE, Merck) : H₂O₂ (30 % EMSURE Iso for analysis, Merck)) over night.

Depending on whether a given measurement is to be carried out in acid or base, different electrolyte supply bottles are used. For acid measurements, a custom-made glass bottle and bubbler is used. A PFA bottle and stopcock system (Savillex) is used for measurements in base (c.f. Figure S3).

The glass supply bottle and bubbler are stored in a ∼ 3 M KOH (85.0 % EMSURE, Merck) bath when not in use and boiled in millipore water prior to use, furthermore the teflon stopcock used is boiled three times in millipore, like the electrochemical cell. The PFA bottle, PFA bubbler with a PTFE frit and related reduction fittings are stored in 2 % HNO₃ (made from 69 % EMSURE ACS reagent Ph.Eur., Merck) and rinsed in warm millipore before being used. When a supply bottle is connected to the inlet tube, warm millipore from a clean glass bottle (also boiled three times in millipore) is flushed through the system before filling it with elec-
trolyte. Additional electrolyte is used to wash away remaining millipore water in the tubes before connecting it to the cell. The electrolyte is continuously bubbled with N₂ (5.0, AGA). See Supporting Information for a more detailed sketch of the tubing and electrolyte flow (Figure S7) plus a description of how the electrolyte is filled into the system and bubbles are removed.

C. Typical experiment

Below follows an outline of a typical experiment:

1. The sample is prepared in UHV
2. STM is performed on the sample while the electrochemical setup is being cleaned and assembled
3. The sample is transferred to the EC cube under vacuum while the dummy working electrode is cleaned electrochemically
4. The cell is mounted with the counter electrode and the dummy working electrode
5. The cube is vented with either Ar or N₂ (6.0, AGA)
6. The cell is raised into the cube that is under over-pressure of Ar or N₂
7. The cell is filled with electrolyte (see Figure S7 and corresponding text) and the electrolyte is allowed to overflow to the overflow volume a few times
8. The electrolyte is slowly sucked through the outlet and towards the reference electrode with a syringe to make contact to the reference electrode.
9. Electrical contact between the counter electrode and reference electrode is confirmed using a multimeter
10. A half-sphere of electrolyte is formed within the perimeter of the inner cylinder of the cell by adding a suitable amount of electrolyte from the inlet until it has the same diameter as the sample above (c.f. Figure 3).
11. The tip of the dummy working electrode is put into the electrolyte and the desired potential for the crystal immersion is set
12. The sample is aligned with the 3-axis manipulator in the x and y directions above the electrolyte
13. The sample is lowered into the electrolyte at this potential thus forming the hanging meniscus configuration and the dummy working electrode is taken out again
14. If necessary, the size of the meniscus can be changed by flowing additional electrolyte into the cell from the supply bottle (c.f. Figure S8)
15. The electrochemical measurement is performed
16. The dummy working electrode is inserted into the meniscus again at the end to remove the sample from the electrolyte under potential control.

After this procedure the cell is taken out of the cube, most remaining electrolyte on the sample is carefully removed using lens paper inserted through the VAT valve, then this valve is closed again and the cube is pumped down to allow for transfer back into the main chamber. The cube can be pumped down to 10⁻⁶ mbar in roughly 10 minutes. If the electrolyte used is volatile, e.g. HClO₄, electrolyte remaining on the sample after the lens paper treatment will evaporate under pump-down and the sample can easily be transferred into UHV. Non-volatile electrolytes like e.g. KOH will instead up-concentrate under pump-down and will make post-EC STM difficult and, at times, impossible.

IV. SAMPLE DATA

In this section we will present two brief sets of data obtained on single-crystal fcc(111) electrodes, i.e. Pt(111) and Cu(111) in 0.1 M HClO₄ (70 %, redistilled, 99.999, Sigma-Aldrich) and 0.1 M KOH (99.995 Suprapur, Merck) respectively. Both the Pt(111) and the Cu(111) single crystal were purchased from MaTeck, Jülich, with a similar hat-shape with a polished top surface of 6 mm in diameter that fits the inner diameter of the cylinder protruding from the cell. After extensive cycles of Ar-ion sputtering (3keV) and annealing to 1200 K the Pt and 1000 K for Cu, both surfaces show large terraces with monoatomic steps typical for the clean surfaces.

The two fcc(111) systems together perfectly illustrate the merits of the system and the advantages/disadvantages of performing measurements like this.

A. Pt(111)

We start out by showing results on Pt(111), a system that has been studied in great detail and has one of the most established CVs by now. Thus it serves as a good system for benchmarking our setup.

Figure 4 shows a typical Pt(111) experiment. Figure 4.a shows a representative image of the clean Pt(111) surface obtained after the Ar-sputter and anneal procedure. The surface consists of rather large, clean terraces separated by smooth steps. Figure 4.b shows the CV obtained after transferring this sample to the electrochemical cell and measuring in 0.1 M HClO₄. It should be noted that even though the current is given as current density it is difficult to know exactly how much of the crystal is wetted by the electrolyte at a given point. We used a geometric surface area of 0.28 cm² but that is likely to be an
overestimation. As can be seen, the current decreases slowly over time as the electrolyte from the meniscus evaporates over the course of the experiment, this will be discussed in more detail in Section V.

The measurement was started at open circuit potential, 0.81 V vs. RHE, as can be seen from the start of the first cycle and was stopped at 0.5 V vs. RHE in the cathodic scan of the 101st cycle. Note how the CV becomes slightly more "rectangular" in the hydrogen UPD region with continued cycling. This CV was obtained with an Argon flow of 7 L/min through the cube. In a range of 2 - 7 L/min we do not see signs of oxygen backflow into the EC cube, below 2 L/min the Pt CV downshifts slowly, indicating oxygen diffusing into the cube. The STM image in Figure 4.c shows the surface of the Pt(111) sample after the electrochemical treatment. It is apparent that
the step edges are no longer smooth. Instead it appears as if they have corroded to some extent. In a recent EC-STM study\textsuperscript{5}, images of the initial steps of corrosion of Pt(111) when cycling to potentials higher than 1.1 V have been reported. Note that the potential window used in the current study is limited to a much lower upper turning potential of 0.9 V vs. RHE. The exact processes of the initial steps of Pt corrosion at such low potential are currently being investigated in more detail and will be presented in a forthcoming publication. In general, we find that quite good post-EC image resolution can be obtained for this type of volatile electrolyte, thus allowing for detailed studies of morphological changes of the electrode surface due to e.g. corrosion processes.

In summary, we have seen that our well-defined, UHV-prepared Pt(111) electrodes indeed show electrochemical behaviour as known from literature, as exemplified by the CVs shown above, thus validating our first aim (transfer of well-defined sample into an EC cell and measurement of good quality EC data). Similarly, our post-EC STM images clearly validate our second aim (post EC characterization with STM).

B. Cu(111)

We have also used our setup to investigate Cu surfaces as Cu has received a great deal of interest in the CO and CO\textsubscript{2} reduction communities. Furthermore, as Cu is often studied in alkaline media, it served as a good way to test our setup under different experimental conditions. Out of the different Cu surfaces investigated so far, we here present data obtained on the same facet as in the case of Pt, i.e. the (111):

Figure 5 shows a typical Cu(111) measurement. Figure 5.a presents an STM image of the clean surface, Figure 5.b shows the CV observed by measuring at 50 mV/s in 0.1 M KOH from −0.2 to 0.45 V vs. RHE. The sample was immersed under potential control at 0.33 V vs. RHE. This is also where the measurement was stopped again.

As can be seen, our Cu(111) CV differs quite a bit from CVs previously reported in the literature\textsuperscript{6}. One reason for this could be that Cu CVs seem to be very sensitive to the actual preparation procedure used, as we were able to show recently by comparing various electropolished and UHV prepared samples\textsuperscript{7}. Given that other single crystal studies on the Cu(111) surface use various combinations of mechanical polishing and electropolishing, it is not surprising that we record a different CV. A full discussion of the Cu CV is, however, outside the scope of this paper and will be presented in a forthcoming publication.

