Electrochemical Insights into Platinum Catalysts for Fuel Cells

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Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

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PhD Thesis:

Electrochemical Insights into Platinum Catalysts for Fuel Cells

by Kim Degn Jensen

Supervisors: Prof. María Escudero-Escribano, Prof. Ifan E. L. Stephens & Prof. Ib Chorkendorff

Technical University of Denmark,
DTU Physics-SurfCat
May 2017, Kgs. Lyngby
Abstract

Development of sustainable energy production, conversion and storage technologies must be considered one of the major challenges of the 21st century. Insight and understanding of the oxygen reduction reaction is imperative in these pursuits. In this work electrochemical investigations and physical characterization of various model systems ranging from extended surfaces, to thin films and nanoparticle electrocatalysts have been presented and discussed. This have been done with a special focus on governing factors controlling the electroreduction of oxygen.

Preparation of Cu/Pt(111) near-surface alloys was conducted and compared to earlier results from our group. In lieu of the Cu amount in the 2nd atom layer the OH adsorption energy could be tuned. This was done for a range of Cu/Pt(111) samples which were investigated in alkaline media, revealing a Sabatier volcano relationship to the relative shift in OH adsorption potential. This work demonstrates, for the first time, that the OH binding energy indeed is a descriptor in alkaline as well as in acidic media. The apparent synergistic effects between the alkali cations and the electrodesurface of the Cu/Pt(111) combined with the optimization of the OH binding energy, resulted in extremely high specific oxygen reduction activities. The maximum ORR activity was recorded to be $100.7 \pm 7.5\, \text{mA/cm}^2$ at $0.9\, \text{V vs. the reversible hydrogen electrode}$. The Cu/Pt(111) system was also used to investigate the oxygen reduction reaction in the presence of poisoning anions from the electrolyte. These experiments revealed that catalyst with optimum activity in non-adsorbate-adsorbate interacting electrolytes, such as $\text{HClO}_4$, also resulted in catalytic surfaces with superior tolerances for phosphate. Suggesting scaling between OH and phosphate adsorption energies. Results on Gd/Pt(111) samples revealed that compressive strain from Pt overlayer formation is of major importance for the observed oxygen reduction activity enhancement. In-situ GI-XRD studies revealed that the overlayer forms almost instantaneous once the electrode is immersed into the acidic electrolyte. Furthermore, the overlayer appeared to be very stable after accelerated stability test.

Pt and Pt-Gd thin film investigation was also conducted. Here X-ray characterization played a central role in ascertaining that oxygen incorporation into the alloy, due to the oxyphilic nature of Gd, was kept at a minimum. Stable Pt and Pt$_5$Gd thin films were produced and electrochemical characterization experiments revealed specific activities of $0.9\, \text{V vs. RHE of } 9.0 \pm 0.6\, \text{mA/cm}^2$ and stability retention of 83%. Both of these metrics were comparable to those reported for bulk polycrystalline Pt$_5$Gd samples in HClO$_4$. 
electrolyte. 
A preliminary electrochemical study of in-house synthesized Pt-Y nanoparticles have also been presented revealing specific mass actives of $0.3 \pm 0.1 \text{ A/mg}_{\text{Pt}}$ in HClO$_4$. The study revealed that extensive optimizations of the Pt-Y nanoparticles are required and their performance is severely impeded by poor electrochemically active areas and maybe also non-conformity of their crystal phase structure.

Præparering af Cu/Pt(111) nær-overflade legeringer er blevet udført og sammenlignet med tidligere resultater fra vores gruppe. Igennem deponeringsmængden af Cu og legering ned i det andet atom lag kunne OH adsorptionsenergien reguleres. Dette er blevet gjort for en række Cu/Pt(111) prøver som blev undersøgt i base, hvilket afslørede en Sabatier vulkan i forhold til de relative skift i OH adsorptionspotentialer. Dette arbejde demon-strerede dermed for første gang at OH binding til overflader er en generel beskrivende aktivitetsfactor i både basiske og syreholdige medier. Den umiddelbare synergetiske efekt imellem alkali kationer og elektrodeoverfladen af Cu/Pt(111) prøvernes, combineret med optimeringen af OH bindingsenergien resulterede i ekstremt høje specifikke oxygenreduktionsaktiviteter med maksimum værdier registreret til 100.7 ± 7.5 mA/cm² ved 0.9 V relativt til det reversible hydrogen elektrode potentiale.

Cu/Pt(111) systemet blev også brugt til at undersøge oxygenelektroreduktion under påvirkning af anionforgiftning fra elektrolyttten. Disse eksperimenter afslørede at katalysatorer med optimeret aktivitet i ikke adsorbat-adsorbat interagerende elektrolytt, såsom HClO₄, også resulterede i overfladelektrolytter optimeret til at modstå fosfatforgiftning. Dette indikerer skalering imellem OH og fosfats adsorptionsenergier.

Resultater fra Gd/Pt(111) prøver afslørede at dannelsen af et sammenpresset Pt overlag var af afgørende betydning for den observerede oxygenreduktionsaktivitet. Ydermere, viste in-situ røntgenstrålediffraktionsstudier at overlager bliver dannes næsten øjeblikkelig efter kontakt med en syreholdig elektrolyt. Det viste sig også at overlager kunne anses som værdende yderst stabilt efter accelereret stabilitetstest.

Undersøgelser af Pt og Pt-Gd tyndfilm er også blevet udført. Her spillede røntgenkarakterisering en stor rolle i og med oxygeninkorporering i legeringen, grundet oxygens affinitet for Gd, ønskedes minimeret. Stabile Pt og Pt₅Gd tyndfilm er blev fabrikeret og elektrokemiske karakteriseringseksperimenter afslørede specifikke aktiviteter ved 0.9 V vs. RHE på 9.0 ±
0.6 mA/cm², samt aktivitet bibeholdelse nær 83%. Hvilket var sammenligneligt med lignende parametre fundet for makroskopiske polykrystallinske Pt₅Gd prøver i HClO₄. Tidligt stadie eletrokemiske undersøgelser af Pt-Y nanopartikler synteseret p˚a DTU er også præsenteret. Disse afslørede specifikke masse aktiviteter på 0.3 ± 0.1 A/mgPt i HClO₄. Dette studie afdækkede også, at omfattende optimering af Pt-Y partikeltypen er nødvendig, eftersom ydeevnen af partiklerne er svært reduceret grundet dårlig eletrokemiske aktive overfladearealer og måske endda også grundet manglende konformitet af deres fasestruktur.
Preface

This thesis has been written and submitted as the part of the required fulfillment for obtaining a PhD degree from the Technical University of Denmark (DTU).
The work has been completed in the time-span from May 2014 to May 2017 at the Department of Physics (DTU Physics) at the Villum Center for the Science of Sustainable Fuels and Chemicals (SurfCat) only interrupted by a two month external stay at the Korean Advanced Institute of Science and Technology (KAIST). SurfCat is funded by the Villum foundation and the work presented in this thesis have been gratuitously funded, under the Korean-Danish Fuel Cell project charter (KDFuelCell), by the Danish fund of innovation (Innovationsfonden).
The work has been conducted under the co-supervision of Prof. Ib Chorkendorff, Prof. María Escudero-Escribano and Prof. Ifan E. L. Stephens at DTU Physics.
The presented thesis has been written using the \LaTeX{} typesetting format.
Acknowledgments

I would like to extend my gratitude and acknowledge my supervisors whom without this work had not been possible Prof. Ib Chorkendorff, Prof. Ifan E.L. Stephens and Prof. María Escudero-Escribano for the opportunity and always being ready with insight, suggestions and (when sometimes needed) critique, all have been heavily appreciated.

I would also like to express gratitude for the funding received under the KDFuelCell project charter and the project partners: DTU Physics and Energy, DPS, EWII and NIAS.

A special thanks is also due to PhD Amado Velázquez-Palenzuela and PhD Christoffer Møleskov Pedersen who together with PhD Arnau Verdaguer-Casadevall and my supervisors took it upon them to introduce me to electrochemistry and the field of electrocatalysis.

All the people of SurfCat and the people whom which this work has been done in collaboration with, most notable PhD Brian Peter Knudsen, PhD Eleonora Zamburlini, PhD Anders Filsøe Pedersen, PhD Elisabeth Therese Ulrikkeholm and others.

Gratitude and thanks is also due to the external collaboration I have had with PhD Jakub Tymoczko and Prof. Aliaksandr S. Bandarenka of the University of Ruhr-Bochum and the Technical University of Munich (TUM), respectively, teaching me near-surface alloys preparation. A thanks also goes to Prof. Jan Rossmieisl of the University of Copenhagen (KU) for theoretical insights of said system. I would also like to thank JeongHoon Lim, Hoon Lee and Prof. EunAe Cho and her entire group for insight into applied fuel cell systems and for making my external stay at KAIST enjoyable and educational.

Recognition is also due to the scientific and administrative staff at DTU Physics notable PhD Kenneth Nielsen, PhD Robert Jensen, Jacqueline McAnulty, Prof. Jakob Kibsgaard and Prof. Jane Hvoldbaek Nielsen and to friends and colleagues whom I have been able to discuss relevant and not-so-relevant topics and especially Georgina Daniell who patiently helped proof-read this thesis work.

I would also like to thank the students whom I have tutored, for their patience and dedication and the learning opportunity they provided me, I hope I was not too demanding. Finally, I like to thank my mom and dad (who also helped proof-read) and my sister for their support, as well as my girlfriends family for theirs. Most importantly I would like to sincerely acknowledge my girlfriend Maria for her unwavering support and admirable patience with me these last three years, thank you.

Sincerely, Kim Degn Jensen (May 2017)
List of Papers

List of Included Papers

Paper I:
Experimental Elucidation of the Oxygen Reduction Volcano in Alkaline Media
Kim D. Jensen, Jakub Tymoczko, Jan Rossmeisl, Aliaksandr S. Bandarenka, Ib Chorkendorff, María Escudero-Escribano, and Ifan E. L. Stephens
Notes: In preparation, manuscript appended, see appendix A.

Paper II:
Enhanced Oxygen Reduction in the Presence of anion poisons through subsurface alloying
Kim D. Jensen, Ib Chorkendorff, Ifan E. L. Stephens, and María Escudero-Escribano
Notes: In preparation, abstract appended, see appendix B.

Paper III:
Benchmarking Pt and Pt-lanthanide sputtered thin films for oxygen electroreduction: fabrication and rotating disk electrode measurements
Notes: Submitted, manuscript appended, see appendix C.

Paper IV:
Active site formation and stability of Gd/Pt(111) for oxygen electroreduction: an in-situ surface X-ray diffraction study
Notes: In preparation, manuscript appended, see appendix D.

List of Non-Included Papers

Paper V:
Probing the nanoscale structure of the catalytically active overlayer on Pt alloys with rare earths
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Introduction

The following thesis work concerns the investigations of platinum-based catalysis for the Oxygen Reduction Reaction (ORR) for use in High- and Low- Temperature Proton Exchange Membrane Fuel Cells (HT- and LT-PEMFCs, respectively). The motivation for this work will be presented in the following ordered introduction by discussion of:

- The broad societal and historical impact our (mostly) fossil based energy consumption has had on the world and the future challenges of such energy consumption.

- The potential technological schemes which have been proposed to address these energy challenges, as well as their respective issues from both a technological and an economic perspective.

- The specific scientific focus and motivation for the study of ORR for PEMFC which is the foundation of this thesis.

- Prior investigations conducted within our group\textsuperscript{[1-3]} and the results of these studies in context to the broader scientific field of PEMFCs and oxygen catalysis research.

It is the hope that the following introduction will act as a conduit for the layman to gain insight into the importance of PEMFC research both from a broad societal, a techno-economic and a fundamental scientific perspective. It is also the hope that this introduction may shed light on the broader range of engineering issues impacting viable PEMFC applications and justify the topics chosen covered within the content of this thesis.
1.1 Motivation

The wealth and prosperity of the human race can fundamentally be accredited to our adaptation and invention of new technologies. Science, as such, is the mediator between ideas and working new technologies. Consequently, scientific endeavors tend to some extent to be aimed at specific fields where clear challenges have been or might be identified. No greater and unavoidable challenges have been identified in today’s globalized society than issues relating to energy and energy sustainability. Some issues are evident and some seem obvious when correlating energy consumption and global economy, population growth, standard of living, fuel availability and sustainability, and the environmental impacts that energy driven societies have on our planet. Some of the aforementioned relations have been exemplified in figure 1.1 to 1.3.

Figure 1.1: Sourced online data\(^{[4-7]}\) showing both annual energy consumption and distribution of resources (blue axis) and annual energy consumption per capita (red axis), the 1/3 of the minimum annual solar energy potential\(^{[6]}\) has been included.

Figure 1.1 shows historic records of annual consumed energy \(E_{\text{Year}}\) (total and per capita). It is evident that renewable energy sources such as wind and solar only occupy a minor role in the global energy consumption at present, but have been growing steadily throughout last decade. From figure 1.1 the global energy consumptions indirect relationship with global economic trends can be observed, hence both the economic crisis around 2007-08 is clearly visible and China’s massive investments in coal power-plants trough the 2000’s are
visible. Figure 1.1 also reveals a general increase in energy used *per* consumer, indicating that a continuous population growth in itself is problematic and in terms of energy consumption from finite (fossil) resources is inherently unsustainable. Linking the energy consumption to atmospheric emission levels is obvious given recent years public discourse. In that context the atmospheric CO$_2$ levels and temperature anomaly, $\Delta T$ measured both from observatory data and ice-core samples have been plotted in figure 1.2.

![Figure 1.2: Atmospheric CO$_2$ levels$^{[8–10]}$ (blue axis) and temperature record$^{[11,12]}$ (red axis) since 1870 up to present (with insert showing the last 400 000 years) gathered from ice-core and atmospheric measurements.](image)

From figure 1.2 it is evident that the anthropomorphic emissions over the last 100 years is strongly related to the energy consumption during that period of time. These emissions are surely inducing changes to the atmospheric CO$_2$ level, correlating with changes in global temperature. From the historic records of the CO$_2$ and temperature it may be noticed that temperature anomalies have been much higher and lower than seen in the last 100 years. However such events often occurred with catastrophic repercussions for many (now extinct) species. Besides the environmental impacts of the energy consumption the energy consumption have also been shown to have an expressed relationship with socio-economic metrics such as the summed Gross Domestic Product accounting for Purchase Price Parity $\sum$ GDP$_{PPP}$ and the Inequality-adjusted Human Development Index IHDI$^{[17]}$ (see figure 1.3). Figure 1.3a shows the growth of national economies (through the GDP) and the average
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**Figure 1.3:** Summed *i.e.* global GDP corrected by purchasing power parity (blue axis) and IHDI (red axis). *a* Plotted from 1870 until 2015 (2015 value was projected). [*13,15*] *b* Plotted as a function of annual energy consumption [*4,5*] with fitted trends.

quality of life (through the IHDI) since 1870. This growth seems to correlate with the energy consumption, see figure 1.3b, over the same period of time and interestingly it seems that GDP scales exponentially while scales IHDI linearly with the energy consumption. Hence, whether the progress of our civilization is described from a metric such as GDP or IHDI the conclusion is clear, continuous growth is predicated upon a significant increase in energy consumption.

From figures 1.1, 1.2 and 1.3 it is clear that there is a problem which can be stated easily in the following manner: Our planet, of finite resources, accommodates a population whose survival and prosperity have so far been predicated on readily available energy predominantly from fossil fuel sources. The energy consumption *per capita* is sure to increase further as the population of less developed countries accounts for more than 80% of the world’s population [*7*] and these countries are for the vast majority, becoming more developed. Shortage or depletion of energy (re)sources have historically resulted in economical stagnation and may severely stifle the production required to maintain a large population, something which has at all times resulted in civil- and national strife. In addition to these socio-economic issues it has become apparent that anthropomorphic changes to our climate follow our emissions of greenhouse gases [*11,12*] such as CO, CO$_2$, NO$_x$ etc. as seen in figure 1.2. This is unfortunate as approximately 86% of global energy consumption [*5*] derives from combustion of fossil fuels emitting exactly these compounds. From a resource availability perspective the situation becomes even more severe as new discoveries of conventional oil and gas resources have steadily declined since the 1980s [*18*]. Moreover, production of more or less all types of fossil fuels is estimated to start decreasing by 2070 due to resource depletion [*19*] *i.e.* human progress in terms of IHDI and GDP is likely to
halt unless new resources or energy solutions are found. From the above problem statement two things are apparent:

1) Discussing the validity of climate change studies and the impact of anthropomorphic emissions are secondary when assessing whether there is an energy problem to be solved or not.
2) The principal problem of finding sustainable resources that will allow both developed and developing countries to maintain and even increase their standard of living may be solved by shifting from chemical fuels forced from the underground in forms of oil(-sands), gas and coal to combinations of renewable sources, such as solar, hydro and wind power.

The latter point is not surprising as the sun delivers approximately $8.64 \times 10^6$ EJ per year to the surface of the Earth, of these between 1575 up to 49837 EJ per year could potentially be collected, which exceeds the present 550.5 EJ annual consumption. Issues regarding the required area for sufficient solar power collection and material availability, device life-times, maintenance and the intermittent nature of solar power generation would have to be addressed. Similar issues also pertain to wind power. Huge research efforts are going into optimizing PhotoVoltaic (PV) devices, thus improving efficiency, durability and overall costs. As of 2017 the German price per Watt of electricity from solar and wind was 78 to 142 €/MWh and 45 to 107 €/MWh, respectively. In some cases these were close to or actually competitive with that of brown coal 38 to 53 €/MWh. Although this seems promising, the most pressing issue for complete energy reliance from solar and wind power persists; at present the technology does not support electricity production and thus consumption in periods when it is neither sunny nor windy. To complicate matters a substantial percentage of the worlds energy consumption goes towards transportation ($\sim 28\%$) and since schemes based on electrification of roads and trains does nothing to alleviate fuel requirements of water and air transport, altogether different considerations must be made. All aspects of the presented wind/solar energy mobility and intermittency problems can be alleviated by the storage of electric power generated by these sources in chemical bonds i.e. fuels and batteries. As the cost and power densities (also volumetric densities) of batteries leaves much to be desired, storage of energy as (chemical) fuels seem like a more promising option, though batteries undoubtedly will still have a role to play in future energy schemes. From the preceding it is clear that generating electrical energy in the future may present challenges, but emerging and old technologies harvesting wind, solar and hydro energy may solve the resource problem. However, renewable energy sources offer no direct solutions for either the intermittency issues (hydropower excluded) or mobility issues arising for transport applications.

---

1 Onshore wind farms.
1.2 Future Energy Schemes

In the following, four schemes for addressing the intermittency and mobility issues have been summarized in context to the future rise in energy demand and finiteness of resources.

1.2.1 Laissez-Faire

The archetypical approach can be described as *Laissez-faire*, in which a minimum amount of new initiatives are being undertaken. This approach is predicated on new fossil fuel sources and as such recent years have seen a rise in biomass consumption and the exploitation of shale gas and oil, both fossil fuel sources deemed too inefficient for usage by earlier generations.\(^5\) It is worth noting that continuous use of progressively less efficient fossil sources (biomass included) hardly can be considered a sustainable approach and comes with a range of ethical, environmental, health and cost issues. Issues that many national governments have pledged to accede to.\(^{25,26}\) Note that at present only \(\sim 0.7\) W/m\(^2\) can be gathered for high yield biomass, whereas the numbers for wind and PVs are \(\sim 4.0\) and \(\sim 12.0\) W/m\(^2\) respectively.\(^{27}\)

1.2.2 Electrification and Batteries

A substantial part of the transport sector can to a wide degree be electrified, as such electrification of buses, trams, trains and in some places even cars is possible. However, this requires centralized (often urban) investments in infrastructure. Battery cars already exist, although their range makes them perform unfavorable outside urbanized areas. Moreover, at present the resource usage of cobalt and other metals used in electric cars makes it hard to scale the technology to support the complete annual car production of ca. 6 million units.\(^{28}\) Despite these shortcomings, technologies relying on batteries and/or road/railway electrification will likely play important roles in the future,\(^{29}\) but as these technologies does little to alleviate the intermittency issues from wind and solar energy nor solve the fuel requirements for air and water transport other considerations must be made.