Finally, Figure 5.c shows the surface after the electrochemical treatment consisting of four cycles as described above and emerging the sample in the fifth cycle at 0.33 V vs. RHE in the cathodic scan. As can be shown, the surface’s morphology has changed considerably and large, monoatomically deep holes have appeared. The exact reason for this is currently under investigation and will

![Figure 5](image_url)

Figure 5. (a) STM image of the clean Cu(111) surface after cycles of Ar sputtering and annealing (\(V_t = 1.25\) V, \(I_t = 0.9\) nA). Besides regular steps, several screw dislocations are visible. (b) CV obtained by scanning at 50 mV/s in 0.1 M KOH with the sample being immersed under potential control and starting at 0.33 V vs. RHE. (c) STM image showing structural changes of the surface after the electrochemical measurement (\(V_t = 0.5\) V, \(I_t = 0.9\) nA).
also be presented in a forthcoming publication.

In summary, we again are able to measure electrochemical behaviour of well-defined, UHV-prepared Cu(111) electrodes, as exemplified by the CVs shown above. Similarly, our post-EC STM images show the potential of post EC characterization with STM.

V. DISCUSSION

In the following, we will address some known issues of our current version of the setup in more detail and present our thoughts on future improvements and actions taken so far:

An obvious weakness of our new setup is the fact that we cannot observe changes on the surface in real-time i.e. while they happen in the electrolyte. In order to do so, an EC-STM clearly would be the first choice. On the other hand, our new setup allows for the preparation of very well-defined samples in UHV, be that flat clean samples or samples of a more exotic nature, which would be extremely challenging to prepare for use in an EC-STM. Furthermore, we know that a thus prepared sample is as close as practically possible to a UHV prepared sample when immersed into the electrolyte. In this way we can get CVs of well-defined model systems which can serve as benchmarks. So, in summary, the EC-STM and our new setup perfectly complement each other.

We assume that the structure visualized with the STM after the EC measurement is identical to the surface structure at the point of emersion from the electrolyte. This is of course very difficult to prove or disprove. Even though related questions like whether electrodes can be emersed with their electric double layer intact or whether there is post-emersion adsorption from the remaining electrolyte have been addressed in literature, the question of possible structural changes during the emersion process still is open. One way to distinguish between structural changes induced by the electrochemical process and those induced by the emersion/transfer could be to use the possibilities of the UHV setup to prepare characteristic surface structures on a given system and investigate whether these structures “survive” an immersion/emersion cycle, i.e. without electrochemical cycling. Possible test structures could be sputter holes in the form of well-defined vacancy islands with their characteristic hexagonal equilibrium shape (on 111) that would be easy to distinguish from mere corrosion induced irregular shaped holes.

As mentioned in Section IV A, the electrolyte evaporates over the course of an experiment. This means that even though the whole crystal face was covered at the start of the experiment, it might not be after some time. This gives some uncertainty in terms of the exact current densities (however it should not have an effect on the morphological phenomena observed on the surface). Here we presented the CVs in terms of current densities as they are likely to be quite precise in the first few cycles.

VI. CONCLUSION AND OUTLOOK

We have presented a novel setup that allows the preparation of single-crystal electrodes in UHV and the investigation of both their electrochemical properties and resultant structural changes after the electrochemical treatment. It is based on a combination of UHV-STM and a custom designed electrochemical add-on chamber. We employed a novel cell design that fits into the spatial constraints of a UHV-compatible add-on cube to the main chamber. Two prototypical systems show the basic validity of our methodology and we are now ready to follow our two aims, i.e. to investigate the influence of changes in the initial structure of the electrodes on the electrochemical properties. Such changes can be made in UHV by e.g. deposition of material onto the surface of by introduction of defects like sputtered vacancy islands. Similarly, we are able to investigate structural changes due to e.g. corrosion during the electrochemical measurement.

VII. SUPPLEMENTARY INFORMATION

See supplementary information for additional pictures of the setup and specific connections. Furthermore, a detailed description of the way the electrolyte is introduced to the EC cell is given in connection with Figure S7.

ACKNOWLEDGMENTS

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E.2  Paper II

Polycrystalline and Single-Crystal Cu Electrodes: Influence of Experimental Conditions on the Electrochemical Properties in Alkaline Media
Albert K. Engstfeld, Thomas Maagaard, Sebastian Horch, Ib Chorkendorff and Ifan E. L. Stephens
Polycrystalline and Single-Crystal Cu Electrodes: Influence of Experimental Conditions on the Electrochemical Properties in Alkaline Media

Albert K. Engstfeld,*[a, b] Thomas Maagaard,[a] Sebastian Horch,[a] Ib Chorkendorff,[a] and Ifan E. L. Stephens*[a, c]

Abstract: Single and polycrystalline Cu electrodes serve as model systems for the study of the electroreduction of CO₂, CO and nitrate, or for corrosion studies; even so, there are very few reports combining electrochemical measurements with structural characterization. Herein both the electrochemical properties of polycrystalline Cu and single crystal Cu(100) electrodes in alkaline solutions (0.1 M KOH and 0.1 M NaOH) are investigated. It is demonstrated that the pre-treatment of the electrodes plays a crucial role in determining their electrochemical properties. Scanning tunneling microscopy, X-ray photoelectron spectroscopy and cyclic voltammetry are performed on Cu(100) electrodes prepared under UHV conditions; it is shown that the electrochemical properties of these atomically well-defined electrodes are distinct from electrodes prepared by other methods. Also highlighted is the significant role of residual oxygen and electrolyte convection in influencing the electrochemical properties.

Introduction

Over the past half century, fundamental studies of single crystal electrodes have facilitated the investigation of more complex, industrially-relevant high surface area materials.[1] Metallic low index (hkl) single crystals (e.g., the face centred cubic (FCC) metal surfaces (111), (110) and (100)) provide atomically flat well-ordered surfaces with a high periodicity of surface atomic structures; they allow the investigation of specific surface sites in a very controlled way.

Electrochemists often deduce the quality of single crystal electrodes on the basis of cyclic voltammetry (CV, which consist of applying a triangular wave potential while recording the current response of the electrode in contact with a supporting electrolyte).[2] The distinct oxidation and reduction features are specific surface sites in a very controlled way. The ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/chem.201803418.
functional theory calculations and gas-phase studies of the same adsorbates.\[9\] Despite four decades of intense study, the electrochemistry community is still discovering new ways to interpret cyclic voltammograms on Pt single crystals.

In this work, we focus on the electrochemical properties of Cu electrodes under aqueous alkaline conditions. The first fundamental studies in this area date back to the beginning of last century.\[10\] This research field has gained an increased importance over the last few decades, due to the potential application of Cu as catalyst material for the electroreduction of nitrate,\[11\] carbon dioxide or carbon monoxide.\[12\] Scientists have also considered it as a potential candidate as coating material in nuclear waste storage containers.\[13\] Experiments show that under alkaline conditions, the oxidation/reduction (including electrode restructuring and corrosion) rate\[14\] and the electrocatalytic properties of Cu electrodes\[12a,15\] strongly depend on the crystallographic orientation of the surface. Several other investigations report analogous findings on Cu, albeit in neutral and acidic aqueous environment.\[12a,16\]

Despite this apparently pronounced structural dependence, only a few reports are dedicated to the detailed elucidation of the cyclic voltammetry of different Cu single crystal electrodes (Cu(hkl)). Unlike Pt, there are no characteristic peaks for *H formation at any pH. In acid, the current density in the hydrogen evolution region is dependent on the crystal orientation.\[16a\] Furthermore, the voltammetric features depend on the anion, such as Cl−, Br−, I− or SO4 2−, in the electrolyte.\[17\] Distinct voltammetric features are also observed for metal under potential deposition (upd) on Cu(hkl) electrodes, such as Pbupd\[16a,18\] and Thupd.\[19\] In neutral solution, the displacement of phosphate anions by CO yields voltammetric desorption features, which are correlated to the coverage of CO at step sites.\[16b\] A great number of Cu single crystal studies have been performed in alkaline solution. In alkaline media, several papers report that the features associated with the oxidation of the surface, that is, the formation of *O and/or *OH, subsurface oxides, bulk oxides and dissolution, are structure sensitive.\[20\] Even so, these features vary significantly between the different studies on Cu (hkl) electrodes. This is exemplarily shown in Figure 1 for CVs of Cu(100) electrodes recorded in alkaline over the last four decades. While most studies show a distinct redox peak at around −0.15 V, the peak number, shape and size at potentials larger 0.30 V vary significantly. As such—in contrast to the situation on Pt single crystals—it is currently challenging to interpret the CV as a measure of quality of the single crystal preparation. The reasons for these discrepancies between the studies could be due to oxide contamination from exposure to air or water, which cannot be avoided when working under laboratory conditions.\[21\] Furthermore, the different preparation procedures employed (see Table 1) do not allow for 1) the complete removal of the native oxide layer\[21a\] from the Cu surface and 2) leveling of the surfaces to atomic flatness. The most common approach to remove the native oxide film is a pretreatment by mechanical polishing and/or chemical etching in acid solutions. In order to level the surface, the most common approach is electropolishing, originally introduced as a method to smooth rough metal surface.\[22\] Several authors have pos-

Figure 1. Cyclic voltammograms of Cu(1 0 0) recorded in alkaline media from the literature. Electrolytes and scan rates are indicated in the respective subfigures. The CVs are adapted from several publications since 1980. The potentials are rescaled to the RHE scale for comparison. The CVs were extracted from the work by a) Droog and Schlenter,\[20a\] b) Jovic´ and Jovic´ from 2002\[21\] and 2003,\[21b\] c) Kunze et al.,\[21c\] d) Schouten et al.,\[21d\] e) Huang et al.,\[21e\] and f) Le Duff et al.\[21f\]

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These are not the final page numbers!
STM[23] and eventually in situ atomic force microscopy (AFM). Only a limited number of publications show both characterization by STM and electrochemical characterization in alkaline, in combination with cyclic voltammetry. This is, importantly of electrocatalytic tests on Cu single crystals, in particular for CO and CO₂ reduction, where electrodes are typically electropolished. It is unclear whether disparities between single crystal studies are due to 1) different test methods employed, particularly in relation to product detection, or 2) the quality of the preparation method: studies on polycrystalline Cu show that the CO and CO₂ reduction activity are strongly dependent on the pre-treatment. [27]

Herein, we present a qualitative description of the electrochemical features of the CVs of polycrystalline and Cu(100) single crystals in 0.1 M KOH or 0.1 M NaOH. We will show and discuss the effect of different pre-treatments available in conventional laboratories. Furthermore, we will report, for the first time, the features observed in the CVs on Cu(100) electrodes in alkaline media, which have been prepared under UHV conditions. We will show that this much less common approach to prepare single-crystal electrodes is mandatory to obtain Cu electrodes with a much more defined surface structure. We will discuss these results in the context of the literature on the electrochemical properties of Cu(hkl) electrodes prepared by different pre-treatments, other than UHV. We will characterise the surfaces under UHV conditions, prior to the electrochemical characterization: we shall determine the structural properties with STM and the cleanliness of the samples with XPS. By employing a hanging meniscus cell and a flow cell we were

### Table 1. Summary of experimental conditions to prepare Cu(hkl) surface over the last decades for studies in alkaline. MP = mechanical polishing. EP = electropolishing.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Year</th>
<th>Cu(hkl)</th>
<th>Electrolyte</th>
<th>Preparation procedure</th>
</tr>
</thead>
</table>
| [28] | 2017 | Cu(111) | 0.1 M KOH | 1. MP in alumina slurries (0.3 μm, Struers)  
Cu(110) 2. EP in a solution of H₃PO₄,H₂SO₄,H₂O (130:120:60) at +2 A cm⁻², t = 1 s  
Cu(100) 3. Rinsed in H₂O and 0.1 M HClO₄ |
| [29] | 2017 | Cu(111) | 0.1 M KOH | 1. EP in 66% H₃PO₄ at +2 V.  
Cu(100) 2. Rinsing with water. |
| [23g] | 2016 | Cu(111) | 0.1 M KOH | 1. MP with suspension of polycrystalline diamond (0.05 μm)  
Cu(110) 2. EP in 85% H₃PO₄ at 2.0 V for 10 s with a Pt CE  
Cu(100) 3. Ultrasoundated and rinsed in deaerated water |
| [23h] | 2016 | Cu(100) | 0.1 M KOH | 1. MP (procedure not specified)  
Cu(110) 2. EP in 85% H₃PO₄ at 2.1 V for 10 s with a 99.8% pure graphite rod as CE  
Cu(100) 3. Pre-reduction at ~0.9 V (SHE) in 0.1 M KOH for 2 h  
Cu(110) 4. Rinsing with water |
| [14] | 2014 | Cu(111) | 0.1 M KOH | 1. MP on a grain paper (<10 μm)  
Cu(110) 2. MP by water-MgO suspension (<1 μm) on suede.  
Cu(100) 3. Chemical polishing in a mixture of concentrated nitric, phosphoric, and acetic acids (1:1:1 by volume)  
Cu(110) 4. Rinsing with water |
| [20d] | 2013 | Cu(111) | 0.1 M KOH | 1. EP in 66% H₃PO₄ at 3 V with a Cu CE for 10 s  
Cu(110) 2. Rinsed with water  
Cu(100) 3. EP in 60% H₃PO₄ supersaturated with Cu²⁺ at 1.80 V with a Cu CE for 5-10 min at RT  
Cu(110) 4. EP in 85% H₃PO₄ at 1.7 V with a Pt CE until current density dropped to a value of 10 mA cm⁻²  
Cu(110) 5. Cleaned for 30 s in 10 vol% H₂SO₄ and rinsed with water |
| [25] | 2003 | Cu(111) | 0.01 M NaOH | 1. MP with Al₂O₃ powder  
Cu(111) 2. EP in HNO₃/CH₃OH (3:7) at 1.8 A cm⁻² for 3 min at RT  
Cu(111) 3. EP on fine grade emery papers (1200, 2400 and 4000)  
Cu(110) 4. Rinsing with water |
| [20b,20c] | 2002 & 2003 | Cu(111) | 0.1 M NaOH | 1. MP on polishing clothes with a suspension of polishing alumina (1 μm, 0.3 μm and 0.05 μm)  
Cu(100) 2. MP on polishing clothes with a suspension of polishing alumina (1 μm, 0.3 μm and 0.05 μm)  
Cu(100) 3. EP in H₃PO₄ (85%) at 1.7 V with a Pt CE until current density dropped to a value of 10 mA cm⁻²  
Cu(110) 4. Rinsed with water  
Cu(111) 5. Cleaned for 30 s in 10 vol% H₂SO₄ and rinsed with water |
| [30] | 2002 | Cu(111) | 0.1 M NaOH | 1. MP with alumina paste  
Cu(111) 2. EP in 60% H₃PO₄, supersaturated with Cu²⁺ at 1.4 to 1.6 V with a Cu CE at j=40-60 mA cm⁻² for 2 min. |
| [23a-f] | 1999 to 2004 | Cu(111) | 0.1 M NaOH | 1. MP with diamond spray 0.25 mm grading  
Cu(100) 2. EP in 85% H₃PO₄ at 1.80 V with a Cu CE for t=5-10 min at RT  
Cu(110) 3. Pre-reduction at 1000 K for 16 h in ultra-pure (6 N) hydrogen  
Cu(110) 4. EP on polishing clothes with a suspension of polishing alumina (1 μm, 0.3 μm and 0.05 μm)  
Cu(100) 5. EP at 1.4 to 1.6 V with a Cu CE at j=40-60 mA cm⁻² for 2 min. |
| [31] | 1995 | Cu(111) | 0.1 M NaOH | 1. MP with 0.5 μm with Al₂O₃  
Cu(111) 2. EP in mixture of 130 mL H₂SO₄ (85%), 20 mL H₂SO₄ 95%, 60 mL H₂O, for 3 min at 2.5 V, with j=2.8 A cm⁻², T<10 °C, in stirred solution  
Cu(111) 3. Heating for 3 h at 600 °C in a N₂ stream (heating/cooling rates 70 °C min⁻¹)  
Cu(110) 4. EP in a mixture Methanol/HNO₃ (85%) (ratio 2:1) at 0 °C |
| [24] | 1995 | Cu(111) | 0.1 M NaOH | 1. EP in HNO₃/CH₃OH (3:7) for 10 min  
Cu(100) 2. EP in mixture of HNO₃/CH₃OH (3:7) for 10 min  
Cu(110) 3. EP in mixture of HNO₃/CH₃OH (3:7) for 10 min  
Cu(111) 4. EP in a mixture Methanol/HNO₃ (85%) (ratio 2:1) at 0 °C |