1.2.3 Carbon Based Synthetic Fuels

A promising approach to the energy challenge\(^{20}\) concerns the use of excess electrical energy from renewable sources, e.g. PV and wind, to make synthetic fuels. The idea is to capture CO\(_2\) and then use the CO\(_2\) as feed gas. Thereby, through careful electrocatalysis with water, in a reaction called CO\(_2\) Reduction Reaction\(^{30,31}\) (CO\(_2\)RR), it may be possible to selectively form hydrocarbons such as methanol or ethanol. Alternatively, by using CO\(_2\) and H\(_2\) one may form desirable hydrocarbons through *Fisher-Tropsch* synthesis.

The benefits of the carbohydrate oxidation scheme are numerous. Carbohydrates have high energy densities (also volumetric) and can be stored, distributed and utilized in a
future energy schemes

fashion similar to how conventional gasoline is used today. It may even be possible to produce more efficient vehicles utilizing electrocatalysis, e.g. through Direct Methanol Fuel Cells (DMFCs), see figure 1.4, although power consumption per vehicle generally exceeds what is considered viable for DMFCs.

![Figure 1.4: Working principle of catalysis, with reactants (A and B) and products (P) exemplified additionally through methane oxidation and ORR.](image)

The benefits of synthesized carbon based fuels are widely predicated on the ability to capture CO$_2$ from both point-sources (district heating plants, factories etc.), but also on the ability to capture CO$_2$ directly from the atmosphere. If CO$_2$ capture from the atmosphere could be realized the technology would to a wide degree be CO$_2$ neutral and likely even aid in diminishing atmospheric CO$_2$ levels. However, if CO$_2$ capture is proved unfeasible CO$_2$ would likely have to be supplied from (upgraded) biomass and may dictate radically increasing CO$_2$ emissions. Moreover, development of an efficient, selective and cheap CO$_2$RR scheme is extremely difficult due to fact that at least a 6$e^-$ process required to get desired products.$^2$

1.2.4 Hydrogen Fuel

Electrochemically producing hydrogen for fuel is the simplest possible electrocatalytic process as it is only predicated on a ”simple” 4$e^-$ transfer process. Water electrolysis for H$_2$ production has been well known since 1800 when William Nicholson and Sir Anthony Carlisle first imposed a potential across two electrodes submerged in water and observed

$^2$Step-wise CO$_2$RR and CORR may circumvention this.
water splitting as H\textsubscript{2} and O\textsubscript{2} evolution at the cathode and anode, respectively. Water splitting follows the simple reaction scheme\textsuperscript{[35]}

\[ 2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2, \quad U_0 = 1.23 \text{ V} \quad (1.1) \]

where \( U_0 \) is the equilibrium potential for the reaction. Splitting of water through equation (1.1) is predicated on two half-cell reactions; the Hydrogen- and Oxygen Evolution Reaction (HER and OER respectively) and the overall reaction is conceptually rather straightforward. However, in terms of efficiency and stability it presents with a range of difficult and complex issues. Hence, at present electrolysis as a means of hydrogen production is out-competed by methane conversion by steam reforming to synthesis gas (or syngas) and the Water-Gas Shift Reaction (WGSR)

\[ \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2, \quad \Delta H = 206 \text{ kJ/mol} \]

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2, \quad \Delta H = -41 \text{ kJ/mol} \quad (1.2) \]

The viability of equation (1.2) reactions as means for a competitive H\textsubscript{2} production is of course predicated on readily available methane, \textit{e.g.} from natural gas. As natural gas reserves are expected to diminish one may assume electrolysis, rather than steam reforming, will be the only viable means of H\textsubscript{2} production in the future. Moreover, H\textsubscript{2} is a very desirable energy carrier as the oxidation produces the benign product of water and abundant water sources for electrolysis are available.

The reverse water-split reaction has been known since 1884 when \textit{Sir William Grover} used a simple electrochemical cell to run a current from H\textsubscript{2} and O\textsubscript{2} gas dissociation into water, thereby converting the stored potential energy of the chemical bonds.

A future hydrogen based energy scheme can be imagined in which water electrolysis from excess renewable power is used to store energy in H\textsubscript{2} bonds for later use in cars or for electrification through reverse reactions, such a scheme has been attempted conveyed in figure 1.5. Hydrogen as an efficient, sustainable and ”clean” energy carrier, as outlined in figure 1.5, is fundamentally predicated on the technological ability to split water efficiently and cost-effectively while at the same time having the ability to consume the hydrogen in a similar efficient and cost-effective manner. Accessing the stored energy in hydrogen is in itself not difficult, combustion of hydrogen as a means of driving gas turbines is a simple, albeit inefficient,\textsuperscript{[16]} method of converting chemical to electrical energy.

Fuel cells provide a promising means of converting chemical energy to electrical energy with lowered losses. Different fuel cell systems have been proposed in literature,\textsuperscript{[36]} most noticeably Solid Oxide Fuel Cells (SOFCs), Alkaline Fuel Cells (AFCs) and PEMFCs. In this thesis fundamental issues regarding mainly PEMFCs and the underlying catalytic process will be treated. It is worth outlining that SOFCs typically operates at high temperatures (400 to 550 °C)\textsuperscript{[37]} resulting in prolonged start-up times. The technology is thereby unsuitable for applications requiring fast responses such as for automotive transport, a sector responsible for approximately 22 %\textsuperscript{[22, 38]} of the world’s total energy consumption. It is also worth noting is that inherent stability issues are associated with the hydroxyl transporting membranes of AFCs.
Figure 1.5: Hydrogen based energy scheme in which excess electricity generated from renewable sources, e.g. PV and wind power, is used for water electrolysis producing $\text{H}_2$ (and secondary valuable $\text{O}_2$). The hydrogen fuel can initially be stored and either reconverted to electricity for the power grid using fuel cells or utilized in the chemical industry or as fuel in automobiles again using fuel cells. Images for the illustration have been sourced online.\textsuperscript{[39–46]} The plot shows the total consumption and production of wind and solar energy for the Danish power grid in the period from 1\textsuperscript{st} to 30\textsuperscript{th} May 2016, especially notice the blue and red areas denoting over and underproduction of renewable energy, respectively.
The benefits of the energy scheme presented in figure 1.5 includes its zero emission nature. Hence, it is favorable in terms of health and climate considerations. Moreover, pure hydrogen and oxygen are both valuable chemicals used by the chemical industry, so a viable hydrogen production through electrolysis may prove economically lucrative as a secondary revenue income for companies generating energy from renewable sources. There are of course also drawbacks to the scheme in figure 1.5. Energy conversion through electrolysis and back-conversion through fuel cells does in each instance present with losses; if these losses together with the cost of the conversion devices become too great the technology will become uncompetitive. Furthermore, in terms of fuel characteristics the power density of hydrogen (compressed to 690 bar at 15 °C) is very good at 142 MJ/kg, but the power per unit volume is relatively low at 5.6 MJ/L, so quite a few issues pertain to hydrogen storage, especially for vehicular applications. Toyota has already gone to market with its 1st generation automobile running on hydrogen named Toyota Mirai. It has an operational range of 502 km which is in close competition with battery based cars, such as the Tesla S 100D which operational range is 594 km. Moreover, hydrogen fuel stations are slowly appearing across Europe, North America and Asia, indicating that hydrogen as the foundation of the future energy economy is slowly gaining trust from investors and industry leaders.

As for any technology to become viable it must be competitive, this can for fuel be reduced to a consideration of power per cost of the fuel. The power per cost of a fuel is usually evaluated considering the Levelized Cost Of Energy (LCOE). Hence, fuels with high energy contents and low conversion costs would increasingly be considered competitive. For hydrogen to make its big entry on the global market for automotive fuels one may simply consider following macroscopic LCOE requirement to be true

\[
c_{\text{gas.}} = \frac{Q_{\text{gas.}}}{C_{\text{gas.}}} \leq \frac{Q_{H_2}}{C_{H_2}} = c_{H_2}
\]

In equation (1.3) \(Q\) denotes the energy content per liter fuel, \(c\) denotes LCOE and \(C\) denotes the cost per liter. The equation (1.3) only holds if the energy is utilized with equal efficiency. Hence, as the fuel efficiency of conventional gasoline and PEMFC vehicles are different the true relationship (assuming similar production costs of the two vehicle types) evaluated should be

\[
\eta_{\text{gas. engine}} \times \frac{Q_{\text{gas.}}}{C_{\text{gas.}}} \leq \eta_{\text{PEMFC}} \times \eta_{\text{el. engine}} \frac{Q_{H_2}}{C_{H_2}}
\]

, where \(\eta_{\text{gas. engine}}, \eta_{\text{el. engine}},\) and \(\eta_{\text{PEMFC}}\) are the gasoline, electric motor and PEMFC ORR and Hydrogen Oxidation Reaction (HOR) conversion efficiencies. From equation (1.4) it is clear that having a PEMFC efficiently converting \(O_2\) and \(H_2\) to water is extremely important. It should in that context be noted that the efficiency of conventional combustion gasoline engines conversion of chemical to mechanical energy are of the order

\[\text{Such as device, maintenance and life-time costs.}\]
of $\eta_{gas.\ engine} \lesssim 0.38$, whereas an electric engine offers efficiencies up to $\eta_{el.\ engine} < 0.90$. It has been estimated that within a reasonable number of years the cost of $H_2$ will be comparable to gasoline,$^{[50,51]}$ thus it follows that one of the main hurdles of $H_2$ PEMFCs market entry concerns the efficiency and life-time cost of the PEMFC.

From an economic point of view the use of emission free fuels, such as hydrogen, may retard anthropomorphic climate changes$^{[9,12]}$ but may also indirectly affects monetary losses arising from pollution due to traffic, especially in heavily urbanized areas, e.g. in Denmark air pollution, mainly from vehicular transport$^4$, has been assessed to cost society roughly 1.7 billion € from health, climate and work loss related issues.$^{[47]}$

From an entrepreneurial point of view there is an vast untapped (and emerging) market relating to $H_2$ based fuel conversion with both huge risks and potentially huge rewards. Moreover, the prices of renewable energy have been steadily declining for the last several years,$^{[5]}$ thus there is an emerging basis for completely novel electrochemical based technologies.

### 1.3 Proton Exchange Membrane Fuel Cells Challenges

As indicated from figure 1.5 water electrolysis relies on the hydrogen evolution and the oxygen evolution reaction. In such reactions a potential is used to drive the splitting of $H_2O$ at the cathode and producing oxygen at the anode, the main losses of this reaction are at the anode where OER takes place. Similarly, losses on the oxygen side at the cathode also occurs when converting $H_2$ and $O_2$ back into water in a fuel cell.

The oxygen and hydrogen reduction reaction can be thought of as two half-cell reactions taking place in a $H_2$ based fuel cell with the overall reaction

$$\begin{align*}
\text{(HOR)} & \quad H_2 \longrightarrow 2H^+ + 2e^- \\
\text{(ORR)} & \quad \frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O
\end{align*}$$

$$\quad O_2 + 2H_2 \longrightarrow H_2O \quad \text{(HOR and ORR)} \quad (1.5)$$

To visualize a fuel cell stack construction and the basic half-cell HOR and ORR mechanism of equation (1.5), taking place within a single stack element, see figure 1.6.

Illustrated in figure 1.6 and indicated in equation (1.3) is that $H_2$ enters through a Gas Diffusion Layer (GDL) to an electrocatalyst (electrode with a catalyst) on the anode side. Here $H_2$ dissociates into protons and electrons. The hydrogen side is separated with a proton conducting membrane and employs an external circuit for electron transport to the oxygen side on which another GDL is placed. On this GDL an electrocatalyst for $O_2$ dissociation is placed and it is thereby possible to drive a current due to the electrochemical potential difference across the cell. At the oxygen (cathode) side oxygen dissociates and combines with protons to form water.

$^4$Predominantly from carbon particulates from combustion engines and decentralized furnaces, but also from car tire particulates.
Figure 1.6: a Schematic showing the main components of a PEMFC stack, e.g. for automobile applications. b Working principle of a single stack element sometimes denoted MEA configuration.

It is generally accepted that platinum based ORR follows a $4e^-$ process\(^{[52]}\) in which $\text{H}_2\text{O}$ and intermediates are reduced step-wise as follows

$$\begin{align*}
\text{O}_2 + \text{H}^+ + e^- & \rightarrow \text{OOH} \quad (1.6) \\
\text{OOH} + \text{H}^+ + e^- & \rightarrow \text{O} + \text{H}_2\text{O} \quad (1.7) \\
\text{O} + \text{H}^+ + e^- & \rightarrow \text{OH} \quad (1.8) \\
\text{OH} + \text{H}^+ + e^- & \rightarrow \text{H}_2\text{O} \quad (1.9)
\end{align*}$$

The above $4e^-$-pathway is usually considered in context to platinum based ORR catalysis, here the * denotes an oxygen adsorption site on the electrocatalyst.

The energy difference from free $\text{H}_2$ and $\text{O}_2$ to $\text{H}_2\text{O}$, \textit{i.e.} the energy which can be released from equation (1.6) to (1.9), can be evaluated as the change in \textit{Gibbs} free energy\(^{[53]}\) and gives insights into the maximum potential induced over the PEMFC. It is generally accepted that ORR happens in discrete steps, as indicated in the equation (1.6) to (1.9) reaction pathway, forming various oxygen intermediates. These steps correspond to changes in \textit{Gibbs} free energy

$$\begin{align*}
\Delta G_1 &= G_{\text{O}_2} - G_{\text{OOH}} \quad (1.10) \\
\Delta G_2 &= G_{\text{OOH}} - G_{\text{O}} \quad (1.11) \\
\Delta G_3 &= G_{\text{O}} - G_{\text{OH}} \quad (1.12) \\
\Delta G_4 &= G_{\text{OH}} - G_{\text{H}_2\text{O}} \quad (1.13)
\end{align*}$$

The maximum downhill reaction of equation (1.10) to (1.13)\(^{[54]}\) has an equilibrium potential of $U_0 = 1.23\text{ eV}$,\(^{[35]}\) \textit{i.e.} this is the maximum load potential available from the PEMFC system, not considering losses, to drive a net current for any conceived application, see figure 1.7 for reaction path.
In equation (1.10) to (1.10) and indeed also (1.6) to (1.6) only reaction-paths from O\(_2\) to water is considered. However, the much simpler 2\(e^-\)-pathway could also be considered

\[
*O_2 + H^+ + e^- \rightarrow ^*OOH \quad (1.14)
\]

\[
*OOH + H^+ + e^- \rightarrow ^* + H_2O_2 \quad (1.15)
\]

Formally, the 4\(e^-\) pathway can be seen as a series of 2\(e^-\) path steps\(^{[56]}\) as

\[
H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (1.16)
\]

Peroxide equilibrium is at 0.7 V.\(^{[57]}\) which means that it is possible to produce peroxide during ORR at large overpotentials (very high currents). For Pt based ORR hydrogen peroxide is typically not relevant.

Nevertheless when designing PEMFCs, system selectivity to the 4\(e^-\) pathway is extremely important because peroxide, which is a severe oxidizing agent, in contact with the acidic PEM will decompose the polymer membrane over prolonged use, especially at elevated temperatures. Though for most PEMFC applications H\(_2\)O\(_2\) selectivity is considered undesirable H\(_2\)O\(_2\) is a valuable chemical and examples of selective ORR systems designed towards peroxide exist.\(^{[57, 58]}\)

Scaling relations\(^{[59]}\) state that intermediates of similar adsorption element (in equation (1.10) to (1.13) oxygen) will bind to the surface in a linear fashion. This implies that the running the reverse reaction of equation (1.6) to (1.9), i.e. the OER reaction, using an electrocatalyst optimized for ORR will induce further losses.\(^{[52]}\)

The fundamentals of how PEMFCs work have now been covered, below the main components of a PEMFC stack or more specifically a Membrane Electrode Assembly (MEA) will be presented purely from and ORR point of perspective.

### 1.3.1 Proton Exchange Membranes

For optimally working PEMFCs, see figure 1.6, it is important that the PEM is stable and proton conducting. Combining good proton conductivity with good stability is challenging, especially since best PEM conductivities have been reached at elevated temperatures. Naﬁon\(^{®}\) based PEMs are the most commonly found in literature for LT-PEMFC systems (\(< 80°C\)), here the PEM electrolyte is H\(_2\)SO\(_4\) based. However, Naﬁon\(^{®}\) destabilizes severely above 100°C.\(^{[60, 61]}\) Hence, for HT-PEMFC applications (120 to 200°C) PolyBenzimidazole (PBI) membranes have been developed\(^{[62–64]}\) using H\(_3\)PO\(_4\) based electrolyte.
Introduction

There are both pros and cons when operating PEMFCs at elevated temperatures. Increased membrane and catalyst deterioration as well as accelerated water evaporation from heating may unfortunately dry out membranes. Conversely, increased temperatures and resulting water evaporation implies lowered water accumulation at the cathode catalyst thereby avoiding “drowning” of the catalyst. Furthermore, the sluggish ORR kinetics\cite{65–67} have been observed to improve at elevated temperatures.

Besides the above, implicit issues are related to the PEM electrolyte and the utilized catalysts e.g. from various adsorbate-adsorbate interactions between electrolyte anions and oxygen intermediates. Relevant examples of this concerns site blockage of platinum by SO$_4^{2−}$ or PO$_4^{3−}$ anions\cite{68} depending on the PEM electrolyte. Furthermore, the PEM/GDL interface, wherein the catalyst is positioned, should also accommodate sufficient electron transport and appropriate reactant availability (see figure 1.8).

**Figure 1.8:** Illustration of GDL/PEM interface (black/green respectively) with catalyst. **a** Typical interface with round catalyst particles. **b** Interface wherein the catalyst is elongated, alleviating some of the issues seen in **a**.

Figure 1.8a shows examples of some relevant PEMFC optimization issues, such as:

A  An ORR catalyst particle completely embedded in the PEM producing water which accumulates thus drowning the catalyst.

B  Idealized case where catalyst is positioned in the interface between PEM and GDL allowing both electron, proton and water transport.

C  Instance where catalyst is well positioned in the GDL/PEM interface, but catalyst activity is retarded due to poor conductivity to the GDL.

D  Deep catalyst embedding within the GDL disfavors proton transport from the PEM.

Besides the above it is of course also important that the catalyst is active and well dispersed and has an optimized surface to mass area. Moreover, ionomers from the PEM or catalyst synthesis are known to limit the activity substantially.\cite{69} Most of the above
issues would be solved by utilizing a catalyst with exceedingly high surface to mass area ratios and utilizing geometries\cite{70-73} which increases the probability of catalyst interfaces are in contact with both GDL and PEM,\cite{74} e.g. nanowires as illustrated in 1.8a.

1.3.2 Gas Diffusion Layers

Gas diffusion layers are also an important and rather complex component of a PEMFC system. The GDL often acts as a support, contact and a gas permeable structure for transport of O\textsubscript{2} to the electrocatalyst and transport of water away from the cathode. GDLs are most commonly carbon fiber based structures as these offers decent chemical stability in acid and at elevated temperatures, while being mechanically durable and good conductors.