STM[23] and eventually in situ atomic force microscopy (AFM).[24] Only a limited number of publications show both surface characterization by STM and electrochemical characterization in alkaline in combination with cyclic voltammetry.[23d,e,25] This is, however, a prerequisite to assign structural properties to the observed electrochemical response in the CVs, as described above for Pt single crystal electrodes.
able to elucidate the influence of trace amounts of oxygen in the electrolyte and the experimental conditions. On the basis of our results, we analyse other reports in the literature on Cu electrodes investigated under alkaline conditions without additional anions or cations.

Results and Discussion

Influence of pre-treatment

It is well known that different crystallographic orientations of Cu electrodes, show distinctly different redox features in a potential range starting from ca. $-0.25 \text{ V}$ up to ca. 0.5 V in alkaline.$^{[20a, 26a, 32]}$ This potential region refers to the initial oxidation of Cu (total transfer of electrons per surface atom is less than or equal to one, for example, formation of an $^\bullet \text{OH}$ adlayer). In order to demonstrate the influence of different pre-treatments on the crystallographic orientation of Cu electrodes, we show first results on different polycrystalline Cu (Cu(poly)) and second on Cu(100) electrodes. The CVs of selected Cu(poly) electrodes are depicted in Figure 2 a to h, where the preparation procedures and electrode materials are indicated in the respective figures and the figure caption. A description of the preparation procedures can be found in the experimental section. The large number of different peaks observed in this potential region suggests that the crystallographic orientation of each of these samples is to some extent unique. Even two foils with the same specifications and the same supplier, but from different batches, can yield a distinct voltammetric feature, as shown in Figure 2 a and b. Both electrodes were pre-treated by electropolishing. Second, pre-treating the Cu foil B by radio frequency heating in a H$_2$ stream (Figure 2 c) changes the crystallographic orientation of the Cu foil B in comparison to the electrode prepared only by electro polishing. However, we observe that on the radio frequency heated and then electropolished sample (Figure 2 e) the features of the originally radio frequency heated sample become more pronounced upon electro polishing. This indicates that the electro polishing procedure is sensitive to the initial crystallographic orientation of the electrode surface. Finally, a mechanically polished Cu(poly) electrode cannot be distinguished from a mechanically polished Cu(100) single crystal (compare Figure 2 g and h). We attribute the similar features by the fact that the surfaces have a similar surface structure, obtained by the same polishing agent in both cases.

For Cu(hkl) single crystals also a large number of different pre-treatments were tested and reported in the literature. Table 1 summarizes the preparation procedures for Cu(hkl) surfaces which have been investigated in alkaline. A comparison of representative CVs in alkaline reported since 1980 for Cu(100) electrodes is presented in Figure 1. We observed that the CVs differ strongly in the potential region $>0.30 \text{ V}$. To compare the influence of different pre-treatments on the voltammetric features in more detail, we pre-treated Cu(100) electrodes by different commonly employed pre-treatments under laboratory conditions. A representative selection of CVs is presented in Figure 3 (solid lines). These comprise in a) an as received electrode from the supplier that is electropolished for 10 s (pre-treatment according to Reference $^{[20d, 29]}$), in b) an electrode exposed to air for 30 days that is electropolished for 90 s (EP pre-treatment according to Reference $^{[26b]}$) and in c) a MP electrode that is subsequently EP for 90 s (pre-treatment based

![Figure 2. CVs of region II (−0.20 to 0.50 V) recorded on various Cu electrodes exposed to different pre-treatments in 0.1 m KOH at a scan rate of 50 mV s$^{-1}$ in a flow cell set-up under stagnant conditions. The CVs of the following electrodes are shown: a) electropolished Cu foil A, b) electropolished Cu foil B, c) radio frequency heated Cu foil B, d) electropolished and subsequently radio frequency heated Cu foil B, e) radio frequency heated and subsequently electropolished Cu foil B, f) Cu(poly) sample prepared under UHV conditions, g) mechanically polished Cu foil B and h) mechanically polished Cu(100).](#)
These CVs are compared with the CV of a Cu(001) electrode prepared under UHV conditions (Cu(100)-UHV, dashed line). A more detailed description of the latter is presented in Figure 4 and described further below. The CVs of all electrodes show redox peaks at around −0.15 V and between 0.35 V and 0.50 V, in agreement with the CVs presented in Figure 1. The redox peaks at −0.15 V vary slightly in size depending on the pre-treatment. The size, position and number of peaks at higher potentials (0.35 V and 0.50 V), however, depend strongly on the pre-treatment. In detail, Cu(100)-UHV shows a single large peak at around 0.47 V. The mechanically polished and subsequently electropolished electrode also has a single redox feature at 0.47 V. The reduction peak is, however, shifted to lower potentials compared to the Cu(100)-UHV electrode. The two electrodes which have been electropolished show a broad shoulder/peak between 0.25 V and 0.45 V, which is more pronounced for the electrode kept in air for 30 days. Further CVs that were recorded on Cu(100) electrodes which were electropolished multiple times during one day of measurements, different electropolishing times or on consecutive days, showed similar features compared to those depicted in Figure 1 and Figure 3 a) and b) (not shown). It has to be noted that different O₂ concentrations in the cell in the different experiments can influence the absolute current densities of the peak at 0.47 V (see below).

Next, we report in detail on the structural and electrochemical properties of Cu(100)-UHV electrodes. In Figure 4 the XPS survey spectrum as well as an STM image of such an electrode is shown. The XPS indicates that the surface was free of the contamination (inadequate UHV-based preparation yields oxygen, carbon and argon contamination). Recall that XPS measurements were performed on different set-ups than samples investigated by STM experiments (see experimental sec-

![Figure 3. Comparison of the CV recorded on a Cu(100) electrode prepared under UHV conditions (dashed line) with a) an electropolished as received Cu(100) electrode from the supplier, b) a 90 s electropolished Cu(100) electrode after storage in air for 30 days and c) a 90 s electropolished Cu(100) electrode after mechanical polishing. All CVs are recorded in 0.1 m KOH and at a scan rate of 50 mV s⁻¹.](image)

![Figure 4. Different characterization methods employed to characterize Cu(100)-UHV electrodes. a) XPS survey spectrum recorded and in the inset a large scale and atomically resolved STM image with sizes of 700 nm x 700 nm and 4 nm x 4 nm, respectively (Recorded with I_T = 1 nA, U_T = 0.1 V and I_T = 0.6 nA, U_T = 0.2 V, respectively). b) First cyclic voltammograms starting at −0.20 V, after the linear sweep from OCP to −0.20 V, recorded in 0.1 m KOH (labels 1–3) and 0.1 m NaOH (label 4) at a scan rate of 50 mV s⁻¹. The CV labeled 1 was recorded in the hanging meniscus cell, where CVs labeled 2–4 were recorded in the flow cell set-up under stagnant conditions.](image)
tion). The surface depicted in the STM image in the inset exhibits large atomically flat terraces extending over several hundred nm, which are separated from other terraces with steps of monoatomic height. The atomically resolved STM image (top left corner of the large scale STM image) shows the quad-ratic arrangement of the surface Cu atoms for the (1 0 0) surface; these images provide no indications of contamination at an atomic scale. The quality of the surface structure of the Cu(1 0 0)-UHV electrode, in terms of terrace size and step density, compares favourably with epitaxially grown Cu(hkt) electrodes\(^{13}\) and Cu(100) electrodes pre-treated under laboratory conditions and investigated with in situ STM.\(^{23}\)

Subsequent to the STM or XPS characterization, the electrodes were transferred under well-defined conditions (without exposure to air) to an electrochemical cell (flow or hanging meniscus cell), as described below. Figure 4 shows the first CVs starting from \(-0.20\) V of a selection of Cu(100) electrodes recorded in 0.1 m KOH (labels 1–3) and 0.1 m NaOH (label 4), between \(-0.20\) V and 0.50 V. All CVs were taken under stagnant conditions. CV 1 has been recorded in the hanging meniscus cell. CVs 2–4 were recorded in the flow cell. CV 2 (recorded in 0.1 m KOH) is also shown with varying upper potential limit. The CVs in both electrolytes show redox peaks at around \(-0.15\) V and 0.47 V. The reduction peak at 0.47 V consists, in most cases, of two peaks, both of which vary in intensity. In the anodic (cathodic) scan, a faint shoulder is observed just negative (positive) of the peak at 0.47 V. We attribute this feature to a small amount of defects on the Cu(100) surface, since we observed a similar feature on polycrystalline electrodes, as shown in Figure 2. STM is a local probe and XPS measurements do not provide any structural information; as such, we are unable to quantify the aggregate amount of defects across the entire electrode surface, prior to the electrochemical measurements.

Variation of the upper potential limit (between 0.20 V and 0.50 V in steps of 0.05 V) has no influence on the size and shape of the redox peak at \(-0.15\) V, both in 0.1 m KOH and 0.1 m NaOH (variation of the potential limit is only shown for an electrode investigated in 0.1 m KOH). On the other hand, the intensity of the peak at 0.47 V varies significantly from one experiment to another, which we will discuss in more detail in below. Furthermore, we generally observed larger current densities using the hanging meniscus cell, in comparison to the flow cell, especially for the peak at around \(-0.15\) V. One possibility could be that the Cu(1 0 0) surface prepared in the UHV-STM set-up is more ordered in comparison to the preparation in the UHV-XPS set-up. A second plausible explanation could, however, be that we overestimate the geometric area for the flow cell set-up, leading to lower apparent current densities in the flow cell system (see experimental part). Finally it is also possible that the rather soft Cu electrodes are prone to mechanical deformation when pressed on the flow cell. Better insights into this observation, could be gained from additional measurements on different cells and eventually different Cu(1 0 0) electrodes.

The shape of the CVs recorded in 0.1 m KOH are identical to those reported in 0.1 m NaOH. Consequently, we consider it appropriate to directly compare CVs taken in KOH to those taken in NaOH. Even so, the type of cation may still play a crucial role in catalytic reactions performed on these electrodes.\(^{34}\) In total, the main difference between the CVs of Cu(100)-UHV electrodes and Cu(100) electrodes pre-treated under laboratory conditions is, that the Cu(100)-UHV electrodes show less/no features in the potential range between 0.3 V to 0.45 V.

The electrodes prepared by different pre-treatments also show distinct features during the first reduction cycles, which were recorded from the open circuit potential (see Figure 5). In Figure 5 a and b we compare the Cu(100)-UHV electrodes investigated in the hanging meniscus cell under stagnant conditions and the flow cell under flow conditions, respectively. In the hanging meniscus cell, only a narrow reduction peak at 0.47 V is observed (see Figure 4b). In the flow cell, a single broad reduction peak is observed with a maximum at around 0.30 V. While we have shown above that the CV of Cu(100) shows a reduction peak at 0.47 V, the peak in the first reduction scan is much larger. This is caused by continuous oxidation of the surface while holding the sample at OCP before the measurement is started (see experimental section), in agreement with literature findings.\(^{35}\) In the hanging meniscus cell, the measurement starts almost immediately after the formation of the meniscus, thus surface oxidation is almost not observed at OCP. In the flow cell set-up, the first reduction peak is larger since the time in between flowing electrolyte and starting the measurement is longer. The first reduction cycles of the electropolished samples investigated in the flow cell are shown in Figure 5 c. Electrodes which are electropolished without any pre-treatment show two reduction peaks at 0.30 V and 0.10 V. The peak at around 0.30 V has a similar magnitude compared to the one observed on the Cu(100)-UHV electrodes in Figure 5 b. The additional reduction peak at 0.10 V varies in size. Interestingly, the largest peak at 0.10 V has been observed for the sample left in air for 30 days (see Figure 3 c). Both the origin of the reduction peak at 0.10 V as well as the change in size observed on the electropolished Cu electrodes is currently unclear and cannot be determined with CV studies only. On electrodes which are pre-treated prior to the electropolishing, either by mechanical polishing or by electrochemical reduction in alkaline in the flow cell in Figure 5 d, only the peak at 0.3 V is observed. In few cases a small peak is observed at 0.1 V. For the sake of completeness we show the first reduction cycles of mechanically polished Cu(100) and Culpoly) electrodes in Figure 5 e and f, respectively. In this case a large reduction peak is observed between 0.30 V and 0.20 V, which is much larger in size compared to the otherwise prepared electrodes and is attributed to the larger surface area of these mechanically polished electrodes. In addition some minor features are observed between 0.10 V to 0.00 V.

Influence of experimental conditions on the initial oxidation of Cu(100) and the HER

In a next step we explored the influence of electrolyte flow compared to stagnant electrolyte conditions on the voltammetric features observed in the CV of Cu(1 0 0)-UHV electrodes.
The CVs were recorded in a potential range between −0.50 V and 0.50 V, which includes the HER and initial oxidation region. Representative CVs of Cu(1 0 0) electrodes (marked with "flow" and "stagnant") recorded at a scan rate of 50 mV s⁻¹ in 0.1 m KOH are shown in the Figure 6a. The CV recorded on Cu(1 0 0) under electrolyte flow conditions shows significant reduction currents at potentials < 0.30 V compared to a Cu(1 0 0) electrode investigated under stagnant conditions. This is attributed to the reduction of residual O₂ present in the electrolyte. Possible reasons for the presence of O₂ in the electrolyte are described in the experimental section. At the lowest investigated potential (−0.50 V) the HER activity is almost identical for both experimental situations. We observed that the HER activity differs strongly from one electrode to another, with large variations in current density. Some samples show much higher current densities than those reported in Figure 6a. Especially, in those cases vivid H₂ bubble formation in the flow cell is an issue at more cathodic potentials than −0.50 V. Under stagnant conditions in the flow cell set-up and in the hanging meniscus configuration, the gas bubbles cannot be removed readily from the sample surface due to lacking transport conditions. This leads to loss of potential control. Additional measurements are required to explore in more detail the relationship between the HER activity and the features observed in the CV, as well as the behavior of the CV at potentials smaller −0.5 V of differently structured electrodes.