1.3.3 Proton Exchange Membrane Fuel Cell Catalysts

State-of-the-art ORR and HOR catalysts in acid media are all based on Pt, which in both instances is the most ORR- and HOR active pure metal catalyst available, \textit{i.e.} in most PEMFC systems Pt is utilized at both the cathode and the anode. Figure 1.9 shows an example of MEA polarization curve suing Pt based catalysts.

\begin{figure}[h]
\centering
\includegraphics[width=0.6\textwidth]{MEAPolarizationCurve.png}
\caption{MEA cell activity of Pt/C (47 wt% TKK) anode and cathode. Adapted from literature.\cite{75}}
\end{figure}

For PEMFC based ORR for automobiles to be scalable the amount of Pt in each Fuel Cell Electric Vehicle (FCEV) should not substantially exceed presently used in catalytic CO to CO\textsubscript{2} converters (\textit{ca.} 5.0 g\textsubscript{Pt}). Hence, the U.S. Department of Energy (DoE) have estimated a conversion for power to Pt mass (or Pt-group metals) conversion ratio of
0.125 kW/gPt corresponding to roughly 11.3 gPt per vehicle in the year 2020.\cite{76,77} Besides the maximum allowed Pt loading per FCEV some requirements for the ORR specific current activity ($j_k \geq 4.4 \text{ mA/cm}^2$) and specific (Pt) mass activity has also been proposed ($j_{k,m} \geq 0.44 \text{ A/mgPt}$). These Pt based catalysts activity goals are dictated as Beginning-Of-Life activities (BOL), however as catalysts deactivate End-Of-Life (EOL) activities corresponding to 60% of the initial performance have also been proposed.\cite{76} From figure 1.9 it can be seen that up to 45% of the energy is lost as heat and of these losses about 70% can be directly attributed to the sluggish ORR kinetics.\cite{78} All the goals set forth regarding Pt usage per FCEV are predicated on the scarcity and cost of Pt and Pt group metals.\cite{20} To circumvent such requirements non-noble ORR (and HOR) catalyst are widely being investigated, although with limited success due to their propensity to degrade in the often very acidic operating conditions.\cite{79,80} In this work only Pt based catalysis will be treated.

### 1.4 Oxygen Reduction Electrocatalysis

The key focus of this thesis has been the investigation of mechanistic effects governing the ORR activity. For the most part this has been done through half-cell investigations of Pt based systems. As already mentioned, Pt is the best pure metal ORR electrocatalyst,\cite{35} however it tends to bind oxygen intermediates too strong e.g. Pt(111) binds oxygen approximately 0.2 eV too strongly.\cite{1,81} Such catalyst activity described as function of intermediate binding strength are defined through the Sabatier principle and states that rate-limiting intermediates in a catalytic reaction should bind neither too weak nor too strong to the surface for optimum activity.

Besides the extrinsic factors pertaining to electrolyte, temperature and pressure control, intrinsic catalyst properties such as catalyst-support interactions,\cite{72,82-86} size and shape control\cite{70,71,73,87-92} and alloying of Pt with a secondary metal,\cite{2,54,93-96} can all have profound impact on catalyst activity, stability and selectivity. Well-defined model studies are often required to distinguish between the many possible synergistic effects\cite{97} and to aptly identify specific mechanisms that describes a catalyst behavior. Within the field of ORR extended surface studies of Pt(hkI) is probably the most well-known example. Pt(hkI) studies have for example shown that in HClO$_4$ the ORR activity order goes as Pt(110)<Pt(111)<Pt(100),\cite{98} while the dissolution order is Pt(110)<Pt(100)<Pt(111).\cite{99} Similarly, model studies on Pt$_xM$ (where M is some alloying metal) have revealed catalytic activity can be tuned by either ligand and/or strain effects.\cite{1,2,100} The activity of any reaction proceeding on a catalyst surface will be dependent on either geometric effects\cite{101} from site availability, e.g. atomic ensemble effects, or electronic effects by changing of the Local Density of States (LDoS) at the catalyst surface.\cite{102} Changing the LDoS of catalysts are typically accredited to ligand and/or strain effects\cite{100} altering the electronic structure at the catalyst surface, elaboration on what strain and ligand effects encompasses have been presented in the following.
1.4.1 Ligand and Strain Effects

Platinum’s relatively good ORR activity is mainly attributed to the \( d \)-band center that allows for good hybridization of \( \text{O}_2 \) molecules near the Pt surface. The hybridization and thus binding is however slightly too strong.\[^{[81]}\] An explanation of the effect of the \( d \)-band have been attempted in figure 1.10.

![Figure 1.10:](image)

**Figure 1.10:** Schematic of \( sp \)- and \( d \)-band of a transition metal hybridizing, thus filling anti-bonding \( \sigma^* \) states and emptying bonding \( \sigma \) states of a homonuclear molecule (such as an \( \text{O}_2 \) molecule) along reaction coordinate \( \Gamma \).

In figure 1.10 a molecule with empty anti-bonding states approaches a surface with a substantial \( sp \)- \( d \)-band overlap, as seen for transition metals.\[^{[59]}\] The delocalized \( d \)-band overlaps with the molecular orbitals. The overlap allows sharing (broadening) of the states and consequent filling of the anti-bonding \( \sigma^* \) states and emptying of bonding states \( \sigma^* \) weakening the intermolecular bond. Although the \( d \)-band model described here mainly gives a qualitative explanation of catalysis, the concepts from the \( d \)-band model have been widely accepted as the basis for tuning catalysts activity both within the fields of heterogeneous catalysis and electrocatalysis. Though the \( d \)-band model applicability may be limited for specific systems, the fundamental concepts of tuning the electronic structure of catalysts surfaces has certainly proven effective.\[^{[54,103–105]}\] In that context two routes for tuning the electronic surface structure of ORR catalyst exists and are denoted under the terms ligand and strain effects, see figure 1.11.

![Figure 1.11:](image)

**Figure 1.11:** Examples of ligand and strain dominated systems. **a** Ligand effect, *e.g.* Cu alloyed into the 2\(^{\text{nd}}\) layer of a Pt(111) surface. **b** Strain effect, *e.g.* a compressed Pt overlayer of a Pt alloy. Courtesy PhD Paolo Malacrida\[^{[106]}\]
Ligand Effects

Extensive studies of the enhancement of ORR activity by ligand effects have been reported in literature.\cite{1,93,103,107} By alloying with an appropriate metal, see figure 1.11a, it is possible to tune the $d$-band center as the filling of the Pt atoms on the surface will be constant. This precipitates a change in the LDoS at the surface, which to a first order approximation scales with the change in hybridization energy and thus the binding energy of the surface. Examples in the literature of the ligand effects include, among others, studies on the $\text{Pt}_3\text{Ni}(111)$\cite{93} and $\text{Cu}/\text{Pt}(111)$\cite{1} near-surface alloys (NSAs). The later Cu/Pt(111) revealed that by controlling the amount of Cu in the 2$\text{nd}$ atom layer of a Pt(111) crystal it was possible to tune OH binding. In this study changes in OH binding energies were approximated to relative shifts in potentials required for 1/6 ML coverages of OH on Pt(111). Consequently a volcano-like Sabatier relationship was found between OH binding energy and the ORR activity at 0.9 V $vs.$ the Reversible Hydrogen Electrode (RHE) as illustrated in figure 1.12 from our group.\cite{1}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{Activity enhancement of Cu/Pt(111) NSAs in HClO$_4$ relative to Pt(111) and kinetic current density at 0.9 V $vs.$ RHE as a function potential shift in OH adsorption and related OH binding. The circular points represent experimental data and the dashed blue line represents theoretical predictions.\cite{1}}
\end{figure}
Strain Effects

Similarly to the ligand effect, surface strain may induce changes in the electronic structure of a Pt based catalyst. Here however, the electronic structure changes arise from the Pt-Pt overlap of Pt surface atoms, see figure 1.11b. Such overlap can be tuned by alloying Pt with a secondary metal. Hence, once the alloy surface comes in contact with an oxidizing media (as in a PEMFC) the secondary metal will, if not noble, tend to leach out forming a thick Pt overlayer. This overlayer will, depending on the underlying alloy unit-cell size relative to a relaxed Pt surface, be under compressive or tensile strain.[2]

An example from our group of how compressive strain of Pt overlayers scales with a wide range of Pt Lanthanide alloys and the effect on ORR activity are shown in figure 1.13 in which polycrystalline Pt$_5M$ ($M=$Lanthanide metal) samples Pt-Pt surface distances were measured before electrochemical tests. Initial ORR activities and post accelerated degradation tests have been shown.

\[ \text{Figure 1.13: Kinetic current density at 0.9 V vs. RHE of polycrystalline Pt}_5M \text{ electrocatalyst surfaces plotted against the lattice parameter of bulk Pt}_5M \text{ (lower axis) and bulk Pt-Pt distance (upper axis), respectively. Both initial (■) and kinetic current densities after 10000 cycles accelerated stability test (●) have been plotted. Dotted and dashed lines represent the experimental trends seen from initial and post stability test measurements.} \]
Extensive X-ray measurements and electrochemical investigations were required to correlate surface strain of Pt overlayers with kinetic current densities of various Pt alloys.\textsuperscript{[2]} The resulting figure 1.13 indicates that a surface strain of approximately 5\% relative to relaxed Pt would result in optimum activity and that such strained active surfaces could be obtained by acid leaching of the surface forming thick Pt overlayers.\textsuperscript{[2,108,109]} When considering Pt based ORR, both ligand and strain effects are aimed at lowering the $d$-band center thereby lowering the hybridization energy and thus the oxygen binding. However, excessive weakening of the OH binding will result in lowering of ORR activity following the Sabatier principle.

In general descriptive analysis such as those conducted for the Cu/Pt(111)\textsuperscript{[1]} or the Pt$_5$M Lanthanide\textsuperscript{[2]} system, using binding energies or alternative metrics, results in volcano-like plots as exemplified earlier in figure 1.12 and 1.13 or more aptly in figure 1.14.

\begin{center}
\textbf{Figure 1.14:}  \textit{Sabatier} volcano-plot of various Pt based ORR catalysts, plotted using ORR activity enhancement as a function of hydroxyl binding energy, $\Delta G_{HO^*}$, both relative to pure Pt(111). Adapted from literature.\textsuperscript{[3,110]}
\end{center}

Figure 1.14 shows a volcano-like activity plot for ORR for a wide variety of extended surfaces using the shift in OH binding to the surface with respect to that of pure Pt(111).\textsuperscript{[3,110]} These alloyed and/or stepped surfaces are more active due to either the aforementioned strain and/or ligand effects. Extended surface studies allows increased control of a range of parameters such as alloying type and phase uniformity,\textsuperscript{[2,93,94]} surface orientation\textsuperscript{[111–116]} and surface modification\textsuperscript{[1,57,68,101,117–121]} compared to that possible for nanoparticulate
studies. Moreover, a range of well-developed surface science and fabrication techniques exist allowing highly controlled experiments. From figure 1.14 one may conclude that OH binding is an universal descriptor predicting catalytic activity. However, others descriptors which indirectly scales with OH binding have also been reported, such as the $d$-band center,[122] elemental composition ratios[123] and strain[2] among others. There are however a few considerations one must take into account when considering descriptors: A volcano-like relationship is predicated on similar reaction pathways, which means that the reaction-limiting step(s) should be the same for any system compared and should also be selective towards the same product. Such thermodynamic considerations are fundamental within catalysis[59] as they allow both a fixed framework of operating with intermediate bindings as activity descriptors, but it also provoke speculation into structures that may break these intermediates scaling e.g. through variation of said reaction pathways, this is often referred to as breaking the scaling relations. An attempt of breaking the scaling pertaining to ORR concerns the Pt-Hg system[57] in which production of H$_2$O$_2$ rather than H$_2$O was attempted. In this study[57] single Pt surface atoms surrounded by Hg were conceived to allow single top-site O adsorption rather than hollow site adsorption while binding would be optimized for O destabilization relative to OOH, see figure 1.15.

![Figure 1.15](image)

**Figure 1.15:** Atomic representation of ORR on a PtHg$_4$(110) surface. The green and red arrows signify the 2$e^-$ and the 4$e^-$ process resulting in either H$_2$O$_2$ or H$_2$O, respectively. Pt, O, Hg and H atoms are represented by gray, blue, red and yellow spheres, respectively. Adapted from the thesis of PhD Arnau Verdaguer-Casadevall.[124]

Figure 1.15 is a good example of how extended surface studies applying simple surface modifications allows for excellent predictive catalytic behavior. However, in practice making Pt-Hg nanocatalysts for H$_2$O$_2$ production proved difficult as the increased Pt undercoordination on NanoParticles (NPs) compared to extended surfaces allowed Pt oxidation sites of the produced H$_2$O$_2$ to H$_2$O and has so far been abandoned. Model studies on both extended surfaces or even on NPs may misrepresent actual cat-
alytic performances, especially when considering the vast difference in environment when conducting clean electrochemical studies or using Ultra High Vacuum (UHV) techniques compared to the "dirty" and ambient MEA setups that mimic real PEMFC operation. In order for model studies to have any relevance for real-world PEMFCs the effects of corrosion, dissolution, contaminants, mass-transport limitations as well as surface (morphology and composition) variations in liquid electrolyte, compared with UHV conditions, all need to be considered carefully. An example where model studies are well suited pertains to anion adsorption on platinum, a subject which have been extensively studied in literature\cite{68,101,112,117,125–137} and in this thesis.

### 1.4.2 Atomic Ensemble Effects

As it will be discussed in chapter 4, a wide variety of approaches have been attempted in literature for countering the effects of anion poisoning and a few of these have been formalized through substantial considerations. However, an \textit{ad hoc} approach have often been adopted in such studies, \textit{i.e.} a catalyst is developed and measured in HClO$_4$, H$_2$SO$_4$ and H$_3$PO$_4$ and compared with some reference system. Such approaches are suitable from an engineering perspective but gives little insight into the atomic effects of anion poisoning and does not offer strategies for avoiding the effects of poisoning.

Surface modification through rational design, utilizing atomic ensemble effects to counter specific adsorption appears to be an attractive route when considering alleviation of the adverse effects of phosphate adsorption.\cite{138}

Examples of this have been reported, in which cyanide modification of the Pt(111) surfaces is seen to counter phosphate site-blocking\cite{68,101,117,118} (see figure 1.16). The cyanide surface modification of Pt(111) showed that available site engineering of the surface made Pt(111) more resilient towards both sulphate and phosphate anion poisoning during the ORR.\cite{68}

The governance of available sites on a Pt(111) surface is not directly applicable to real life (many faceted) NP Pt catalysts, as surface order will be severely reduced, but as a proof-of-concept the idea of site engineering is intriguing.

This doctoral thesis aims to elucidate mechanisms of Pt based ORR electrocatalysts in terms of relevant surface adsorption phenomena. This is important as catalytic processes in electrolyte are insufficiently described by the catalyst surface, but rather by
Oxygen Reduction Electrocatalysis

As mentioned, the interface between catalyst and electrolyte can have a profound effect on the catalytic activity and selectivity. For instance, the data in figures 1.14, 1.12 and 1.13 have all been obtained in 0.1 M HClO₄ acid, which incidentally is an electrolyte showing minimum anion adsorbate effects on Pt. However, strong adsorbate-adsorbate interactions are observed when subjecting Pt based surfaces to HCl, H₃PO₄ or H₂SO₄.\(^{125,126,135}\) Hence, one could easily imagine a Pt based surface with good intrinsic ORR activity when measuring in HClO₄, but for practical relevant electrolytes such as H₃PO₄ the surface is less active due to adsorbates blocking the sites needed for ORR, see figure 1.17 in which PO₄³⁻ have been imagined on a Pt(111) surface.

Strong adsorption may also induce surface restructuring and oxygen solubility and thus mass-transport limitations may be impeded by changes in the double-layer. Besides ligand-, strain- and atomic ensemble effects the pH of the electrolyte are also expected to affect OH adsorption\(^{140}\) though reports of ORR activity independence\(^{141}\) disputes this. Understood from purely Nernstian considerations reduction potentials will vary with local pH. The pH dependence on equilibrium conditions of a half-cell potential compared to the standard potential \(U_{\text{red}}^0\) can be described by\(^{142}\)

\[
U_{\text{red}} = U_{\text{red}}^0 + \frac{k_B T}{e} \ln \left( \frac{[C]_{\text{red}}}{[C]_{\text{ox}}} \right) \quad (1.17)
\]

In equation (1.17) \(e\), \(k_B\) and \(T\) denote the elemental charge, Boltzmann’s constant and temperature respectively. While \([C]\) denotes concentration of reduced and oxidized species, *i.e.* the logarithmic term of (1.17) should scale with pH. Nb macroscopic electrolyte pH are not necessarily the same as the local pH in the catalyst electrolyte interface,\(^{143}\) thus complicating matters.

Clavilier’s reports\(^{144–146}\) of flame-annealing techniques allowing preparation of clean and well-ordered Pt single and polycrystalline surfaces widely predicates this work. Moreover, abundant literature covering topics of such well prepared Pt surfaces has resulted in invaluable insight into Pt based catalysis. Both in terms of Pt effects from surface modification,\(^{1,57,68,101,117–121}\) electrolyte,\(^{125,126,135,147,148}\) surface morphology\(^{3,149,150}\) as well as ligand\(^{1,93,151–156}\) and strain\(^{2,100,103,108,109,157–159}\) effects. Consequently, there is also an impressive back-catalog of NP (and cluster) catalyst studies in which the experience gathered from the extended surface studies has been applied.\(^{88,91,96,97,139,160–166}\)

Due to many NP studies are closer to actual application studies,\(^{92}\) such investigations often presents with an increased focus on good catalyst performances rather than the more esoteric description of the catalytic surfaces. Hence, focus is often placed on the evalu-
Introduction

ation of good metrics for a catalyst, such as stability, activity and costs of the material and NP processing. Interestingly it is worth noting that stability is often predicated on material nobility, thus extremely stable and active catalyst can be obtained,\cite{167} however cost and availability considerations\cite{20} often makes such catalysts non-viable for market applications.\cite{76,77}

1.5 Thesis Outline

The work encompassed in this thesis has been presented in the following order:

**Chapter 1**- Introduction and motivation for this Pt based ORR study and presentation of prior arts within the field.

**Chapter 2**- Description and discussion of some of the experimental methods and setups utilized in this work.

**Chapter 3**- Results and discussion pertaining to Pt based surfaces, especially Pt(111) and Cu/Pt(111) NSAs performances in alkaline electrolyte and the effect of cations.

**Chapter 4**- Results and discussion of Pt based model surface sensitivity towards the phosphate anion.

**Chapter 5**- Results and discussion of Pt(111) and Gd/Pt(111) single crystal studies in acid.

**Chapter 6**- Presentation and discussion of a study of Pt and Pt$_5$Gd thin films.

**Chapter 7**- Pt/C and Pt$_x$Y/C nanoparticle studies and their performance in MEA systems.

**Chapter 8**- Conclusion and outlook.
In the following a short overview of the experimental methods utilized for this thesis will be presented. Focus will be mainly on the electrochemical methods used as electrochemical studies make up the majority of the reported results of this thesis. However, a range of surface science techniques adopted for this work will also be covered, most of them conducted at the Technological University of Denmark (DTU).

2.1 Electrochemical Setups

A wide range of electrochemical techniques have been utilized in this thesis work, a vast majority of the experiments utilized state-of-the-art Rotating (Ring-) Disk Electrode (R(R)DE) techniques in one form or another. Hence, in the following a quick description of the setups, crystal preparation for RDE test and typical RDE experiments, such as Cyclic Voltammetry (CV), will be presented.