On the other hand, the experimental conditions, flow vs. stagnant, significantly influence the peak structures and current densities of the peaks around 0.47 and −0.15 V. We focus first on the anodic peak located at 0.47 V. The size of the peak in Figure 6b remains almost constant during electrolyte flow and continuous cycling. When the electrolyte flow is turned off, the current density of the peak decreases by almost 50% (Figure 6c). Upon continuous potential cycling (increasing time) the sizes of the peaks decrease further, indicated by the CVs of the first potential cycle compared to the CVs obtained after 10 and 50 potential cycles, respectively. The first assumption is that the surface is poisoned by impurities from the flowing electrolyte[36]. This causes a decrease of the current density in the voltammetric features, due to irreversible blocking of impurities on certain sites. This effect should in principle be more pronounced during electrolyte flow, where a continuous...
supply of impurities is supplied by the electrolyte from the supply bottle, for example, dissolved Si from KOH etching of the glassware [26b, 37] and other carbonaceous species originating from the PFA tubing connecting the supply bottle and the flow cell. The second possibility would be that the peak observed at 0.47 V is caused by oxidation of surface sites by molecular O₂. This is in agreement with the work by Droog et al., where the authors propose that the peak preceding the Cu₄O formation at potentials < 0.5 V is attributed to O₂ electroadsorption [26a, 31a]. Thus the peak remains unchanged when O₂ is continuously supplied to the electrode under flow conditions, where under stagnant conditions the residual O₂ content in the cell is slowly reduced in subsequent potential cycles. Upon flowing fresh electrolyte through the cell when the electrode is almost deactivated and a stagnant situation is again restored, the peak at 0.47 V shows almost identical intensity as the initial CV recorded under stagnant conditions (see Figure 6c CV marked with restored). A similar behavior has also been observed for measurements in the hanging meniscus cell on Cu(100)-UHV electrodes, for Cu(100) electrodes prepared via electropolishing, as well as for Cu(poly) electrodes prepared both under UHV conditions and via electropolishing (data not shown). A more qualitative evaluation of the peak (peak charge) makes little sense, since it depends strongly on the residual O₂ content in the electrolyte. This is also the reason for the strong difference in peak size of the CVs shown in Figure 4.

The influence of the electrolyte flow compared to the stagnant situation on the more cathodic peak around −0.15 V is shown in Figure 6d and e, respectively. The peak is shown for two different lower potential limits, −0.2 V (black solid trace) and −0.5 V (red dashed trace). Under flow conditions (Figure 6d) the peak at −0.15 V remains almost unchanged when the lower potential limit is decreased. Under stagnant conditions (Figure 6e) the oxidation peak is shifted to slightly more positive potentials. Possible reasons for this behavior are discussed further below.

Discussion

We demonstrate that the voltammetric features observed in the CV of Cu(poly) electrodes in alkaline in a potential range of −0.30 V to 0.50 V ("fingerprint region"), strongly depend on the crystallographic orientation of the electrode surface (Figure 2). This in turn depends on the manufacturing process as well as on the pre-treatment of the electrode. In the literature, only very few studies report the fingerprint region of the CV for the initial oxidation of Cu(poly) in alkaline [26a, 26, 32a, 38]. The CV can be particularly useful for studies of Cu as an electrocatalyst, both to compare different types of electrodes within a single study and to relate reports from different laboratories. For example, some reports show that the CO electroreduction activity depends on the ratio of the different peaks observed in the fingerprint region [26]. By comparing the CVs of two electropolished Cu foils from the same supplier but different batch number, we show that the voltammetric features do not depend on the pre-treatment but rather on the initial crystallographic orientation of the surface. Therefore it is crucial to report the CVs of the investigated electrodes, in addition to the exact pre-treatment procedures.

In order to deduce the crystallographic orientation from the different features observed in the CV, a more detailed understanding of the electrochemical features observed in the fingerprint region is mandatory. Despite some attempts to attribute these features with those observed in CVs of Cu single crystal electrodes [26a, 26] a complete picture is still missing. Since the reported CVs for example for Cu(100) differ strongly one from another (see Figure 1). Therefore a direct comparison of
the CVs recorded on complex Cu(poly) materials with literature data of Cu(hkl) is not straightforward.\cite{26a}

Our CV results for Cu(100)-UHV electrodes (Figure 4) show similarities to the CVs reported in the literature and electrodes prepared under laboratory conditions in this work (see Figure 3). However, the CV of the Cu(100)-UHV electrode does not show any distinct features in the potential region from 0.30 V to 0.45 V, which are normally observed for electrodes prepared under laboratory conditions (Figure 1). Our STM results show only very few steps on large scale images compared to in situ STM images recorded on Cu(100) electrodes prepared under laboratory conditions.\cite{22a,34,35} We attribute the additional peaks observed in the CVs in the literature to an increased number of different facets/steps on the surface. The most comparable voltammogram to our Cu(100)-UHV electrode is obtained for electrodes that were first mechanical polished and subsequently electropolished, a preparation procedure which is widely used in studies of Cu(hkl) electrodes in acid medium. Interestingly in the work by Huang et al. a similar pre-treatment has been employed to prepare Cu(100) single crystals,\cite{35a} but the reported CV (Figure 1e) is very different to the one obtained in the current work. The difference could be caused by the different choice of electropolishing conditions (different electropolishing solution and polishing time).

Distinct differences between the Cu(100) electrodes prepared by different pre-treatments and investigated in different set-ups become apparent from a comparison of the first reduction scans recorded starting from the OCP (Figure 5). Cu(100)-UHV electrodes, mechanically polished electrodes and electropolished electrodes that were pre-treated by mechanical polishing or electrochemical reduction in alkaline in the flow cell, show a single reduction peak in between 0.20 and 0.50 V. This additional peak could be caused by the reduction of a native Cu oxide layer, resulting from storage in air in between the experiments, that is, different days of measurement,\cite{21a} which is not removed from the Cu electrodes during the electropolishing procedure. An indication that this is the case provides the experiment, where the electrode was pre-treated by mechanical polishing before the electropolishing. Such an approach is used in a number of publications listed in Table 1. Mechanical polishing is considered as the most straight forward approach to remove the native oxide layer.\cite{21a} Thus, since the peak at 0.1 V is not apparent on these electrodes and the CVs are rather similar to those obtained on the Cu(100)-UHV electrodes, (which are shown to be free of oxide by XPS and STM), we assume that electropolishing does not remove the native oxide completely. Applying a sequence of mechanical polishing followed by electropolishing, is also consistent with the general procedure to prepare smooth metal surfaces described in detail in the comprehensive reviews for EP of metal surfaces by Landoldt\cite{22a} and Yang et al.\cite{22b} The procedures described in the reviews by Landoldt\cite{22a} and Yang et al.\cite{22b} are, however, primarily addressing leveling of rough polycrystalline surfaces. To the best of our knowledge, the literature lacks any guidelines for producing Cu single crystal electrodes with atomically well-defined crystallographic orientation on a micrometer scale. In addition, there is still a huge debate in the literature whether or not a passivating film or oxide structures are formed during the electropolishing process, which might prevent perfect leveling of the surface.\cite{22b} Furthermore, we speculate that during the electropolishing of an as received or air stored non-mechanically polished Cu electrode, two processes are competing: 1) electrochemical oxidation of the surface Cu atoms, where the Cu ions are dissolved by an electrochemical process in the electrolyte (fast) and 2) chemical dissolution of Cu-oxides, which does not require potential because Cu is already present in its oxidized state (slow).

Further investigations are required to identify the reasons for the different structural and electrochemical properties observed on electrodes pre-treated in different ways other than preparation under UHV conditions. In addition, in order to get a more detailed picture of the actual surface structure formed during the electropolishing procedure of single crystal electrodes more concise and detailed studies are required. It has been discussed that the following effects have an influence on the polishing quality on Cu(poly); influence of etching agent concentration, potential dependence on passive film formation, flattening and pitting,\cite{32b,39} polishing time,\cite{19} photocatalytic effects,\cite{16c,40} rotation speeds (electrolyte flow)\cite{39b,41} or Cu ion concentration in the etching agent.\cite{42} To gain a systematic insight on the influence of pre-treatment on the electrode quality only a limited number of pre-treatments reported in the literature were tested in this work. Other pre-treatment procedures described in the literature to prepare Cu single crystal electrodes, summarized in Table 1 for Cu(hkl) surfaces prepared for studies under alkaline conditions, where no CVs were reported to demonstrate the quality of the electrode surface, also have to be revisited and both the structural as well as electrochemical properties have to be compared with existing data.