2.1.1 The Three-Electrode Setup

Almost all electrochemical data presented in this thesis has been gathered using a three-electrode cell as illustrated in figure 2.1.
As seen in figure 2.1 the cell simply consists of a glass container with two Pt-wire (Mateck, \( \varnothing = 0.5 \text{ mm}, 99.995 \% \)) electrodes; a Counter Electrode (CE) and a ”substitute” Working Electrode (WE). The benefit of the substitute WE lies in when immersing an electrocatalyst sample into the cell the potential can be firmly maintained (potential control).
The cell of figure 2.1 is covered in another glass ”jacket” into which a water inlet and outlet can be connected. Thus, by connecting the water jacket of the cell to a heat bath (Grant,
Figure 2.1: Three electrode cell. a Illustration with associated cell components such as RDE rotator, tip and shaft as well as potentiostat. b Photo of a RRDE three electrode setup courtesy of PhD Eleonora Zamburlini.\cite{168}

TC-120) the cell can be tempered and electrochemical reactions investigated at various temperatures from \textit{ca}. 15 to 90\degree C\footnote{Lower temperature limit is governed by the available cooling water supply.}. Moreover, the heating jacket allows the cell to be rinsed using heat assisted desorption. Hence, for all experiments the cell was heated from 86 to 89\degree C for 15 minutes and rinsed with ultra clean water, denoted Millipore water or H$_2$O-mQ (Millipore, 18.2 M\Omega cm). This were repeated five times for all Pt based electrochemical nanoparticle and thin film experiments and ten times for all Pt(111), Cu/Pt(111) NSAs, Gd/Pt(111) and Pt\textsubscript{Poly} experiments. Figure 2.1 also shows a Luggin capillary in which a Reference Electrode (RE) could be placed. For studies in acid a Hg\textsubscript{(l)}|HgSO\textsubscript{4(s)} reference electrode (Schotts Instruments) with 0.6M K$_2$SO\textsubscript{4} solution was utilized and in alkaline media a Saturated Calomel Electrode (SCE) (Hg$_2$Cl$_2$) was utilized instead. The placement of reference electrodes in a Luggin capillary instead of the main cell-compartment prevented molecular transport to and from capillary to sample electrode, while still allowing electronic transport. Hence, reference electrodes and the inside of
the Luggin capillary were allowed to be relatively contaminated without influencing the electrochemical measurements. In that context it should be mentioned that all glassware was cleaned for at least 24 hours in "piranha" solution consisting of sulfuric acid (Merck, 98% H₂SO₄, Emsure®) and hydrogen peroxide (Merck, 30% H₂O₂, Emsure®) which was volumetrically mixed 3:1. Other cleaning approaches such as the use of *aqua regia* (Merck, Nitric acid 69%, Emsure® mixed 1:3 with hydrochloric acid 37% from VWR) and concentrated KOH (Sigma Aldrich, Semiconductor grade) were also used to a certain extend when thought to have merit. All (Teflon and) glassware utilized for electrochemistry were cleaned in piranha and rinsed a minimum of five times in H₂O-mQ before use. Moreover, no beaker, cell nor bottle was ever left without being filled with H₂O-mQ as this lowered the amount of atmospheric dirt capable of adsorbing within the cell.

The three-electrode cell in figure 2.1 also had a small bubbler for dosing electrolytes with various gas compositions, see table 2.1.

Moreover, the cell of figure 2.1 was connected to a RDE setup consisting of a rotator (Pine instruments) where a RDE tip containing a cylindrical Pt or glassy carbon sample could be mounted and connected to a potentiostat (Bio-logic WMP-2 or SP-150). Utilizing the EC-lab software (Bio-logic) the potentiostat could be controlled from a desktop PC. Three different RDE tips were utilized: 1) A standard RDE tip in Teflon (PTFE). 2) A PEEK RRDE tip with a Pt ring. 3) A standard PTFE RRDE tip with a Pt ring. The standard Teflon RDE tips were mostly used in experiments with NPs on glassy carbon. The PEEK tip were only used for a few extended Pt crystal experiments at elevated temperature. Hence, most of the data were collected using the PTFE RRDE type tips as these proved versatile and quite stable for most temperature, mediums and electrocatalytic measurements.

An analogue to the three-electrode glass cell in figure 2.1 is the three-electrode Teflon cell. This type of cell were utilized in some instances where catalysts were investigated in alkaline electrolytes as some basic electrolytes, such as KOH, tend to etch the glassware, thereby leaching out contaminants from within the glass. However, using the Teflon-type cell was quickly abandoned as no change was observed in electrochemical performance of Pt(111) in the Teflon cell compared to that of the glass cell (likely due to the low molarity of the KOH used). Moreover, as the Teflon-type cells bubbling mechanism was very poor and the requirements for separating the reference electrode from the main cell compartment required the troublesome used of Nafion® or PTFE membranes, the use of the Teflon cell was quite limited and will not be treated any further.

**Table 2.1**: Gasses utilized from AGA for electrochemical tests and crystal preparations.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Type</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>N5.0</td>
<td>Base CVs etc.</td>
</tr>
<tr>
<td>Ar</td>
<td>N5.0</td>
<td>Base CVs etc.</td>
</tr>
<tr>
<td>Ar/CO(1%)</td>
<td>N5.0</td>
<td>Crystal preparation</td>
</tr>
<tr>
<td>H₂/CO(2%)</td>
<td>-</td>
<td>CO poisoning</td>
</tr>
<tr>
<td>Ar/H₂(5%)</td>
<td>-</td>
<td>Crystal preparation</td>
</tr>
<tr>
<td>CO</td>
<td>N3.7</td>
<td>CO oxidation</td>
</tr>
<tr>
<td>H₂</td>
<td>N4.5</td>
<td>HER/HOR</td>
</tr>
<tr>
<td>O₂</td>
<td>N5.0</td>
<td>ORR</td>
</tr>
</tbody>
</table>
2.1.2 Electrodeposition Cell

A versatile cell for electrodeposition, e.g. of Hg, was also utilized during the project. This cell relied on the same basic layout of the three-electrode setup as seen in figure 2.2.

The electrodeposition cell consisted of a small open compartment adjoined to a Luggin capillary. The cell’s functionality in terms of allowing versatile gas saturation of electrolyte and immersion of electrodes under potential control were difficult and seldom relevant for the cell’s applications. Moreover, rotation in the cell was not possible.

The cell was mainly used to immerse polycrystalline Pt samples in HgClO$_4$ to form a surface Pt-Hg alloy, presented in section 4.2.1. In some instances the electrodeposition cell was also used to calibrate Hg$|$HgSO$_4$ electrodes relative to the RHE, albeit with some practical difficulties.
2.1.3 Closed Three-Electrode Cell

A closed three-electrode cell, or just "closed cell", was used extensively for a range of electrochemical investigations. The closed cell was vital for the modification of Pt(111) crystals by alloying Cu into the 2\textsuperscript{nd} atomic layer forming Cu/Pt(111) NSAs, as will be discussed later in section 2.3.3.

An illustration of the closed cell can be seen below in figure 2.3.

\textbf{Figure 2.3:} Schematic of the closed cell with working, counter and reference electrodes. For this setup these were connected to a Bio-logic SP-150 potentiostat.
The closed cell of figure 2.3, has the benefit of being able to contain a crystal sample in a controlled gas environment, while allowing sequential voltammetry and crystal annealing to be conducted. Sample heating could be conducted using an inductive heater (Inductive Heating Machine, SP-15AB). The ability to keep the cell closed with a light overpressure of any desired atmosphere was extremely important when preparing Pt(111) and Cu/Pt(111) NSAs as any oxygen would allow either Pt or Cu oxides to form on the surface while heating, thus preventing the correct formation of Cu in the 2nd atomic layer of the Pt(111) crystal. Nb not seen in figure 2.3 is the two glass-bubble valves that ensures there were no back-flow of atmospheric air into the cell from the exhausts.

The closed cell comprises of a main cell in which a small "ladle" is placed. The ladle constitutes the unit volume in which the electrolyte for electrochemistry is placed. This small volume has two benefits: 1) The system becomes more tolerant to contamination as it is easy to flush clean. 2) Low amounts of electrolyte were needed per experiment. This ladle can be flushed with electrolyte from a reservoir denoted gas bubbler of figure 2.3, i.e. electrolytes were always gas saturated prior to entering the ladle in which electrochemical measurements took place. Nb only N\(_2\)-saturated electrolytes were ever used for the closed cell in this work. The ladle and connecting counter, substitute working and reference electrode allowed for electrochemical measurements in a hanging meniscus configuration using a potentiostat (see figure 2.3).

The inductive heater was capable of heating Pt samples to ca. 900\(^\circ\)C, depending on gas flow velocity. The crystal temperature could be monitored using a thermocouple (type-K, NiCr/Ni-Alumel) and a multimeter reader (AMPROBE, TMD90A).

### 2.2 Electrochemical Methods

In the following the electrochemical techniques used will be presented.

The main electrochemical methods utilized in this work were based on cyclic voltammetry using RRDE setups, albeit Electrochemical Impedance Spectroscopy (EIS), ChronoAmperometry (CA) and MEA single-cell tests have also provided useful techniques to investigate catalytic performance on a wide range of electrocatalysts.

#### 2.2.1 Electrochemical Impedance Spectroscopy

EIS relies on frequency modulated Direct Current (DC) signals (Alternating Current (AC) on a DC signal) giving insight into resistive and capacitive effects of the three-electrode setup.\([142,169]\) The three-electrode setup allows the current from WE to RE to be discerned from that of the CE to the RE, thus giving insight into the actual current response at the WE. However, as the electrolyte and contacts of the three-electrode setups are not perfect conductors, current induced lowering of the potential across the WE to the CE may result in lowering of perceived currents at the designated potentials. Thus, Ohmic-drop compensation has been utilized.\([170-172]\) Quite complex equivalent circuit models can be utilized when considering conduction through an electrolyte, as (parasitic) capacities
and series resistances between electrolyte and the different electrodes in the setup most certainly exist. However, in this work Ohmic-drop compensation has mainly been used to compensate for the electrolyte resistance of the simple equivalent circuit model of a parallel-capacitor and a charge transfer resistor in series with a global system resistor\cite{173} as seen in figure 2.4.

**Figure 2.4:** a Equivalent circuit model for a working electrode in electrolyte.\cite{173} b Nyquist plot at 23°C of PtPoly and Pt(111) in a RDE setup in N₂-saturated 0.1 M HClO₄ at 0 rpm.

The equivalent circuit of figure 2.4a assumes a Helmholtz-layer (double-layer) capacitance $C_{HL}$ at the interface between the electrocatalyst and the electrolyte. Moreover, a charge transfer resistance $R_{CT}$ is also present in this layer and a global series resistance $R$ encompassing residual resistance contributions have also been considered. Using frequency modulated DC signals it is possible to evaluate frequency dependent impedance contributions $Z(f) \approx \Re(Z) + i \Im(Z(f))$. I.e. plotting the impedance response in a Nyquist plot allows to a first-order approximation to determine the intersect where no frequency dependent impedance takes place\(^2\) $R_{sol} \approx \Re(Z)|\Im(Z(f))=0$. This would correspond to the global series resistance convoluted with all other linear resistance contributions $R_{sol}$ not included in the model, figure 2.4 exhibits examples of $R_{sol}$ evaluation from impedance spectra obtained from PtPoly and Pt(111) crystals.

The evaluation of $R_{sol}$ has for all instances been done by maintaining electrodes at potentials typically associated with the double-layer region i.e. 0.5 V vs. RHE. The system resistance is evaluated by linear regression of the impedance in an appropriate frequency $f$ range

$$\Im(Z(f)) \approx \alpha \Re(Z) + Z_0 \Rightarrow 0 = \alpha R_{sol} + Z_0 \Rightarrow R_{sol} = \frac{-Z_0}{\alpha}, \quad f \in [60 \text{ Hz}; 400 \text{ Hz}] \quad (2.1)$$

\(^2\)For $< 1$ MHz frequency dependent resistance is negligible.
Using the linear regression $R_{sol}$ values can be found as seen in figure 2.4b. The found series resistance on the electrochemical three-electrode system can always be compensated, thus allowing comparison of systems utilizing different electrolytes or with varying degree of series resistance

$$U = U_{applied} - IR_{sol}$$ \hspace{1cm} (2.2)

, where $U_{applied}$ is the potential applied by the potentiostat and $I$ is the current.

### 2.2.2 Rotating Ring-Disc Electrode

When electrochemically probing electrocatalysts the ability to control the mass-transport of reactant species to the surface is often preferred as insight into steady-state reaction kinetic can be obtained.\[142]\) The mass-transport to the sample can be controlled by rotational speed, meaning a disk electrode embedded on a tip mounted on a shaft as shown in figure 2.1 and 2.2 can be rotated at various speeds. This rotation will through centrifugal forces acting on the electrolyte induce convection of reactants in the electrolyte to the disk double-layer. In the case of electrochemical ORR measurements oxygen would be the reactant. This double-layers thickness have been estimated to\[142]\)

$$\delta = 1.61D_{O_2}^{1/3}v^{1/6}\omega^{-1/2}$$ \hspace{1cm} (2.3)

, where $D_{O_2}$ is oxygen’s diffusion coefficient in the electrolyte, $v$ is the viscosity and $\omega$ is the rotation speed. By controlling the rotation the double-layer thickness and thus the speed in which reactants can be supplied to said layer can be controlled. Assuming the electrocatalytic disk depletes reactants instantaneous through a given catalytic reaction the maximum electrocatalytic current will be that dependent on the maximum mass-transport to the surface defined as the diffusion-limited current $j_{diff}$. This current is intimately related to the double-layer thickness of equation (2.3) as given below for the case of the ORR\[142]\)

$$j_{diff} = I_{diff} = n_eC_{O_2}F\frac{D_{O_2}}{\delta} = 0.620n_eFA_{geo}D_{O_2}^{2/3}\omega^{1/2}v^{-1/6}C_{O_2}$$ \hspace{1cm} (2.4)

, where $n_e$ is the electron transfer number, $F$ is Faraday’s constant, $A_{geo}$ is the electrode area and $C_{O_2}$ is oxygen’s concentration.\[174]\) Hence for first order reactions the RRDE rotation controls the mass-transport to and from the relative to the catalysis driven kinetic current sample following the Koutecky-Levich relation\[142]\)

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_{diff}}$$ \hspace{1cm} (2.5)

, where $j$ is the overall current density and $j_k$ is the kinetic current density, \textit{i.e.} by knowing the total current and the diffusion limited component it is possible to isolate the catalysis driven kinetic current of a RRDE.\[142,175]\)
2.2.3 Cyclic Voltammetry

Cyclic voltammetry is a widely used technique, which, as indicated by the name, consists of cycling the potential between the working and reference electrode of figure 2.1 between two potentials $U_{\text{max}}$ and $U_{\text{min}}$ at a fixed scan-rate $\frac{dU}{dt}$ a certain number of times $N$, see figure 2.5. Various CV based experimental techniques exist allowing the investigation of different electrocatalytic phenomena, some of the techniques have been be presented in the following.

Hydrogen Electrocatalysis

A useful CV experiment concerns the HER/HOR voltammogram for RHE evaluation in which is a CV of Pt based electrodes are used in $\text{H}_2$-saturated electrolyte. PtPoly and Pt(111) examples of HER/HOR CVs can be seen in figure 2.6. From figure 2.6 the intersect of the HOR/HER region can be evaluated as the average of the cathodic and anodic sweep from a positive to negative current i.e. the zero-current intersect corresponding to equilibrium between HOR/HER, also know as the RHE potential. For simplicity (unless otherwise stated) all electrochemical cell potentials have been given with respect to the RHE potential and with Ohmic-drop compensation

\[ U_{\text{RHE}} - IR = U_{\text{ref.}} - \Delta U_{\text{ref.}-\text{RHE}} - IR \]  

(2.6)

, where $\Delta U_{\text{ref.}-\text{RHE}}$ is the potential shift from associated with the the difference form the reference potential and that of the RHE. From equation (1.17) the $\Delta U_{\text{ref.}-\text{RHE}}$ in equation (2.6) is dependent on both temperature and pH. Other insights can also be gained from HOR/HER CVs, for example the steepness of the HOR curve and the half-wave potential relay information about the HOR and HER activity. Furthermore, as seen from figure 2.6, one may plot the current relative to the HOR diffusion current $j/j_{\text{diff}} - 1$. This metric gives insight into the H to OH competition and OH onset near the ORR potential region and may elucidate why some samples are more active than others. Almost all data in this thesis have been supplied with respect to the Ohmic-drop and RHE compensation of equation (2.6) and currents given by the relevant current densities, $j \equiv I/A$, where $A$ is the relevant electrode area. For an extended well ordered crystal this area corresponds to the geometric area, while for rough or nanoparticulate catalysts has to be derived from evaluation of the ElectroChemically active Surface Area (ECSA).
Experimental Methods and Setups

Figure 2.6: CVs of Pt\textsubscript{poly} and Pt(111) samples in a RDE setup in H\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} electrolyte at 1600 rpm at 23°C. The gray region denotes the potential region where the diffusion limited HOR current was evaluated and the insert shows the relative current response in the OH region.

Base Cyclic Voltammograms

Base CVs of Pt samples incorporate a lot of fundamental information about adsorption of relevant species such as H and OH. Information that is crucial for understanding Pt based ORR. Base CVs denotes CVs in non-interacting gas saturated electrolytes (N\textsubscript{2} or Ar). In this work base CVs have usually been obtained in RRDE setups at room-temperature at 400 rpm using scan-rates of 50 mV/s.\cite{171}

Examples of base CVs for Pt\textsubscript{poly} and Pt(111) have been shown in figure 2.7. From figure 2.7 the regions associated with OH and H adsorption and desorption have been highlighted.\cite{67,176-179} Hence, the Hydrogen UnderPotential Deposition (H\textsubscript{UPD}) region is designated from the hydrogen onset (and offset) potential $U_{H-onset/offset}$ from the local absolute current minimum of the anodic sweep (or cathodic sweep) double-layer region down to 0.05 V \textit{vs.} RHE as below this potential HER and HOR start to be contributing factors to the CV, \textit{i.e.} CV irreversibility. The H\textsubscript{UPD} region has been used by many to evaluate the ECSA of Pt based catalysts by simply tallying up the adsorption induced
Figure 2.7: Base CVs in N\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} (23 °C, 50 mV/s, 400 rpm). \textbf{a} Voltammetric cycle (black) and current signal (blue) for Pt\textsubscript{Poly}. \textbf{b} Voltammetric cycle (black) and current signal (red) for Pt(111). \textbf{c} Base CV from the potential and current signal data for Pt\textsubscript{Poly}. \textbf{d} Base CV from the potential and current signal data for Pt(111). The regions of hydrogen underpotential deposition have been sketched, as well as the regions designating approximately 1/6 of an adsorbed OH monolayer from the OH onset potential.

charge transfer to and from the catalyst surface\textsuperscript{[171, 180]} Any such evaluation of such a charge $Q_{ECSA}$ can be done by\textsuperscript{[168]}

$$Q_{ECSA} = \frac{dt}{dU} \int_{U_{onset}}^{U_{offset}} (I - I_{off}) \, dU$$

, where $I_{off}$ is the background signal current when there is no adsorbed relevant species e.g. for hydrogen the start of the double layer region. Given the charge it is possible to
estimate the actual ECSA geometric area $A_{ECSA}$ by assuming pure Pt sites are responsible for the relevant adsorbed/desorbed species.

Formally one may consider H$_{UPD}$ charge reference measurements of extended surfaces to find the charge density of the relevant species such a hydrogen. This also implies that if one has a catalyst with a certain charge area on can, by using the reference measurements, evaluate a corresponding area\[^{168}\]

$$Q_{ECSA}^{\text{ref.}} = \sigma_{ECSA}^{\text{ref.}} \Rightarrow A_{ECSA}^{\text{ref.}} = \frac{Q_{ECSA}^{\text{ref.}}}{\sigma_{ECSA}^{\text{ref.}}} \quad (2.8)$$

, where the charge per area $\sigma_{ECSA}^{\text{ref.}}$ is some relevant reference experimental value, usual values of $\sigma_{\text{Pt(111)}}^{\text{H}_{\text{UPD}}}$ and $\sigma_{\text{PtPoly}}^{\text{H}_{\text{UPD}}}$ of 210 $\mu$C/cm$^2$ and 240 $\mu$C/cm$^2$ are used in literature.\[^{181,182}\] Specific reference values for both Pt(111) and polycrystalline Pt have been found, as will be presented and discussed later in chapter 4.

**Hydrogen Adsorption Based Area Evaluation**

As indicated in figure 2.7 the H$_{UPD}$ region consists of both an anodic sweep and cathodic sweep region. In this work an average of the two are used, meaning both the hydrogen adsorption and desorption are taken into consideration as from equation (2.7)

$$Q_{H_{\text{UPD}}} = \frac{dt}{2 dU} \left[ \int_{U_{\text{H-onset}}}^{U_{\text{H-offset}}} (I - I(U_{\text{H-onset}})) dU \right] \quad (2.9)$$

The H$_{UPD}$ charge areas can be seen as the sketched region below 0.5 V vs. RHE in figure 2.7c and d. The lower limit of 0.05 V vs. RHE in equation (2.9) has been established empirically as it is unclear when the Pt surface goes from hydrogen adsorption to HER.\[^{178,180}\] Unfortunately, it is generally well known that there exist an inherent error when assigning fixed charge densities to surfaces for which either the distribution of uncoordinated sites or the surface adsorption energies are not the same.\[^{1,179,182}\] Moreover for NPs charge area inconsistencies related to particle dispersion/proximity have been reported to influence ECSA evaluation.\[^{97}\] For example, assigning the charge per area derived from an extended polycrystalline Pt surface\[^2\] to values for polycrystalline Pt NPs an error is knowingly being introduced to the area evaluation.\[^{100,171,179,182}\] However, the technique is commonly used for large surface area Pt catalysts\[^{177}\] as it is a relatively quick and simple method widely used within the ORR community.
Hydroxide Adsorption Potential

Indications have been included in figure 2.7 showing the OH adsorption onset potential given by the intersect between linear fit from the double-layer and OH region. The OH adsorption varies for different Pt based surfaces depending on their binding to oxygen intermediates such as OH. Hence, one may plot the relative shift in OH adsorption potential. This has been done on selected catalyst surfaces by simply considering the cathodic sweep required for a certain fraction $\theta_{\text{OH}}$ associated with a full MonoLayer (ML) OH coverage, as dictated by

$$Q_{\theta_{\text{OH}}^*\text{OH ML}} = \frac{d\theta}{dU} \int_{U_{\text{OH-onset}}}^{U_{\theta_{\text{OH}}^*\text{OH ML}}} [I(U) - I(U_{\text{OH-onset}})] dU$$

(2.10)

where the $Q_{\theta_{\text{OH}}^*\text{OH ML}}$ charge fraction utilized are usually $[1, 2, 183]$ 1/2, 1/3, 1/4, 1/6 or 1/8 *OH ML. Given the likeness of specific samples being investigated, charges area values related to full coverages of either polycrystalline or Pt(111) single-crystals were utilized, these are 210 $\mu$C/cm$^2$ and 240 $\mu$C/cm$^2$, respectively.$[1, 177]$

Carbon-Monoxide Oxidation Based Area Evaluation

CO oxidation, also known as CO-stripping$[168, 171, 177, 184, 185]$ is strongly related to the H$_{\text{UPD}}$ based ECSA evaluation. Similarly, this allows for evaluation of the ECSA, in this instance the desorption (or oxidation) charge of CO are used as an estimate for an area

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2e^-$$

(2.11)

Utilizing CO oxidation, as of equation (2.11), for area evaluation involves the potentiodynamic measurements of the electrochemical adsorption and oxidation of CO, for which a reference CO coverage for the Pt electrode surface is known.$[186, 187]$ Thus, similarly as for the H$_{\text{UPD}}$ region a comparison between measured charge and expected charge per area allows the estimation of the active surface area of the Pt based catalyst. However, excess CO-saturated electrolyte will result in an added CO oxidation current during cyclic voltammetry. Hence, for CO charge evaluation CVs were taken in Ar-saturated electrolyte in a potential region where OER and HER do not usually take place on Pt based catalyst, i.e. from 0.1 V to 1.0 V vs. RHE. Two to three consecutive CVs were measured ensuring stable features. Consequently the working electrode was held at minimum potential (0.1 V) for ca. 15 minutes. During the 15 minutes CO gas was dosed into the cell for 2 minutes, in which time charge adsorption from the CO could clearly be monitored from the potentiostats’ current signal. After the 2 minutes of CO dosage the gas was switched back to Ar for the remaining ”potential hold time”, thus ensuring complete purging of CO from the electrolyte. Consequently only CO adsorbed on the surface of the sample would be present. After the hold time the CVs were allowed to proceed and for the first cathodic sweep a clear CO oxidation peak would be visible as shown in figure 2.8.
After the CO-strip an additional two to three CVs were collected, thus ensuring the electrolyte were completely desaturated of CO as any residuals will result in oxidation currents. The additional CVs were also used to verify that CO, due to its strong adsorption energies,\cite{177} had not altered the sample surface seen as changes in CV features. CO has been reported to smoothen Pt(111) single-crystalline surfaces\cite{184,188} but roughen Pt/C nanoparticles.\cite{189} After these additional CVs the sample was held again for 15 minutes at 0.1 V. The next cycle after this potential hold was used for background subtraction as the electrode in this instance had been under the same adsorption conditions immediately prior the CO-stripping cycle, \textit{i.e.} any cathodic adsorption errors would (hopefully) cancel out when subtracting the CO-strip peak with the base CV\cite{168,171} as

\begin{equation}
Q_{\text{CO}} = \frac{\text{d}t}{\text{d}U} \int_{U_2}^{U_1} (I - I_{\text{background}}) \text{d}U
\end{equation}

From figure 2.8 the CO oxidation potential onset $U_1$ and offset $U_2$ are observed as the background CVs (with background current $I_{\text{background}}$) intersects with the anodic CO-stripping cycle. From figure 2.8 a clear difference in CO-strip peak potential is observed between $\text{Pt}_{\text{Poly}}$ and Pt(111) showing a clear surface dependence on the CO oxidation. Hence, CO desorption peak(s) do to some extent give information on surface uniformity and morphology, such as information on steps, terraces, kinks and/or edge sites.\cite{182,184,187,190,191} As CO-stripping, as assumed in equation (2.11), is likely a $2e^{-}$ transfer process, the charge area from the CO-strip should be approximately twice that from the H$_{\text{UPD}}$, assuming similar site density for carbon-monoxide as for hydrogen, \textit{i.e.} for $\text{Pt}_{\text{Poly}}$ values of 420 $\mu$C/cm$^2$ have usually been used in literature.\cite{177,180,181} Although more realistic
values of $\sim 340 \mu C/cm^2$ have also been reported.$^{[171,192]}$ Just as for the $H_{\text{UPD}}$ charge evaluation CO reference values have been estimated in this study for Pt(111) and Pt$_{\text{Poly}}$ as seen in chapter 4.

The CO-strip measurements conducted in this study were usually done at $23^\circ C$ in a RDE setup using scan-rates and rotational speeds of $10 \, \text{mV/s}$ and $200 \, \text{rpm}$. The low scan-rate allowed for better resolution of the CO oxidation features from the stripping peak, but did add to the risk of poising from the added experimental time. Low rotational speeds have been used as a compromise between minimizing mass-transport to the sample surface, thus lowering the contamination rate, while still maintaining a rotation minimizing the chances of bubbles being trapped on the sample electrode causing disruption to the experiment.

Both ECSAs evaluated from CO-stripping and from the $H_{\text{UPD}}$ region have been utilized in this thesis to various extents. Both techniques carries benefits and drawbacks which should be considered when forming conclusions from the ECSA results.

### Oxygen Electrocatalysis

CVs in $O_2$-saturated electrolyte are of fundamental electrocatalytic importance when considering the oxygen reduction reaction. In this work such experiments have usually been conducted using RDE with rotational speeds and scan-rates of $1600 \, \text{rpm}$ and $50 \, \text{mV/s}$. Although various scan-rates have been reported in literature. Within the MEA community low scan-rates of $5 \, \text{mV/s}$ mimicking the mass-transport limited kinetics of a MEA system are typical. Whereas the RDE community tend to use $20$ to $50 \, \text{mV/s}$ as this allows better evaluation of the intrinsic catalytic activities by minimizing unwarranted adsorption effects.$^{[171]}$

Based on the CVs in $O_2$-saturated electrolyte and the isolation of the kinetic current density of equation (2.5) the kinetic current magnitude of the sample in question can be found

$$j_k = \frac{j_{\text{diff}} j}{|j_{\text{diff}} - j|}$$

(2.13)

Often the sample activity towards ORR is exemplified by specific current densities, also simply know as specific ORR activities, at for which the current density at specific potential (usually $0.9 \, \text{V vs. RHE}$) is used as metric for activity.$^{[171]}$ Moreover, it is from equation (2.4) noted that by measuring the ORR CVs at various rotational speeds one can isolate the electron transfer number, thus giving insight into the dominating reaction mechanism of the electrocatalyst. This can be seen in figure 2.9 where Pt(111) and Pt$_{\text{Poly}}$ have been measured at $400, 900, 1600$ and $2500 \, \text{rpm}$ and such so-called Koutecky-Levich plots have been derived from such analysis.

From the Koutecky-Levich analysis (figure 2.9) an average electron transfer number at the various potentials can be derived using appropriate electrolyte/reactants parameters in equation (2.4). For both Pt(111) and Pt$_{\text{Poly}}$ an electron number near $\bar{n}_e \approx 3.8$ has been found using values from Yin et al.$^{[174]}$ This indicates that the $4e^- \text{- reaction pathway}$
Figure 2.9: RDE data for Pt(111) (red) and PtPoly (blue) in O₂-saturated 0.1 M HClO₄ (23°C, 50 mV/s) at various rotation speeds.  

- Anodic sweeps.
- Koutecky-Levich plot derived from $I_{\text{diff}}$ at 0.40, 0.48, 0.56, 0.64, 0.72 and 0.80 V vs. RHE.

...dominates the ORR. The *Koutecky-Levich* relation of equation (2.5) combined with the anodic sweep data of figure 2.9a allows *Tafel* plots of the kinetic current density to be plotted as seen in figure 2.10.

Figure 2.10: *Tafel* plots of Pt(111) (red) and PtPoly (blue) in O₂-saturated 0.1 M HClO₄ (23°C, 50 mV/s) at 400, 900, 1600 and 2500 rpm. Highest rotational speed corresponds to the plots with highest activity *i.e.* least mass-transport limited.
The \textit{Tafel} plot of figure 2.10 reveals kinetic limitations are less of a constraint when rotation is very fast. However, as fast rotation also increase the likelihood of contamination,$^{[171]}$ ORR activities have mostly been evaluated at 1600 rpm. The \textit{Tafel} slope can be evaluated using the plots in figure 2.10 by

\[
\beta = \frac{\partial U}{\partial \ln(\text{j}k)} \bigg|_T \tag{2.14}
\]

Equation (2.14) provides great insight to the ORR catalysis as it, just as the electron transfer number, gives insight to the exponent of the \textit{Butler-Volmer} equation.$^{[142,193]}$ Other useful metrics concerning the ORR can be evaluated from the anodic sweeps of the CVs in \text{O}_2-saturated electrolyte as indicated in figure 2.11.

\textbf{Figure 2.11}: Anodic sweep RDE data for Pt\textsubscript{Poly} in \text{O}_2-saturated 0.1 M HClO\textsubscript{4} at 23 °C at 50 mV/s and 1600 rpm. The region usually used in \textit{Tafel} plots is highlighted (red), as well as sketches of how evaluation of diffusion limiting current, half-wave and ORR onset potentials were defined. Illustration of relevant ORR parameters and their evaluation can be seen in figure 2.11, these include ORR onset potential $U_{\text{onset}}$, half-wave potential $U_{\text{half-wave}}$ and diffusion limited current. These parameters and the \textit{Tafel} slope$^{[125,142,194]}$ and specific activities $\text{j}_k$ (and when relevant specific mass-activity $\text{j}_{k,m}$) have been used to gain insight into the fundamental performance of various Pt based ORR catalysts. RDE derived ORR activities are an extremely useful and important parameter when investigating the catalytic performance of any catalyst. However, ORR stability is also important as for any actual catalyst application substantial life-time considerations must be made, \textit{e.g.} catalyst dissolution is often observed in real catalyst systems. Interestingly such dissolution will often result in changes in the number of available sites on the catalysts. This is observable by changes in the H\textsubscript{UPD} region (or from the CO charges) and can
easily be triggered by going to high anodic potentials, \textit{i.e.} Pt is known to oxidize above 1.2 V \textit{vs.} RHE.\textsuperscript{99,195–197} Moreover, effects of poisoning or strain relaxation \textit{etc.} can be observed in ORR activity plots. To investigate ORR stability performances accelerated stability tests in RDE setups are often used and have in certain instances also been applied in this thesis work.\textsuperscript{168,198} Accelerated tests usually encompass cycling of the electrocatalyst from 0.6 V to 1.0 V \textit{vs.} RHE for 10 000 cycles in O\textsubscript{2}-saturated electrolyte with no electrode rotation at 100 mV/s.\textsuperscript{171,199,200} After stability tests relevant electrochemical measurements are often re-obtained, both before and after changing to new electrolyte.

### 2.2.4 Miscellaneous Electrochemical Methods

Other techniques such as chronoamperometry and single-cell MEA tests have also been utilized in this project. Chronoamperometry simply consists of maintaining a working electrode at a fixed potential and monitoring the evolution of the current. As the potential will shift due to the Ohmic-drop, real-time compensation need to be utilized. The utilized potentiostat for this project, was however not able to completely compensate for the full Ohmic-drop but only 85\%, which is worth noting.

Another technique used was a single-stack testing bench as illustrated in figure 1.6a which have been utilized for MEA investigation of NP catalysts.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.12.png}
\caption{Photo of the Wontech SMART-II test bench utilized at KAIST. Consisting of a control unit hooked up to a PC and gas supply for test of a MEAs.}
\end{figure}

The setup (Wontech, SMART-II) utilized (see figure 2.12) was used during a collaborative stay at the Korean Advanced Institute of Science and Technology (KAIST). The system consisted of a control unit able of controlling both the pressure and flow of gasses though the MEA, as well as the electrical load of the MEA. Moreover, the temperature could be controlled by two thermal units, thus simulating both LT- and HT-PEMFC operation.
2.3 Platinum Crystal Preparation Methods

Various methods were utilized for the preparation of extended Pt electrodes. An overview the methods used for preparing polycrystalline Pt (and Pt-Hg), single-crystalline Pt(111) and Cu/Pt(111) NSAs will be presented in the following.

2.3.1 Preparation of Polycrystalline Platinum

To prepare polycrystalline Pt the techniques of Clavilier\textsuperscript{[144]} have been widely utilized. Pt crystals (Mateck or Pine, $h \times \varnothing = 5 \times 0.5$ mm, 99.999\%) were placed surface-up on a ceramic stand. By using a Liquid Petroleum Gas (LPG) torch (Proxxon) the crystals were heated until glowing bright orange. The flame was placed at an angle towards the surface so that no direct, and consequently very local, heating occurred. The crystals were heated for 3 minutes followed by cooling in a bell-jar with pure Ar atmosphere.

Following the annealing the Pt\textsubscript{Poly} was allowed to cool for 5 minutes and then removed after a clean droplet of hydrogenated H\textsubscript{2}O-mQ had been placed on top of the crystal. The crystal could now be moved, using clean Teflon tweezers, face down onto a polypropylene film (SpectroCertified\textsuperscript{®}) which had been sonicated (BANDELIN, SONOREX DIGITEC) for 15 minutes in a clean beaker with H\textsubscript{2}O-mQ.

The electrode could now be carefully dried from the sides and back using lens paper (Assistents, LinsenPapier) and mounted on a RRDE tip using clean U-cups (Pine) and fixed onto a rotator-shaft and rinsed with Millipore water.

The shaft, with RRDE tip, could now be mounted in the rotator and submerged into the three-electrode setup under potential control at $U < 0.1$ V vs. RHE, as such low potentials would minimize any surface oxidation of the electrode. For insight into the electrochemical performance of polycrystalline Pt see section 4.1.

If the Pt\textsubscript{Poly} crystal performed electrochemically as expected from other studies\textsuperscript{[171]} the electrode could be removed from the three-electrode setup of figure 2.1 to the setup of figure 2.2 for Pt-Hg alloying of the surface through Hg deposition.\textsuperscript{[57]}

2.3.2 Preparation of Pt(111)

Preparation of Pt(111) (Mateck, 99.999\%, $\pm 0.1^\circ$, $h \times \varnothing = 3 - 5 \times 0.5$ mm) crystals were a little more demanding but fundamentally required the same preparation\textsuperscript{[144]} as Pt\textsubscript{Poly} except the Pt was allowed to cool in another atmosphere. Initial attempts using inductive heating to 850 °C for 2 minutes in Ar/H\textsubscript{2}(5\%) followed by 2 minutes in Ar/CO(1\%) following earlier reports from our group\textsuperscript{[201]} did not work in an expected fashion. Electrochemical characterization indicated unknown elements alloyed into the Pt(111) crystal when cooling in Ar/CO, while the CO were supplied from a vast gas delivery system and not a locally placed gas-bottle. It was speculated that nickel-carbonyl formed by the CO from the stainless steel gas connects (Swagelock\textsuperscript{®}) could effuse into the Pt(111) crystal during heating, thus altering the electrochemical response. Such speculation was supported by the
increased ORR activity of such prepared Pt(111) samples and by considering the vapor-pressure of nickel-carbonyl. Using Ar/CO(1%) from a locally placed gas bottle, where the lines could be extensively purged, allowed the formation of Pt(111) surfaces. However, it was found that annealing using the inductive heater and including CO in the cooling was unnecessary and often resulted in subpar Pt(111) surfaces. Flame-annealing of the Pt(111) crystal and cooling in a designated cooling-flask with roughly 50/50 Ar/H$_2$ were found to result in the best Pt(111)-like surfaces. The cooling-flask has been illustrated in figure 2.13.

The preparation of Pt(111) crystals thus relied on them being mounted on a holder using Pt-wire (Mateck, $\varnothing = 0.25$ mm, 99.999%). The crystals were then heated for ca. 3 minutes while glowing orange, before removing the stopper from the Ar/H$_2$ filled cooling-flask and quickly moving the electrode into the flask. Due to the high hydrogen content, oxygen in the atmosphere and the very hot crystal a small "pop" could be heard as hydrogen were ignited. This procedure were repeated two to three times and sometimes for longer annealing times e.g. when receiving new crystals or after sputter cleaning procedures.

After the Pt(111) annealing the electrodes were released from the Pt-wires and mounted in the RDE setup utilizing a Teflon holder system (figure 2.14).

The three parts of the electrode holder system in figure 2.14 allowed easy mounting of the Pt(111) crystals into the RDE tip as similarly done for Pt$_{\text{Poly}}$. The polypropylene film was also used for the Pt(111) crystals, but as no discernible changes in the CVs could be found using the Teflon holders over the film and the holders made demounting so much easier this approach was favored. Before each use the Teflon tools were cleaned in piranha and rinsed five times with H$_2$O-mQ before being heated to 70 °C while sonicating.
2.3.3 Preparation of Cu/Pt(111) Near-Surface Alloys

Cu/Pt(111) preparation relied heavily on the earlier work\cite{1,151–156} by our and other groups. In order to optimize the methodology for Cu/Pt(111) NSA preparation many issues had to be overcome and, although the majority were solved, some persisted throughout the work.