Another aspect that has to be considered in the interpretation of CVs on Cu electrodes is the residual content of O₂ in the electrolyte. We demonstrate that this has a strong effect on the shape and size of the two main redox peaks at ~0.15 V and 0.47 V (Figure 4), as shown in Figure 6. The size of the peak at 0.47 V decreases with decreasing amount of O₂. It can be restored upon supplying fresh electrolyte with residual O₂ in the electrolyte to the working electrode. This means that some sites are more easily oxidized by O₂ than by H₂O or OH⁻. The interpretation of the changes in the peak at ~0.15 V are more complicated. In almost O₂ free solutions we observe a shift of the peak to more positive potentials, when the lower potential limit is decreased into the HER region (lower potential limit of ~0.5 V). In O₂ containing electrolyte such a shift is absent. Matsuoka et al. reported a similar shift on a Cu(111) electrode.\cite{25} In their study, the first oxidation peak shifts by almost 250 mV to more positive potentials when the electrode is cycled into the HER region.\cite{25} They argue that the position of the oxidation peak depends on the degree of reduction of the oxy-overlayer.\cite{25a} This experimental observation is in agreement with earlier DFT-based calculations,\cite{48} which suggest H sorption in this potential range. Further in situ STM studies in acidic conditions on Cu(111) and Cu(100) indicate that H can intercalate in the Cu lattice at HER potentials. This process
leads to a reversible potential dependent reconstruction of the surface.

Beyond Cu, such a peak shift is observed in cyclic voltammograms on Ru(0001) recorded in 0.1 m HClO₄. According to these results, the "Nernstian" shape of the peak at about 0.15 V on Cu(100) could be the formation of *OH in the negative going scan and the reoxidation to *O in the positive going scan. Upon excursion to higher overpotentials (HER onset/region), *H is able adsorb on the surface by displacing *OH. This displacement of *H in turn leads to a peak shift in the positive going scan due to kinetic limitations in *OH/*O formation on the surface. Hence, we take the view that hydrogen could also adsorb on Cu(100) at a potential of −0.5 V. The presence of *H shifts the oxidation potential at −0.15 V to more positive potentials. However, when the electrolyte contains significant amounts of residual O₂, the *H is removed at more negative potentials, which is why no shift in peak position is observed in our experiment under flow conditions. This phenomenon could be due to competitive adsorption of *H with *O or *OH derived from O₂.

**Conclusion**

This work comprises a detailed study on the interpretation of CVs of Cu electrodes recorded under alkaline conditions (0.1 m KOH and NaOH). We presented results on various polycrystalline Cu electrodes and Cu(100) single crystal electrodes prepared by different pre-treatments and explored under different experimental conditions. The key findings of this study are the following:

According to our CV study, the crystallographic orientation of polycrystalline Cu electrodes depends both on the initial crystallographic orientation and the pre-treatment of an electrode. For example, while electropolishing preserves the crystallographic orientation, radio frequency heating in a H₂ stream changes the crystallographic orientation of the surface.

We show the CVs of Cu(100) electrodes recorded in 0.1 m KOH and 0.1 m NaOH. The electrodes were determined free of contaminants by XPS. Atomic flatness has been verified by STM imaging. As such, the CV recorded on Cu(100)-UHV electrodes can be considered as benchmark for further studies on Cu(100) single crystals.

The Cu(100) electrodes prepared under ambient laboratory conditions show additional features in the CV in the potential region from 0.30 V to 0.50 V. We attribute these features to defect sites and different facets on the surface. We conjecture that the preparation procedures reported in the literature are not optimized to produce atomically flat well defined Cu(100) surfaces. As reported earlier for Cu(poly), removal of the native oxide by mechanical polishing is crucial for a good polishing quality of single crystal electrodes.

With flow cell measurements under flow and stagnant conditions we show that the voltammetric features depend on the amount of residual O₂ in the electrolyte. In the presence of O₂, a pronounced oxidation feature is observed at 0.47 V, which decreases with decreasing amount of O₂ in the cell.

We have thus addressed a number of open questions in our understanding of the electrochemical properties Cu electrodes under alkaline conditions. Further studies, especially with respect to benchmarking the CVs of Cu(hkl) electrodes, are mandatory to compare the results between different research groups. Electrocatalytic reduction reactions, such as CO₂/CO and NO, should be revisited on well-defined Cu(hkl) electrodes in order to determine in how far the quality of the investigated electrodes plays a role in the electrocatalytic activity and product distribution.

**Experimental Section**

In the present study, we investigated the electrochemical properties of several Cu electrodes, namely Cu(100) single crystals, polycrystalline Cu crystal electrodes and polycrystalline foils. We use (i) an electrochemical flow cell and (ii) a hanging meniscus cell, operated in a load lock chamber. Both are attached to an UHV set-up under inert gas atmosphere. The electrodes have been prepared both in UHV and ex UHV.

**Materials and electrochemical solutions**

Two Cu(100) single crystals were purchased from Mateck GmbH (Purity 99.9999%, diameter 6 mm and 8 mm, thickness 2 mm). The 6 mm sample was used in the UHV-STM and the 8 mm sample was used in the UHV-XPS set-up (see below). Using two different samples allows us to check the reproducibility of our approach.

The Cu foil was purchased from Alfa Aesar Supratronic® (Purity ≥ 99.9999%, 0.1 mm thickness) where foil A has the LOT number S29C040 and Foil B has the LOT number M18D049.

The Cu wire (serving as counter electrode during electropolishing and used to mount the Cu foils in the RF heater) were purchased from Goodfellow (Purity ≥ 99.999%, 0.5 mm diameter).

The ultrapure deionized water (MilliQ) used for rinsing the electrodes and mixing the solutions was obtained from a Millipore MilliQ Integral purification system. The 66% H₃PO₄ (Merk EMSURE, 85%) used for electropolishing was prepared from mixing 85% H₃PO₄ with MilliQ water.

The 0.1 m alkaline electrolytes used for the electrochemical characterization were prepared from MilliQ water and KOH (potassium hydroxide monohydrate, Merck Suprapur®, ≥ 99.9995%) or NaOH (sodium hydroxide monohydrate, Merck Suprapur®, ≥ 99.995%), respectively.

**UHV set-up**

In this work two, UHV set-ups have been employed: (i) the flow cell is attached to an UHV chamber with an XPS setup (UHV-XPS) or (ii) the hanging meniscus cell is attached to UHV chamber with an STM (UHV-STM).

The UHV-XPS set-up consists of three parts, that is, (i) a UHV chamber dedicated to XPS measurements (details see below) provided by Thermo Fischer (pbase = 1 × 10⁻⁹ mbar), (ii) a UHV preparation chamber (pbase = 1 × 10⁻¹⁰ mbar) equipped with standard facilities for sample preparation such as a manipulator for sample heating via electron bombardment, an Ar⁺ ion sputter gun and several valves serving as gas inlets (O₂, H₂, Ar, etc.) and (iii) a load lock chamber, which allows for lock in or lock out of samples. Furthermore, the load lock chamber serves as a working compartment to mount an electrochemical flow cell. For the electrochemical measurements the samples were transferred from the preparation chamber to the load lock, which is subsequently flooded with N₂.
XPS measurements after EC were achieved by pumping the N₂ from the transfer chamber until a base pressure of \(p_\text{base} = 5 \times 10^{-8}\) mbar was reached, before transferring the electrodes into the main UHV chamber.

The UHV-STM set-up consists of two parts, that is, (i) a main UHV chamber \(p_\text{base} = 1 \times 10^{-10}\) mbar) containing both an STM (Aarhus Type STM) and similar facilities for sample preparation as mentioned above and (ii) a similar load lock chamber \(p_\text{base} = 5 \times 10^{-8}\) mbar) for the electrochemical characterization equipped with a newly designed hanging meniscus cell. The procedure for the sample transfer between the different chambers was performed in the same way as described above.