Prepared Pt(111) crystals (flame-annealed and cooled in 50/50 Ar/H\textsubscript{2} atmosphere using the cooling-flask\cite{102} of figure 2.13) were carefully mounted on a molybdenum wire using the already attached Pt-wires. The molybdenum wire ”stage” was then lowered into the closed cell of figure 2.3. Prior or during the annealing of the Pt(111), the Ar filled closed cell was purged with at least 2L H\textsubscript{2}O-mQ and N\textsubscript{2} was bubbled into the 0.1 M HClO\textsubscript{4} electrolyte by the gas bubbler. After approximately 10 minutes the cell, now with the Pt(111) crystal, was assumed to be oxygen free and fresh electrolyte were flushed into the ladle three times. CVs of the substitute working electrode of the closed cell (see figure 2.3 for cell) were used as an indicator of cell cleanliness. Afterward the Pt(111) was lowered into the ladle under potential control at 0.1 V \textit{vs.} RHE. It is worth noting that the RHE compensation for the Hg\textvert:HgSO\textsubscript{4} reference electrode had to be done in another cell.

After the submerging of the Pt(111) electrode into the ladle electrolyte, in a hanging meniscus configuration, the substitute working electrode was disconnected and cyclic voltammetry proceeded from 0.05 V to 1.00 V \textit{vs.} RHE at 50 mV/s.

Due to the nature of the hanging meniscus configuration the initial CVs appeared rather erratic due to the unintended wetting of the crystal sides. Changing the CVs range down to 0.00 V \textit{vs.} RHE and increasing the scan-rate to 100 mV/s for 20 to 100 cycles were in most cases enough for cleaning the Pt(111) surface and allowed the crystal sufficient time to ”dry” its sides. CVs of Pt(111) could be obtained and compared with state-of-the-art results\cite{172} by either transferring the electrode to a RDE setup or by conducting a CV in a hanging meniscus configuration in the closed cell (see figure 2.15).

After ensuring a well-ordered Pt(111) surface had formed from CV observations, the electrolyte in the closed cells’ gas bubbler seen in figure 2.3, was switched to one that contained Cu\textsuperscript{II}. The electrolyte containing Cu\textsuperscript{II} was formed by mixing 5 mM Cu\textsuperscript{II}O\textsubscript{4} (Sigma Aldrich, 99.999 %) into a pre-prepared 0.1 M HClO\textsubscript{4} solution. After N\textsubscript{2}-saturation
of the Cu$^{II}$-containing electrolyte in the gas bubbler the electrolyte was flushed into the ladle while holding the Pt(111) electrode potential at $\sim 0.1$ V and with the substitute working electrode connected ensuring that there was no loss of potential control. After flushing with the Cu$^{II}$-electrolyte CVs in the range from 0.4 V to 1.0 V vs. RHE using a scan-rate of 20 mV/s were collected. For each CV the potential was held for 3 minutes at 0.4 V allowing increasingly stable Cu oxidation peaks to be observed, see figure 2.16a. Once the Cu-stripping peaks were stable, the lower potential limit $U_{\text{dep}}$ was shifted to appropriate values. By holding for 3 minutes above 0.4 V sub-monolayer Cu $\theta_{\text{Cu}}$ could be adsorbed and consequently desorbed by oxidation as co-adsorption of OH would become increasingly predominant.$^{[1,151–156]}$ Examples of the Cu oxidation can be seen below in figure 2.16.

![Figure 2.16](image)

**Figure 2.16:** Measurements in 0.1 M HClO$_4$ at room-temperature in inert gas-saturated electrolytes. **a** Hanging meniscus with 5 mM Cu$^{II}$ in the electrolyte, measured in the closed cell at 20 mV/s. Cu oxidation charge corresponds to $\theta_{\text{Cu}} = 0.70$ ML. **b** Pt(111) and a Cu/Pt(111) sample after Cu deposition and annealing measured in a RDE setup at 50 mV/s at 400 rpm.

After the Cu oxidation peaks stabilized after consecutive stripping at the fixed deposition potentials, a final deposition was conducted (again for 3 minutes) at which time the potential was maintained at $U_{\text{dep}}$ while the substitute WE was reconnected and the ladle was flushed with clean 0.1 M HClO$_4$ electrolyte, thus removing excess Cu. Consecutively, the sample was raised from its hanging meniscus position, disconnected and dried using a lens paper only touching the sides of the crystal, not disrupting the Cu OverLayer (OL) on the Pt(111). The Cu/Pt(111) OL electrode was repositioned in the Ar/H$_2$(5%) filled closed cell and using the inductive heater the sample was heated for 2 minutes at 400 $^\circ$C and then cooled for an additional 10 minutes. This annealing and cooling in a reducing hydrogen atmosphere allowed overlayer Cu to switch places with underlying Pt atoms, thus forming
a Cu/Pt(111) NSA. A schematic of the different steps can be seen in figure 2.17.

![Figure 2.17: Illustration of Pt(111) surface followed by sub-monolayer Cu deposition forming a surface overlayer, which by annealing in Ar/H₂(5\%) at 400°C for 2 minutes allows the formation of a Cu/Pt(111) NSA.]

It was found to be extremely important that absolutely no oxygen was present in the cell during the annealing. This was because oxygen appeared to facilitate Cu oxidation at the surface \textit{i.e.} copper would be positioned at the surface rather than in the 2\textsuperscript{nd} atomic layer. It is worth mentioning that Cu deposition was not found to induce any changes in the Pt(111) surface. This was verified by conducting CVs of a Pt(111) surface before and after subjection to Cu deposition, separated by extensive flushing of clean electrolyte.

2.4 Thin Film Sputter Deposition

Investigations of Pt based thin films were conducted by preparing samples using a UHV sputter deposition system (from AJA), see figure 2.18. Deposition and optimization was conducted by PhD Eleonora Zamburlini. The sputter system used is capable of co-sputtering up to three targets at a time, thus allowing binary (or even ternary) alloys to be formed. The chamber has been equipped with a Quartz Micro Balance (QCM) for monitoring deposition rates, a shutter for controlling deposition times, a rotating substrate.

![Figure 2.18: Photo of sputter deposition of Ti. Courtesy PhD Eleonora Zamburlini.\textsuperscript{[202]}]

\[\text{Substrate holder} \quad \text{Target} \quad \text{Target shutter}\]
holder for uniform deposition and a substrate heating system able to heat to 850 °C.
A schematic of the co-sputtering process have been provided in figure 2.19 with an example of a typical glassy carbon (HTW Hochtemperatur-Werkstoffe, $h \times \varnothing = 5 \times 5 \text{ mm}$) substrate and the influence the island-like thin film growth mechanism\cite{203} will have on an alloy when subjected to acid leaching.

Prior to any deposition the glassy carbon substrates were polished (using polishing paste and disks from Struer), sonicated and Ar sputter cleaned. Moreover, for each deposition a glassy carbon slab were placed in the setup allowing for larger area deposition samples which were useful for X-Ray Diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) tests.

![Schematic of the sputter deposition process.](image)

**Figure 2.19:** Schematic\cite{168} of the sputter deposition process, here for a Pt$_5$Gd thin film. Ar gas is ionized to plasma to form Ar$^+$ (blue). A negative bias is applied on the target material (gray), which causes the Ar$^+$ to bombard the surface and knock atoms loose. Some of the target atoms then deposit on the grounded substrate. Magnets confine the plasma near the targets. A insert of the glassy carbon substrate have been included as well as the island-like growth of Pt and its alloys and the impact of thickness will have when subjected to acid leaching.\cite{203}
To avoid incorporation of oxygen in the thin films the following steps were taken:  

1. Glassy carbon substrates were loaded into the chamber load lock and when the pressure was below $10 \times 10^{-7}$ mTorr the samples were transferred to the main chamber.  
2. The substrates were heated to 200 °C to evaporate water traces.  
3. Ar sputtering on the substrates was performed for 45 minutes removing all surface adsorbed contamination.  
4. The shutter was positioned so as to obstruct substrate deposition and Ti was sputtered in the chamber for 30 to 45 minutes, acting as a Ti sublimation pump, thus lowering the oxygen pressure in the chamber.  
5. The chamber was pumped down until a base pressure of $10 \times 10^{-9}$ mTorr had been reached.  
6. Sputter deposition at 180 W of Pt and if required a secondary material could now be conducted, this was done at 4 mbar with a 50 sccm Ar flow using various film thicknesses and annealing temperatures.  

Some optimization of thin films’ thickness and annealing temperature were identified, for instance film thicknesses below 27 nm were observed to allow pinholes formation. Moreover, annealing temperatures above 400 °C resulted in rather erratic electrochemical performances of the thin films as discussed in chapter 6.

As indicated in figure 2.19, it was found that for Pt based alloy films at least 3 nm thick films were needed to avoid the secondary metal to completely leach out during electrochemistry. This would otherwise correspond to a pure Pt surface with no benefit from the alloying. This observation fits very well with earlier report, suggesting Pt$_x$M $(M=\text{Gd, Y})$ NPs should attain diameters $\gtrsim 6$ nm for any positive effect from the strain induced Pt overlayer formation on the ORR activity from Gd or Y alloying.

### 2.5 X-Ray Diffraction

XRD and relies on emission of X-rays of wavelength $\lambda$ onto a surface. Surface crystallinity and the consequent atomic periodicity will result in constructive diffraction following Bragg’s law $n_i \lambda = 2 d_{hkl} \sin(\theta)$, where $n_i$ is an integer number, $d_{hkl}$ denotes the crystal spacing for the $(hkl)$ plane where $h$, $k$ and $l$ are Miller indices, see figure 2.20.  

Hence, by impinging X-rays onto samples at various angles crystal structure information can be obtained through interference patterns. This can be done both on ex-
Figure 2.21: Examples of XRD data. a Here of commercially available Pt/C (49.8 wt%) NPs exhibiting a crystal size of 6.8 nm from Rietveld analysis. b Same catalyst as a after alloying synthesis procedure, see chapter 7. Courtesy PhD Brian Peter Knudsen.\cite{204}

tended surfaces and on Powders (P-XRD), examples of the latter have been presented in figure 2.21 of NPs before and after an alloying synthesis procedure (see chapter 7). A PANalytical XPert Pro or EMPYRIAN XRD system, both with 1.54 Å X-rays from the Cu $K\alpha$ line and angular measurement ranging from 20 to 90° have been utilized. Grazing Incidence-XRD (GI-XRD) using synchrotron radiation were also performed for some Gd/Pt(111) samples.\cite{198,206} These measurements were conducted at the synchrotron source at Stanford Synchrotron Radiation Lightsource (SSRL). For specific samples (see chapter 5) in-situ GI-XRD in a three-electrode setup in a hanging meniscus configuration was utilized, such setup has been illustrated in figure 2.22.

Figure 2.22: Schematic of the in-situ GI-XRD setup used at SSRL.\cite{157,206}
2.6 X-Ray Photoelectron Spectroscopy

XPS relies on the emission of X-rays of ideally monochromatic wavelengths and is based on the photoelectric effect \( E_\gamma = h\omega_\gamma \). By bombarding a sample surface with X-rays of specific energies and using an electron energy analyzer e.g. a Hemi-Spherical energy Analyzer (HSA) with an electron multiplier, electrons with shell-binding energies \( E_b \) can then be detected, as

\[
E_b = E_\gamma - (\Phi + E_{\text{kin}}) \tag{2.15}
\]

where \( E_{\text{kin}} \) is the kinetic energy of the electron detected by the HSA and \( \Phi \) is the work function\(^3\). Inherent of equation (2.15) and implicitly to Fermi’s-golden rule\(^2\) is that electron occupancy densities can be probed, due to the excitation probability of the electron \( P \propto |\langle \phi_{\text{initial}} | \hat{H}(t) | \phi_{\text{final}} \rangle |^2 \), where \( \hat{H}(t) \) is a the Hamiltonian and \( \phi \) the initial and final state.

There is some uncertainty associated with the X-ray source and analyzer. Uncertainties relating to the X-ray sources arise from spin-orbit band-splitting and Heisenberg uncertainties \( \Delta E \Delta t \geq \hbar \). Moreover, as primary excitations \( K\alpha \)’s are observed in pairs this give rise to a Full Width Half Maximum (FWHM), typically in the order of 0.7 to 0.85 eV. An illustration of the XPS principle is shown in figure 2.24.

\[3\] Energy required for an electron to become a free electron from the Fermi to the vacuum level.
Figure 2.24 gives good insight into the working principle of XPS while stating that due to ionization of the core-shells during the adiabatic photoelectric excitation of electrons, the apparent binding energies may shift and/or relax i.e. satellites and shake-ups have to be considered. Moreover, binding energies may also shift due to differences in chemical states, hence equation (2.15) can be modified by

\[ E_b \rightarrow E_b + E_{ar} + E_{car} + E_{chem} \]  

(2.16)

, where \( E_{chem} \) designates any chemical shift from the surroundings of the atoms, for instance surface oxide formation is easily observed using XPS.

The X-ray sources (for suitable photon energies) are typically in the order of 1 to 2 keV (for ionization regime see figure 2.23) and can be generated by potential excitation of anode materials. In this work an Al source of \( E_{\gamma,Al,K\alpha} = 1486.6 \text{eV} \) were used. The XPS system used in this work was a Theta Probe instrument (Thermo Scientific). The base pressure in the XPS chamber was between \( 8.0 \times 10^{-9} \) and \( 5.0 \times 10^{-10} \text{mbar} \), unless the chamber flood-gun or Ar sputter capabilities were utilized, in which case the pressures were ca. \( 1.1 \times 10^{-7} \text{mbar} \). Sample tilting was never applied and the beam spot size was \( 400 \mu\text{m} \) for all measurements. An image of the Theta Probe XPS chamber with its main components can be seen in figure 2.25.

![Theta Probe XPS chamber and components](image)

**Figure 2.25:** Theta Probe XPS chamber and components. Adapted from PhD Paolo Malacrida.\textsuperscript{[106]}

XPS has mainly been used for evaluation of contamination, surface chemical states and to gain insight into the profile of sample surfaces. To do this the software Avantage incorporated with the Theta Probe system have been utilized.

XPS is a non-destructive (soft X-ray) UHV technique giving average peak information of chemical states of the first few atom layers of a sample, it does not give any structural information about the surface. \( Nb \) charging of samples will severely change the kinetic energy of the excited electrons, hence samples should ideally be conducting and grounded.
2.6.1 Conventional X-ray Photoelectron Spectroscopy

Quantitative XPS of element $A$ excitation of electrons from shell $\kappa$ relies on evaluating the XPS signal arising from the probabilities of photoelectrons excitation and escape through the surface (given by cross-section $\sigma_A$ and the number of incident X-ray photons $F$). This can be evaluated as the atom density $N_A$ for a sample with inelastic mean-free path length of $\lambda_A$ and transmission $T$ to the analyzer

$$I_{A,\kappa} = \sigma_{A,\kappa} N_A \lambda_{A,\kappa} F_{\text{inc}} T(E_{\text{kin}})$$  \hspace{1cm} (2.17)$$

From this a relation for the intensity in depth $z$ and of thickness $dz$ can be estimated and, following a Beer-Lambert relation, can be formulated for an overlayer $B$ on $A$

$$dI_{A,\kappa} = \frac{I_{A,\kappa}}{\lambda_{A,\kappa}} \exp \left(-\frac{z}{\lambda_{A,\kappa}}\right) dz \Rightarrow I_{A,\kappa}(z) = I_{A,\kappa} \exp \left(-\frac{z}{\cos(\theta)\lambda_{B,\kappa}}\right)$$

$$I_{B,\kappa'}(z) = I_{B,\kappa'} \left(1 - \exp \left(-\frac{z}{\cos(\theta)\lambda_{B,\kappa'}}\right)\right)$$  \hspace{1cm} (2.18)$$

The effective probing depth can be tuned by changing the analyzer angle $\theta$ this allows for some measure of depth profiling. For an isotropic surface the ratios of atoms can be evaluated from the intensity peaks (or rather their area)

$$C_A = \frac{I_{A,\kappa}}{\sum_{i=1}^{N} I_{A,i}} \times 100\%$$  \hspace{1cm} (2.19)$$

The sensitivity factors $S_i$ of the various elements is dependent on the elements interaction cross-section, the transmission probability and the atomic density i.e. $S_i(\sigma_i, T, N_i)$. In this work sensitivity factors from the National Institute of Standards and Technology (NIST) database were utilized, matching those pre-installed in the Avantage software package.

2.6.2 Angle Resolved X-Ray Photoelectron Spectroscopy

Besides conventional XPS, in which electron energies are measured over all incoming angles, it is possible to gain information about the surface profiles by measuring the angle dependent electron energies.$^[1,106] E.g. an overlayer $B$ on $A$ can be described by

$$\frac{I_{B,\kappa'}}{I_{A,\kappa}} = \frac{I_{B,\kappa'}^\infty}{I_{A,\kappa}^\infty} \left[ 1 - \exp \left(\frac{-d_{OL}}{\lambda_{B,\kappa'}(E_{B,\kappa'} \cos(\theta))}\right) \right]$$

$$\exp \left(\frac{-d_{OL}}{\lambda_{A,\kappa}(E_{A,\kappa} \cos(\theta))}\right)$$  \hspace{1cm} (2.20)$$

, where $I_{A,\kappa/B,\kappa'}^\infty$ signify signals from infinitely thick layers. Equation (2.20) shows that it is possible to describe the surface profile of a simple two layer system e.g. an overlayer on a sample substrate. Using the build-in Angle Resolved (AR-)XPS tool in the Avantage software package it was possible to construct AR-XPS surface profiles.
An example, seen in figure 2.26 the Cu2p, Pt4f, O1s and C1s peak of a Pt(111) crystal prior, post Cu overlayer deposition and after near-surface alloying with Cu.

Figure 2.26: AR-XPS plot measured at angles from 21.875 to 78.125° over 16 steps, blue low angles, red high angles. a O1s peak. b C1s peak. c Pt4f peak. d Cu2p\(_{3/2}\) peak.

The data of figure 2.26 reveals how peak positions are dependent on surface chemical state changes, in this example a Pt(111) subjected to Cu near-surface alloying as described in 2.3.3.

Using the maximum entropy fitting tool of the Avantage software allows a profile to be plotted, see figure 2.27. AR-XPS is a powerful tool for overlayer investigations of extended surfaces. However, the technique is quite sensitive to surface roughness, which will ”smear” out the angle dependence. Moreover, as surfaces transferred through air are subjected to adsorption of oxygen and carbon species.

Figure 2.27: AR-XPS surface profile of a Cu/Pt(111) NSA.
such surface species should ideally be accounted for when conducting AR-XPS, see figure 2.27 for AR-XPS profile of a Cu/Pt(111) NSA for which surface contamination of oxygen and carbon has been taken into account. AR-XPS is not the only technique to give XPS information on the surface profile; soft Ar sputtering 0.5 μA over 20 minutes of a 6 × 6 mm² area are expected to remove ca. 9nm pure Pt. Hence, by alternating between sputtering and XPS measurements a rough profile can be derived. However, contrary to AR-XPS sputter profiles are destructive and when considering systems with multiple sputter rates forming an actual depth profile becomes very difficult.

### 2.7 Miscellaneous Techniques

Besides the physical and electrochemical experimental methods and setups utilized in this thesis work, other techniques have peripherally been used and/or discussed. No in-depth explanation of these techniques will be given, but such relevant techniques include Ion Scattering Spectroscopy (ISS), Low Energy Electron Diffraction (LEED), (CO-)Temperature Programmed Desorption (CO-TPD), Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), Extended X-ray Absorption Fine Structure (EXAFS), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), ThermoGravimetric Analysis (TGA) and reactor based[34,204] NP synthesis.

### 2.8 Conclusions

In the above the relevant electrochemical cells, setups and procedures used in this work have been presented. Moreover, in-depth state-of-the-art electrochemical methods used to estimate relevant parameters for ORR electrocatalysts have been presented and discussed, and concepts such as specific activities, Tafel slopes, ECSA and Ohmic-drop compensation have been defined.

Methods for preparing extended catalyst surfaces such as Pt_{poly}, Pt(111) and Cu/Pt(111) NSAs have been presented, as well as sputtering deposition of Pt based thin films.

A range of setups for catalyst characterization have been presented, together with the insights such techniques may provide.
Electrolyte Effects on Pt-Part I: Cations

ORR is one of the most important chemical reactions known to the human race. It is of paramount importance within energy conversion as any efficiency limitations of this reaction will manifest implicitly as an efficiency constraint applied to the overall conversion, whether it be for PEMFCs or batteries. Consequently vast research efforts have been devoted towards elucidating the specific factors governing ORR and due to the huge commercial potential of PEMFC systems noticeable focus has been placed on acidic media ORR. Unfortunately, acidic media based ORR only supports very noble materials such as Pt based catalyst for stable and active applications. Dissolution and corrosion, coupled with poor selectivity and activity for non-Pt based electrocatalysts in acid virtually exclude all other materials for ORR. Recent years have shown an increase in the effort to explore neutral or alkaline electrolytes. ORR catalysis in alkaline media have especially received increased attention as stability requirements for the catalyst are eased, in many cases at the expense of the membrane durability and efficiency in fuel cells, thus allowing non-noble catalyst materials. In context to such investigations no clear descriptors for ORR activity have been found, not even for a well-reported material such as pure Pt. This is in contrast to acidic media ORR, for which both theoretical and experimental studies supports Sabatier volcano-like relationships of OH intermediate surface binding being the main descriptor of activity. Considering the research efforts into elucidating the relevant ORR descriptors in acid and their resulting success, it is surprising that similar identification of descriptive models for ORR in alkaline media have not had a similar rate of success.

Thorough work on stepped Pt single crystals have revealed Pt(111) activity enhancement over other Pt surface morphologies, in a fashion that seemingly differs from that
expected for an OH binding energy descriptor. Furthermore, cation dependence\cite{227, 228} on the Pt(111) activity has been investigated and it has been found that the alkali (cation) present in the electrolyte has a substantial influence on the resulting ORR activity. The following relationship in 0.1 M alkaline media has been reported\cite{68} for Pt(111) \( j_{k,LiOH} < j_{k,NaOH} < j_{k,KOH} < j_{k,CsOH} \).

It may be surprising that the apparent ORR activity enhancement on Pt(111) in alkaline electrolyte is not shared for all surface morphologies. Indications of the poorly understood interaction between cation and surface morphologies have been attempted exemplified in alkaline electrolyte by RDE tests of Pt\textsubscript{Poly} electrodes first measured in KOH followed by HClO\textsubscript{4} and also in the reverse order (see figure 3.1).

![Figure 3.1: RDE measurements of a Pt\textsubscript{Poly} sample (23 °C, 50 mV/s) in 0.1 M KOH alkaline and then in 0.1 M HClO\textsubscript{4} acidic media. a Base CVs in N\textsubscript{2}-saturated electrolytes at 400 rpm. b Tafel plot with anodic sweep insert taken at 1600 rpm in O\textsubscript{2}-saturated electrolyte, the specific activity points at 0.9 V shows the average activities (with errors) for two samples both measured in KOH followed by HClO\textsubscript{4} and vice versa.](image)

As seen from figure 3.1, interestingly no surface activity enhancement of polycrystalline Pt in KOH has been observed here or by others\cite{89} (0.96 ± 0.03 mA/cm\textsuperscript{2}, roughly half of that in HClO\textsubscript{4}). Moreover, these Pt\textsubscript{Poly} experiments in KOH revealed by careful immersion and retraction of Pt electrodes under potential control, separated by a simple rinse in Millipore water, allowed same electrodes to be electrochemically investigated in both HClO\textsubscript{4} and KOH without loss of activity. However, it was found that without rinsing the electrode was poisoned, possibly from KCl formation.

For any scientific investigation it is useful to consult literature, this has been done in this study pertaining to Pt based alloys ORR activity in alkaline media. Interestingly there is not strong consensus with regard to the ORR activity of Pt in alkaline media, not even...
for quite reproducible model surfaces such as Pt(111) and Pt\text{poly}, selected Tafel plots and specific activities from literature have been shown in figure 3.2.

![Tafel plots and specific activity values of selected Pt based catalysts from literature in alkaline media.](image)

**Figure 3.2:** Tafel plots and specific activity values of selected Pt based catalysts from literature in alkaline media.\[68, 89, 147, 150, 164, 224, 226]\]

The exceedingly high ORR activity of Pt\textsubscript{3}Ni(111)\[226\] in KOH shown in figure 3.2 is especially interesting, as this is a surface on which activity was found to scale with oxygen intermediates in acidic media,\[93\] in strong contrast to results on stepped Pt in NaOH.\[150\]

In the following, investigations of Pt based ORR catalysis in alkaline media have been presented with a special focus on the effect of weakening OH binding using Pt(111) and Cu/Pt(111) NSA\[1\] model systems.

### 3.1 Pt(111) in Alkaline Media

Pt based electrocatalysts have been investigated by various groups and widely varying results have been found as indicated in figure 3.2. Using the methods and setups presented in chapter 2, preparation of Pt(111) electrodes and electrocatalytic performances in alkaline media were conducted and compared to other literature results,\[68, 150\] an example of this have been given in figure 3.3.

Figure 3.3 shows Pt(111) base CVs in 0.1 M KOH and NaOH compared to CVs from literature.\[68, 150\] Interestingly of the CVs in KOH, NaOH and CsOH exhibit almost the same features and only LiOH of the alkaline metals gives rise to CVs with fundamentally different features. A wide range of Pt(111) electrochemical parameters in KOH were found from extensive RDE experiments and some of these have been presented in table 3.1.
The data of table 3.1 for Pt(111) oxygen electroreduction requires some interpretation. Especially, in regards to the $H_{\text{UPD}}$ charge area, which upper potential limit, i.e. hydrogen adsorption onset potential, is rather uncertain due to the slight (100) features\[^{228,230}\] in the double-layer region. The slight (100)-features from surface steps are likely to increase estimates of the hydrogen charge for Pt(111) and furthermore distort any evaluation requiring a fixed hydrogen adsorption potential onset.\[^2\]

The stability of Pt(111) surfaces in alkaline media are severely limited as any trace metals tend to adsorb to the Pt(111) surface during RDE experiments,\[^{229,232}\] especially after fast rotations like the 1600 rpm utilized during ORR evaluations.

Figure 3.4 shows a base CV of a Pt(111) surface before and after ORR evaluation in a RDE setup. Here a small redox-couple presents in both the anodic and cathodic scan after ORR, features which have been well reported in literature.\[^{232}\]

From the base CV measurements of Pt(111) it became obvious that any RDE based investigation of Pt ORR electrocatalysis would have to be done under extremely clean conditions and had to be executed in a reduced time frame compared to the time required for Pt(111) studies in acidic conditions. This extreme sensitivity to surface contamination

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**Figure 3.3:** RDE base CVs of Pt(111) in alkaline media at room-temperature. \(\text{a}\) In 0.1 M KOH measured at 50 mV/s and compared to literature CV.\[^{68}\] \(\text{b}\) In 0.1 M NaOH measured at 50 mV/s and compared to literature CV\[^{150}\] (narrower potential limits have been applied the reference CV).

**Table 3.1:** Electrochemical parameters for Pt(111) gathered in 0.1 M KOH at 23°C from 7 distinct measurements. *Evaluated at 0.9 V vs. RHE.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{Pt}(111)}$</td>
<td>$141.6 \pm 12.9 \mu \text{C/cm}^2$</td>
</tr>
<tr>
<td>$j_k^*$</td>
<td>$7.8 \pm 0.8 \text{mA/cm}^2$</td>
</tr>
<tr>
<td>$\beta^*$</td>
<td>$45.52 \pm 5.9 \text{mV/dec.}$</td>
</tr>
<tr>
<td>$U_{\text{onset}}$</td>
<td>$962 \pm 8 \text{mV}$</td>
</tr>
<tr>
<td>$U_{\text{half-wave}}$</td>
<td>$908 \pm 7 \text{mV}$</td>
</tr>
</tbody>
</table>
in KOH also meant that although a ca. 4-fold improvement of Pt(111) activity in KOH compared to HClO$_4$ were observed, the uncertainty was relatively large, see table 3.1. It is definitely the case that Pt(111) exhibits a substantial activity enhancement as reported by others.[147,150,226] Interestingly it was found that if Pt(111) (or Cu/Pt(111) NSAs) exhibited peaks after ORR similar to those seen at the cathodic scan at $\sim 0.57$ V vs. RHE in figure 3.4, it was possible to ”reset” the features of the CV by performing a single CV in HClO$_4$ (all transfers under potential control) and re-immersing in KOH. This strongly suggests that in KOH some oxidized species can irreversibly adsorb on the Pt surface, but can be dissolved in acid in agreement with literature reports.[232]

As indicated, having a basis for reference of the Pt(111) crystal’s electrochemical performance in KOH allowed the use of standard RDE techniques to probe Cu/Pt(111) NSAs under similar alkaline conditions, in the hope that the relevancy of OH binding as ORR descriptor in alkaline media could be elucidated.[150,226]

### 3.2 Cu/Pt(111) Preparation and Characterization

Using the NSA preparation approach explained in chapter 2, it was possible, by Cu underpotential deposition[137] and consequent annealing, to form Cu/Pt(111) NSAs. Earlier reports[1] found these to allow tuning of oxygen intermediates binding to the surface by controlling the Cu concentration in the 2$^{nd}$ atomic layer. Hence, the system was very interesting as it would allow insight into some of the governing factors of the anomalous Pt(111) ORR activity in KOH and allow us to probe the system activity in terms of initial amounts of Cu deposition coverage $\theta_{Cu}$.

Four different Cu deposition cycles have been plotted in figure 3.5 and using the expected full monolayer Cu deposition charge area of 480 $\mu$C/cm$^2$[1,233] $\theta_{Cu}$ have been calculated.
Figure 3.5: Closed cell Cu deposition on Pt(111) crystals done at room temperature in 5 mM Cu dissolved in 0.1 M HClO$_4$, N$_2$-saturated electrolyte at 20 mV/s after 3 min potential hold.  

$a$ $\theta_{Cu} = 0.17$ ML.  $b$ $\theta_{Cu} = 0.27$ ML.  $c$ $\theta_{Cu} = 0.79$ ML.  $d$ $\theta_{Cu} = 0.98$ ML.

From the examples in figure 3.5 of Cu oxidation peaks and earlier reports\cite{1,100,151,152,183} it is clear that Cu deposition amounts is a non-linear function of potential, \textit{i.e.} for each deposition extensive cycling and consequent hold times were needed to obtain specific Cu coverages. Interestingly the Cu deposition appeared to be insensitive to the Cu concentration present in the electrolyte, supporting a fixed potential dependent coverage equilibrium. Hence, the reason for the non-linear dependence remains elusive.

Typically five to ten deposition cycles with consequent Cu-stripping were required for stable Cu oxidation peaks. This extensiveness of measurement may in itself represent a source of experimental uncertainty, as maintaining low $U_{dep}$ will exacerbate any unwarranted adsorption. Morphology changes from the strong Cu adsorption on the Pt(111)
was found unlikely to be an issue as base CVs of Pt(111) before and after CVs in Cu containing electrolyte reverted to their original form, albeit extensive flushing with fresh electrolyte were required.

After the Cu deposition the samples were dried and annealed in Ar/H$_2$(5%), see section 2.3.3. Following the Cu/Pt(111) NSA samples were moved to the RDE setup for testing or quick base CVs in the closed cell were obtained, both methods ensured that CVs compared to those expected from literature\cite{1} had formed. In some cases the NSAs were moved to a UHV chamber for AR-XPS after deposition and CV verification, see figure 3.6.

**Figure 3.6:** AR-XPS profiles of corresponding Cu/Pt(111) of figure 3.5, evaluated from the Pt4f, Gd4d, C1s and O1s peaks from data collected by the Theta Probe and consequent analysis using the Avantage software.  

- a $\theta_{Cu} = 0.17$ ML.  
- b $\theta_{Cu} = 0.27$ ML.  
- c $\theta_{Cu} = 0.79$ ML.  
- d $\theta_{Cu} = 0.98$ ML.  

Note the maximum profile Cu content $\theta_{Cu,Profile} \neq \theta_{Cu}$.
The AR-XPS profiles of figure 3.6, which all rely on the sample examples of figure 3.5, reveal that there is little consistency between the initial Cu deposition $\theta_{\text{Cu}}$ and the AR-profile Cu content denoted $\theta_{\text{Cu,profile}}$ as this quantity (seen as the maximum of the relative Cu signal of figure 3.6) results from an unknown fitting model of the Avantage software suite rather than physical meaningful values. By instead using the angle dependence of the relative signal for low incident angle electrons (from 20 to 35°), the most surface sensitive, Cu:Pt ratios could be evaluated and compared to earlier reported NSA behavior, as done in figure 3.7 and co-plotted with an earlier model.\cite{1}

**Figure 3.7:** Cu:Pt intensity ratio, from XPS, for different Cu/Pt(111) NSAs. The analysis was based on the Pt4f and Cu2p photoelectrons emitted at four different angles between 20 and 35° to the sample normal. The Cu:Pt intensity ratio is corrected for the excitation cross section, the mean free path and the analyzer transmission. The error bars show the standard deviations over the angles. The dashed line shows the earlier modeled ratio\cite{1} relative to the initial Cu deposition. The open circled data point shows the Cu:Pt ratio after electrochemistry. The blue points show data points for a range of Cu/Pt(111) that produced unexpected CVs.

Using the data of figure 3.7 it was possible to map out average Cu:Pt ratios from 20 to 35° for a wide range of Cu/Pt(111) NSAs. It is worth noting that figure 3.7 mainly includes data points for Cu/Pt(111) NSAs which CVs features matched those expected from earlier reports, i.e. there were cases where deposition seemed to have failed due to loss of potential control etc. These samples’ CVs looked either unfamiliar, had a strong resemblance to Pt(111) or exhibited a noticeable Cu stripping peak when cycled in acidic electrolyte. A few points where samples with unexpected CVs have been included in figure 3.7. These data points revealed that if something went wrong during the preparation it could clearly be seen in the CVs. In instances where the CVs did not look as expected the samples were usually cycled to very positive potential stripping all Cu from the subsurface and the electrodes were re-prepared. Unfortunately, this also meant that no clear understanding
of error modes were identified, although any failed NSA formation were thought mainly to be due to oxygen contamination. The model\cite{1} of figure 3.7 plots the expected AR-XPS Cu:Pt ratio if only Cu in the 2\textsuperscript{nd} layer was present. Hence, it is appears that some Cu likely to have migrated into the bulk, which has also been corroborated from earlier studies.\cite{1,234,235}

From figure 3.7 it is clear that Cu/Pt(111) NSAs, that exhibits similar behavior as reported earlier, can be formed and that the Cu content in the 2\textsuperscript{nd} atomic layer indeed tunes the OH binding, seen as a OH suppression in the OH potential region of such samples CVs (see figure 3.8).

![Figure 3.8](image)

*Figure 3.8:* RDE obtained base CVs of Cu/Pt(111) NSAs in N\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} taken at 23\degree C, 50 mV/s and 400 rpm.

Figure 3.8 clearly exemplifies the OH suppression from Cu alloying and thus the initial Cu deposition coverage $\theta_{\text{Cu}}$. Further, the data suggests that a substantial effect from the change in OH binding occurs even at low Cu depositions.

From the above and the methodology of sections 2.1.3 and 2.3, an usable framework for tuning the OH binding for Cu near-surface alloying of Pt(111) have been presented.

### 3.3 Cu/Pt(111) Activity in Alkaline Media

Cu/Pt(111) NSAs with varying amounts of Cu in the 2\textsuperscript{nd} atom layer were prepared and measured. Base CVs in (Merck, Suprapur\textsuperscript{®}, 70 \%) HClO\textsubscript{4} were obtained ensuring that appropriate NSAs vs. Cu coverages had been formed. Following this the NSAs were removed from the RDE setup containing acid and moved to a KOH containing one (Merck, Suprapur\textsuperscript{®}, 99.995 \%). All immersions and extractions were done under potential control
and separated by a quick rinse in Millipore water. The full procedure used for electrochemical characterization of Cu/Pt(111) NSAs has been summarized in the following approach:

**Step 1** - Cu/Pt(111) NSAs were loaded into a three-electrode RDE setup containing 0.1 M HClO$_4$ and base CVs were obtained, followed by EIS and RHE evaluation.

**Step 2** - NSAs were transferred to a three-electrode setup containing 0.1 M KOH separated by a rinse with Millipore water and base CVs were collected.

**Step 3** - ORR activity was measured followed by EIS and RHE evaluation and additional base CVs were obtained to check for any changes.

**Step 4** - Electrodes were moved back to the RDE setup containing acid separated by electrode rinsing in Millipore water.

**Step 5** - Base CVs in acid were re-obtained and changes noted.

**Step 6** - Sample was stripped for any Cu by cycling to 1.6 V vs. RHE.\[1\]

Base CVs of Cu/Pt(111) NSAs in acidic and alkaline media can be seen in figure 3.9.

![Figure 3.9](image)

**Figure 3.9:** Base CVs of Cu/Pt(111) NSAs with varying $\theta_{\text{Cu}}$. Measurements taken at 23°C, 400 rpm and 50 mV/s in N$_2$-saturated electrolytes. *a* In 0.1 M HClO$_4$. *b* In 0.1 M KOH.

The shift in the OH onset potentials coupled with the suppression of the OH region, has from earlier studies\[1, 236–238\] been found to correspond to shifts in OH binding energies. Assuming 50% coverage of OH, the expected 1/3 Pt(111) OH saturation coverage\[236\] and a full charge layer corresponding to $\sigma_{\text{OH}}^{\text{Pt(111)}} = 240 \mu\text{C/cm}^2$ \[1, 236\] it is possible to estimate the relative shift in OH binding energy required to cover the Cu/Pt(111) surface (1/6 *OH
ML) halfway relative to the total number of Pt(111) sites and correlate this to shift in OH adsorption potential

$$\Delta \Delta E^*_{\text{OH}} = \Delta E^*_{\text{Pt(111)}} - \Delta E^*_{\text{Cu/Pt(111)}} \approx e[\Delta U^*_{\text{Pt(111)}} - \Delta U^*_{\text{Cu/Pt(111)}}] = e \Delta U_{1/6 \cdot \text{OH ML}} \quad (3.1)$$

The potential evaluation was calculated by finding integration limits relative to the OH onset as proposed from equation (2.10) (see figure 2.7d for example of $U_{\text{OH-onset}}$ determination) by considering the following

$$\theta_{\text{OH}}^*_{\text{PT(111)}} = \frac{dt}{dU} \int_{U_{\text{OH-onset}}}^{U_{\text{OH-ML}}} [j - j_{\text{background}}] \, dU \quad (3.2)$$

where $\theta_{\text{OH}}$ is the OH coverage fraction (e.g. 1/6) and $\Delta U_{\theta_{\text{OH}} \cdot \text{ML}} = U_{\text{OH-onset}} - U_{\theta_{\text{OH}} \cdot \text{ML}}$. Figure 3.6 shows the OH adsorption region and the integration done for select Cu/Pt(111) NSAs and pure Pt(111) in acid and in alkaline media.