**Sample preparation**

*Under UHV conditions:* Two slightly different preparation procedures were employed. (i) The electrodes were exposed to Ar⁺ ion sputtering \(p_\text{base} = 4 \times 10^{-4}\) mbar, \(U = 2\) keV) for 1 hour, annealed at 1000 K for 1 hour, Ar⁺ ion sputtered at 1000 K for 1 hour and a final annealing step at 1000 K for 10 minutes. The quality of the samples was either investigated with XPS or STM depending on the used UHV chamber. (ii) The electrodes were exposed to 3–5 cycles of \(\text{Ar}^+\) ion sputtering 5–10 monolayers \(p_\text{base} = 4 \times 10^{-4}\) mbar, \(U = 2\) keV) and then heating to 1000 K for 300 s. The first cycle is sputtered while the crystal is at room temperature. Subsequent sputter cycles were carried out as the crystal is still cooling down from 1000 K, that is, to around 800 K.

**Mechanical polishing (MP):** The electrodes were polished mechanically by hand on a polishing cloth (Struers, MD-Mol) first with 0.1 \(\mu\)m Alumina powder for 10 minutes and further 10 minutes with 0.05 \(\mu\)m Alumina powder (Buehler MicroPolish) until a mirror like finish was observed by naked eye and were subsequently thoroughly rinsed with MilliQ water. Residual water had to be removed carefully from the sample face with a paper tissue, without touching the electrode surface, prior to mounting the sample on the flow cell set-up.

**Electropolishing (EP):** The electrodes were EP in 66% H₃PO₄ solution at approximately 2 V vs. a Cu wire serving as counter electrode, used as cathode. The potential was controlled with a power supply (EA Elektro-Automatik EA-PS 7016-10 A) and was set at the point just prior to the onset of bubble formation on the electrode, which would be related to the oxygen evolution reaction (OER) on the electrode. Performing the electrolysis at a more positive potential leads to pitting and restructuring of the surface, which can be observed with the naked eye. The electrodes were electropolished for 90 s unless otherwise mentioned. After the electropolishing the electrodes were thoroughly rinsed with MilliQ water. Residual water had to be removed according to the procedure described for MP electrodes above.

**Radio frequency heating (RF):** The Cu foils were attached to a Cu wire and mounted in the RF heater (MTI Corporation SP-15A Portable High Frequency Induction Heating Unit). The samples were heated in a gas mixture of H₂/Ar : 5/95 (AGA, purity: 5.5 H₂ and 6.0 Ar).

**Chemical induction (RI):** The cylinder has three in-/outlets, where the first inlet is used to mount a Pt wire as counter electrode, the second inlet is used to introduce the electrolyte in the cell from a glass supply bottle, connected via PFA tubes (high purity plus PFA–IDEX Health & Science) to the cell and the third outlet is leading to the reference electrode and an electrolyte waste container. The potential was controlled with a BioLogic SP-200 potentiostat.

In both electrochemical cells a homemade RHE electrode was used and all potentials are given vs. the RHE scale, unless otherwise mentioned. The electrochemical data were collected with the BioLogic EC-Lab V11.12 software.

The glassware (Electrolyte supply bottle) was cleaned with highly concentrated KOH (Merck ENSURE potassium hydroxide 85%) and boiled prior to the experiment in MilliQ water. Prior to each experiment the tubes leading to the flow cell and the hanging meniscus cell were rinsed with deaerated MilliQ water (purged with Ar, AGA 5 N) and subsequently with the respective deaerated electrolyte (purged with Ar, AGA 5 N).

**Procedure to record CVs in the flow cell set-up:** First, the electropolished polycrystalline Cu sample was mounted on the cell to test
that the set-up is contamination-free (comparison between the CVs for the initial oxidation of an electropolished Cu electrode for each day of measurement). Subsequently, the flow was stopped, the polycrystalline Cu sample removed. During electrochemical tests of the electrodes prepared under UHV conditions, the flow cell was mounted in the load lock chamber. The freshly prepared electrodes (both from UHV or non-UHV treatment) were mounted on the cell and electrolyte flow was started. Next, the bubbles were removed from the system with a set of syringes, the working electrode was connected and the measurement was immediately started. The time between the commencement of the electrolyte flow and the measurement was approximately 20 seconds. Ten cycles were recorded between −0.2 and 0.5 V to stabilize the background pressure of residual O₂ in the cell compartment until a reproducible CV was recorded in this potential range. At this point, CVs were either recorded with electrolyte flow, or the flow was stopped to investigate the surfaces with CVs under stagnant conditions.

Procedure to record the reported CVs in the hanging meniscus set-up: In the hanging meniscus set-up, the cell was raised vertically into the load-lock before the electrolyte cylinder was filled with electrolyte. Ten cycles were recorded between 0 and 0.1 V for each sample. The actual surface area can be slightly smaller: when the electrode is pressed against the O-ring, its contact with the electrolyte is reduced. Thallium UPD[15,16,18] or double layer capacitance.[19,47] Due to technical reasons we only explored the latter (if necessary), since this approach allows for monitoring changes in surface area during the measurement.

Evaluation of the electrochemical surface area (ECSA)

Throughout the article the current is normalized to the geometric surface area. For the single crystal Cu(100) electrodes investigated in the hanging meniscus cell the electrode geometric surface area corresponds to the diameter of the sample (6.0 mm, d₀ in Figure 7) and in the flow cell the geometric surface area is determined by the inner diameter of the employed O-ring (4.4 mm, d₁ in Figure 7). In the latter case, the actual surface area can be slightly smaller: when the electrode is pressed against the O-ring, its compression leads to a reduction of the inner diameter, due to its lateral expansion (d₂ in Figure 7). This can lead to small differences in the absolute currents, when CVs recorded in the different electrochemical cells are compared. For the single crystal Cu(100) electrodes the actual electrochemical surface area (ECSA) of polycrystalline Cu electrodes can be determined by a number of different techniques such as Lead UPD,[15,16,18] Thallium UPD[19,47] or double layer capacitance.[32,46] Due to technical reasons we only explored the latter (if necessary), since this approach allows for monitoring changes in surface area during the measurement.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: copper · cyclic voltammetry · electrochemistry · model catalysis · single crystals

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These are not the final page numbers!
Polycrystalline and Single-Crystal Cu Electrodes: Influence of Experimental Conditions on the Electrochemical Properties in Alkaline Media

Pre-treatment matters: The electrochemical properties of Cu(100) single-crystal electrodes prepared with different pre-treatments were investigated by cyclic voltammetry in alkaline media. Since the atomically flat Cu(100) electrodes prepared under ultrahigh vacuum (UHV) conditions show a distinct electrochemical response compared to those prepared under laboratory conditions, the CV recorded on Cu(100)-UHV electrodes provides a benchmark for further studies on Cu(100) single crystals.
E.3 Paper III

Grazing incidence X-ray diffraction of polycrystalline copper under CO reduction conditions

Søren B. Scott, Thomas V. Hogg, Alan Landers, Thomas Maagaard, Erlend Bertheussen, John Lin, Ryan Davis, Jeffrey W. Beeman, Drew Higgins, Walter Drisdell, Christopher Hahn, Apurva Mehta, Brian Seger, Thomas F. Jaramillo and Ib Chorkendorff

Notes: In preparation, November 2018, cited as [91] in this thesis

Abstract

In-situ studies are necessary to understand electrocatalysts in their active state. In this study, we use in-situ grazing incidence x-ray diffraction (GIXRD) to investigate the surface composition and morphology of a polycrystalline Cu electrode in 0.1 M KOH electrolyte during electrocatalytic reduction of CO. By monitoring the Cu$_2$O(111) and Cu(111) peaks as a function of time during the initial cathodic sweep from open-circuit potential to $-0.4$ V vs RHE, we observe that the surface is fully converted to the metallic phase between approximately 0.5 and 0.3 V vs RHE. No oxidized phases of copper are detected at potentials relevant to CO reduction. We also observe that the ratio of the Cu(200) to Cu(111) GIXRD peak increases at $-0.4$ and $-0.5$ V vs RHE in CO-saturated electrolyte but not in Ar-saturated electrolyte, indicating that CO promotes a restructuring favoring the (100) surface facet. This helps explain why polycrystalline Cu shows a similar product selectivity to single-crystalline Cu(100).
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