**Figure 3.10:** Integration of OH charge (top) from base CVs zoom-ins (bottom) of the relevant OH region of Cu/Pt(111) NSAs from figure 3.9. Measurements were taken at 23 °C, 400 rpm and 50 mV/s in N$_2$-saturated electrolytes. **a** In 0.1 M HClO$_4$. **b** In 0.1 M KOH.
Figure 3.10 further demonstrates that the Cu content tunes the OH adsorption compared to pure Pt(111), although the exact relationship is unknown. It is also evident that the OH adsorption charge per potential shifts dramatically when changing from pure Pt(111) to Cu/Pt(111) NSAs. Specifically, fundamental differences are observed between $\theta_{Cu} \leq 0.2$ ML and the $\theta_{Cu} > 0.2$ ML coverage range. In the range $\theta_{Cu} > 0.2$ ML in KOH it appears as if the OH charge accumulation begins to follows the same slope as function of potential ($dQ/dU \approx 282 \pm 30 \mu C/Vcm^2$), indicating a rapid modification of the Pt(111) electronic surface structure followed by a more gradual one.

Potential shifts have all been evaluated relative to literature values for the total charge area of Pt(111) assumed to be 240 $\mu C/cm^2$. It is however likely that OH coverage as a function of applied potential (from OH onset) in 0.1 M HClO$_4$, will not be the same as in 0.1 M KOH and moreover assuming identical OH saturation coverage in HClO$_4$ as in KOH is questionable. Although low adsorbate-adsorbate interactions of the electrolyte would support this assumption, any relative shift in OH coverage potentials will introduce an error when evaluating the “true” potential shifts. The potential shift in OH adsorption should rather be seen as relative shifts compared to Pt(111), which is known to bind OH intermediates approximately 0.1 eV too strongly$^{[1,81]}$ from that optimal for ORR and thereby simply gives an indication of stronger or weaker OH binding of the system relative to Pt(111).

From base CVs in acidic and alkaline electrolytes the relative potential shifts in OH charging are shown (figure 3.9 and 3.10) to follow similar trends to those reported earlier$^{[1]}$ in acid. The relative shifts in OH potential as a function of the initial Cu deposition coverages are shown in figure 3.11.

Figure 3.11 shows a similar trend of weakening of OH binding as a function of the Cu amount which is initially deposited on the Pt(111) electrodes prior alloying. However, for intermediate $\theta_{Cu}$ values there seems to be a discrepancy in the observed shift relative to that observed in earlier work.$^{[1]}$

At present no good explanation has been conceived to account for this discrepancy, but it is worth noting that the variation in trend in acid can mainly be accredited to a single point corresponding to $\theta_{Cu} = 0.71$ ML, though three consecutive measurements supports its validity. One may speculate whether there could be an inherent instability associated with producing Cu/Pt(111) NSAs due to geometric constrictions, i.e. certain Cu coverages would be preferred on the surface.

*Figure 3.11:* Cu/Pt(111) NSAs’ initial Cu coverage relative to OH potential shifts in KOH and HClO$_4$ (both from this and earlier studies$^{[1]}$) with guides for the eyes (lines).
Cu/Pt(111) Activity in Alkaline Media

The total OH coverage possible in KOH may differ significantly relative to that observed in HClO$_4$. As the main (111) feature in alkaline is broader than in acidic media, one may speculate that Pt(111) experiences different OH saturation coverage or at the very least different coverage as a function of potential in KOH relative to HClO$_4$.

After obtaining base CVs in acid media and successful transfer to electrolyte KOH containing (again verified by CVs), ORR activity were evaluated as indicated in figure 3.12.

![Figure 3.12: Tafel plots showing the Cu/Pt(111) NSAs’ ORR activities in O$_2$-saturated 0.1 M KOH taken at 23°C, 50 mV/s and 1600 rpm, insert shows the utilized anodic scans.](image)

Figure 3.12 reveals that in KOH the Cu/Pt(111) NSA system experiences gradual improvement in activity as function of Cu coverage. Peaking at a staggering specific activity at 0.9 V vs. RHE of 100.7 ± 7.5 mA/cm$^2$ at ca. $\theta_{Cu} = 0.77$ ML. The activity is enhanced by a factor of up to 12.9 times that of pure Pt(111) at the same potential in KOH.

Comparison of the maximum specific activity at 0.9 V vs. RHE of the Cu/Pt(111) NSA system in HClO$_4$ of 11.7 mA/cm$^2$[1] and with the maximum activity in KOH an enhancement of NSAs of 8.6 is observed when moving from HClO$_4$ to KOH. Curiously this value is almost double that observed when measuring activities of pure Pt(111) in HClO$_4$ and KOH where an enhancement factor of ca. 4.4 was observed.

Figure 3.13 shows reasonable agreement of activity enhancement in KOH as a function of initial Cu deposition coverage compared to that reported in HClO$_4$[1]. This suggests
similarity in between the Cu/Pt(111) NSAs Cu dependence in acid and alkaline media, i.e. same OH binding trends.

Moreover, as Pt(111) activity has been reported\cite{147} to be dependent on cation type, a few measurements of Cu/Pt(111) in 0.1 M NaOH (Merck, Suprapur®, 99.995%) were also collected. In agreement with literature\cite{147} the samples were found to be more active in KOH than in NaOH as indicated in figure 3.14.

\textbf{Figure 3.14:} Tafel plots of Cu/Pt(111) NSA with selected Cu coverages in 0.1 M KOH and NaOH, taken in O$_2$-saturated electrolyte, 23°C, 50 mV/s and 1600 rpm.
The evaluated activity enhancements were plotted as a function of the observed shifts in OH adsorption potential (see figure 3.15).

Figure 3.15: Volcano-plot of the potential shift in OH adsorption vs. activity enhancement in 0.1 M NaOH (green), KOH (red) and HClO$_4$ (blue). A thermodynamic (black) and kinetic volcano (gray) for the 4e$^-$ ORR have been included together with results of Pt$_3$Ni(111) in HClO$_4$ and KOH at 60 $^\circ$C and single crystal values of Pt(775) and Pt(755) surfaces in 0.1 M NaOH evaluated from specific activities at 0.8 V vs. RHE.

Reasonable agreement between ORR enhancement in acid and alkaline media are observed as a function of the shifts in OH adsorption potential, tuned by Cu alloying, in the figure 3.15 volcano plot. This proves that OH binding is an activity descriptor for ORR activity in alkaline media. However, the activity points of Pt(755) and Pt(755)$^{[150]}$ suggest, OH binding is not the sole descriptor of the ORR activity. It seems an intricate interplay exists between the cation of the alkaline electrolyte and the Pt surface morphology.

Figure 3.15 also shows that more active surfaces than Cu/Pt(111) NSAs exist in alkaline media such as Pt$_3$Ni(111)$^{[226]}$ which specific activity at 0.9 V vs. RHE is so high that it breaks the Koutecky-Levich relation of equation (2.5). Interestingly, the Koutecky-Levich
relation for the Pt(111) and the Pt$_3$Ni(111) sample$^{[226]}$ also appears to fail at higher potentials than 0.9 V vs. RHE. Moreover, the kinetic volcano limit$^{[81]}$ appears to be superseded in numerous instances in alkaline media suggesting either changes in reaction pathways from the apparent cation-effect or change in the scaling due to entropy induced changes of the intermediate reaction steps.

From evaluation of pure Pt(111) $U_{OH-onset}$ values there is a shift in OH onset potential of ca. 47 mV between KOH and HClO$_4$. Explicitly it seems that OH binds weaker in KOH. Consequently, it seems to counter intuition that higher Cu coverages in KOH will result in better activity relative what have been reported in HClO$_4$$^{[1]}$ as one would expect less weakening of the OH binding to be required. This becomes more curious as there appear to be a coinciding relative shift of ca. 53 mV between the HClO$_4$ and KOH volcano maximums. This indicates that, although OH binding is a descriptor for the activity another factor plays an important role for the ORR activity e.g. the cations in the electrolyte relative to the OH binding. This further suggest that the OH coverage profiles (as a function of applied potential) in KOH and HClO$_4$ are not identical, something figure 3.10 verifies. Hence, by plotting the potential shift of OH adsorption as a function of coverage $\theta_{OH}$ used in the evaluation in equation (2.10) (of the 240 μC/cm$^2$ Pt(111) surface) clear trends can be observed. This has been done for a few NSAs (see figure 3.16).

![Figure 3.16](image-url)

**Figure 3.16:** Relation between the potential necessary to adsorb 1/8, 1/6, 1/4, 1/3 and 1/2 *OH ML from the CVs OH adsorption region. It is clear that the relative shift increase with coverage (and also the uncertainty).
The coverage dependent variation of the shift in OH adsorption potential in figure 3.16 reveals that if the potential dependent OH coverage in KOH is not the same as in HClO$_4$ a shift in the volcano maximum would be expected. This have been exemplified by the re-evaluated Cu/Pt(111) NSA volcano in KOH utilizing different OH coverages as metrics for the OH binding weakening relative to Pt(111) (see figure 3.17).

From the alkaline investigation of the Cu/Pt(111) NSA system the electrolyte influence on ORR can be summarized as $j_{k_{,\text{HClO}_4}} < j_{k_{,\text{NaOH}}} < j_{k_{,\text{KOH}}}$ as expected.$^{[147]}$ Various explanations for the activity changes between acid and alkaline electrolytes have been proposed, perhaps most prominently pH dependence on ORR activity are cited.$^{[129,131,141,143,240]}$ However, though pH certainly can have an effect it does not account for the huge difference in activity on Pt(111) observed when going from NaOH to KOH ($j_{k_{,\text{NaOH}}} = 4.0 \pm 0.7 \text{ mA/cm}^2$ and $j_{k_{,\text{KOH}}} = 7.8 \pm 0.8 \text{ mA/cm}^2$).

Extensive studies on Au($hkl$) surfaces by other groups$^{[210,225,226]}$ have revealed that Au(100) exhibits slightly elevated ORR activity in 0.1 M KOH compared to Pt(111). However, Au(100) has been seen (below 0.7 V vs. RHE) to strongly favor the $2e^{-}$-pathway, forming peroxide over water and thus suggesting a different ORR mechanism than for the case of Pt(111). Surface stabilization of ”water-complexes” (HO*···H$_2$O*) by MOH (where M here is an alkali metal) has been proposed$^{[226]}$ to account for this new ORR mechanism. In this mechanism, water is placed in a surface configuration allowing super(hydroxide)oxide (O$_2$ and HO$_2$) intermediates to form, which may provide favorable
ORR kinetics as the effects from "oxygen" site blockage (self-poisoning) of the electrodes are minimized. The scheme proposed\(^{[226]}\) do not take into account effects from the surface binding of oxygen intermediates. However, from the work presented here and proposed by others,\(^{[210]}\) it is evident that OH binding, besides the water-complex stabilization and resulting OH destabilization, would indeed affect the ORR. Competing explanations for the Au(100) and Pt(111) activities in alkaline media, other than that of the water-complex stabilization\(^{[226]}\) exist and although aspects of this model certainly seem plausible, it does also raise some critical questions. For example, the effect of the cation. The water-complex stabilization model\(^{[226]}\) seems very dependent on cation stabilization on the electrode surface. To test this effect dosing experiments of KOH into a three-electrode cell with a Pt(111) electrode in HClO\(_4\) were attempted (results not presented). However, these experiments were abandoned as the only observation made was a gradual poisoning of the Pt(111) surface, likely from KCl precipitation.\(^{[112]}\) This in-ferred from equivalent experiments with KCl (Merck, Suprapur\textsuperscript{®}, 99.999 %) that yielded similar poisoning. Ideally, KClO\(_4\) should have been used.\(^{[101, 241]}\) Further discussion of the water-complex stabilization model\(^{[226]}\) also opens up the question of the cation type. Alkali metal of increased covalent-radii and electronegativity are known to result in increased Pt(111) activity,\(^{[68]}\) although whether covalent-radii and/or electronegativity have any influence on the activity is unknown.

From the results of this work and others the following is evident for ORR electrocatalysis in alkaline media:

1. Macroscopic pH insufficiently account for the significant ORR activity enhancement of the Pt(111) NSAs in alkaline media though pH is not without some effect.\(^{[242, 243]}\)
2. Non-covalent interactions between the alkali metal cations and the electrode surface are fundamental when attempting to explain the enhanced ORR activity in alkaline compared as to that observed in acid.
3. The relative weakening of OH binding through \(\theta_{\text{Cu}}\) for the Cu/Pt(111) surfaces proves, that OH binding is a valid activity descriptor in alkaline electrolyte, although it is not a sole descriptor.

As indicated from the above, when optimizing catalysts to operate in alkaline media a descriptor model including both OH binding and non-covalent interaction from the cation with the surface is required and it is in part this convolution which has confounded the field.

Working models have been proposed\(^{[226]}\) to account for the cation effects. However, one could just as easily propose a model that only relies on static field considerations from cation induced entropy changes in the double-layer. Such a model may even take into account morphology considerations, as it would rely on the relative entropy changes of adsorbed OH in the presence of a cation. Experimental work by the group of Feliu and coworkers\(^{[241]}\) suggests water orientation on Pt(111) is strongly dependent on the presence of KClO\(_4\), which modulates the free charge density, \textit{i.e.} surface order and thus entropy is most definitely affected by cations. Interestingly this study\(^{[241]}\) cites pH influence on the
free charge density of Pt(111) as the governing factor, although no direct link to ORR is presented. Although it has certainly been ascertained that pH is not the dominant factor for Pt(111) (or Au(100)) ORR activities in alkaline media, the exact effect is still widely discussed.\cite{131,140,141}

As a final side note, it should be mentioned that though impressive ORR activities have been observed for the Cu/Pt(111) NSA system, it exhibits poor HOR activity in KOH, exemplified in figure 3.18 by a Pt(111) measurement.

![Figure 3.18: RDE CVs in H₂-saturated electrolyte at 23°C, 1600 rpm, 50 mV/s of Pt(111) and a Cu/Pt(111) NSA in 0.1 M KOH and HClO₄.](image)

From extensive HOR/HER measurements (used to determine RHE) on the Cu/Pt(111) system, it were found that the half-wave HOR potential were virtually non-existent in acid for pure Pt(111) and Cu/Pt(111). However, in alkaline Pt(111) HOR half-wave potentials attained values of $U_{HOR,\text{half-wave}} = 214 \pm 32\text{mV}$, interestingly once any Cu were alloyed into the 2nd atomic layer the HOR half-wave potential stabilized to $U_{HOR,\text{half-wave}} = 146 \pm 22\text{mV}$, i.e. roughly 3/4 of pure Pt(111). This minor effect may be due to slight surface rearrangement from annealing instead of the actual NSA formation. From an application point of view the added HOR overpotential for Pt based alloys in KOH is not important, as other (more abundant) usable HOR catalyst materials exist, e.g. for us in AFCs.
3.4 Conclusion

In the preceding electrochemical investigation the Cu/Pt(111) NSA system has been used to elucidate the apparent synergistic effect of cations and OH bindings. Following earlier reports \[1,151,154\] Cu/Pt(111) NSA formation and characterization were executed. In that context a procedure for electrochemically verifying expected Cu/Pt(111) NSAs had formed with respect to $\theta_{\text{Cu}}$ was established. This verification relied heavily on HClO$_4$ CVs and that transferring the electrodes between acid and alkaline media had no observable effect on CV features or ORR activity. Moreover, AR-XPS techniques were also employed verifying expected NSA formation.

Stability issues pertained to measuring Cu/Pt(111) and Pt(111); in KOH due to irreversible adsorption of metal-oxides and in acid due to the dissolution.\[154\]

The cation effects on model Pt(111) extended surfaces and the substantial increase in ORR activity from measuring in KOH relative to HClO$_4$ have been reported in terms of the specific activity at 0.9 V vs. RHE. Specific activities for Pt(111) in KOH of $7.8 \pm 0.8$ mA/cm$^2$ was found relative to $1.7 \pm 0.1$ mA/cm$^2$\[157\] in HClO$_4$. This corresponds to a roughly 4.5-fold improvement in Pt(111) activity between KOH and HClO$_4$ and a 2.3-fold enhancement in NaOH relative to HClO$_4$ ($4.0 \pm 0.78$ mA/cm$^2$ in NaOH).

Using the Cu/Pt(111) NSA system it was seen that, just as in the HClO$_4$ electrolyte,\[1\] it was possible to tune the OH binding in KOH electrolyte by the initial Cu deposition amounts. Hence, a clear Cu coverage dependence $\theta_{\text{Cu}}$ to the OH potential shift could be observed, although a slight variation to that reported earlier was noted (figure 3.11). The influence of the Cu near-surface alloying was seen to coincide well with the relative ORR activity enhancement at 0.9 V vs. RHE in acid reported earlier.\[1\] Indicating similar OH binding dependence (figure 3.13). Which could be verified from figure 3.15. The relative activity enhancement was seen to scale with the OH potential shifts of Cu/Pt(111) NSAs in a volcano-like fashion equivalently proving that OH binding is a valid descriptor in alkaline media, as it has observed to be in acid.

The Cu/Pt(111) NSA system in 0.1 M KOH was shown to exhibit a maximum activity of $100.7 \pm 7.5$ mA/cm$^2$ at $\theta_{\text{Cu}} \approx 0.77$ ML corresponding to a ca. 13-fold improvement over Pt(111) in KOH and a 58-fold improvement for Pt(111) in HClO$_4$. From the exceptionally high activity and the corresponding base CVs it can be deduced that OH binding is a descriptor for ORR activity in alkaline. According to figure 3.15 and consequent analysis of the OH coverage dependence $\theta_{\text{OH}}$, it appears that the saturation coverage dependence relative to OH onset differed between acid and alkaline media, although no quantification of this effect was attempted.

Besides OH binding is an universal descriptor for ORR activity in both acid and alkaline media it was found that some (as of yet unknown) descriptor governing the effect of the cation are needed to successfully account for the apparent synergistic effects on the ORR actives. Literature\[226,241\] has suggested both water-complex stabilization by cations, slight activity modulation by pH and entropy driven static field models, but at present the true nature of the cation effect on electrocatalysis remains elusive.
Electrolyte Effects on Pt-Part II: Anions

In this chapter the ability of ligand effects to tune the binding of adsorbates on single crystal Pt(111) has been investigated and discussed. In order to achieve this the Cu/Pt(111) NSA system, discussed extensively in chapter 3 and elsewhere,\textsuperscript{[1,151–156]} has been utilized to gain insight into the immediate effect of anion poisoning of Pt based catalysts. Ionomer and anion adsorbates on ORR catalyst and their influence on performance have been extensively investigated in literature when dealing with both Nafion\textsuperscript{®} and PBI based PEMFCs\textsuperscript{[125,126,135]} as discussed in section 1.3. Adsorption and site blocking from proton conducting acid groups from the membrane electrolyte both SO$_4^{2–}$ or PO$_4^{3–}$ from Nafion\textsuperscript{®} and PBI respectively, lowers PEMFC efficiencies.\textsuperscript{[147]}

This work focuses on the effect phosphate has on the ORR performance of Pt based catalysts. This has been done by electrochemical investigation of extended surfaces. From a fundamental point of view temperature and anion concentration (and pH) are important parameters, when trying to understand the mechanism of (phosphate) anions, as kinetics would be expected to change depending on the effects from adsorption coverage of non ORR intermediate species in the catalyst interface. Moreover, as oxygen binding is expected to scale directly with oxygen containing anion intermediates, such as SO$_4^{2–}$ and PO$_4^{3–}$, the influence of ligand effects tuning the adsorption have been investigated. This has been done by: 1) Studying the fundamental issues that arise when adding known ORR poisons to well-ordered Pt surfaces. 2) Investigation of Pt surface modification using Hg. 3) Studying the effect of phosphate when tuning the OH binding using Cu/Pt(111) NSAs.\textsuperscript{[1]}
4.1 Anion Poisoning on Pure Pt

Phosphate (and sulphate) adsorption on Pt electrodes has been extensively studied with varying conclusions by others.\cite{68, 125, 135} The effect of the lowered ORR activity is however generally attributed to the strong adsorption of anions such as phosphate and the consequent blocking of available sites for O\textsubscript{2} dissociation. Figure 4.1 illustrates a Pt(111) surface with and without anion adsorbates in the interface.

![Illustrations of Pt electrolyte interface during 4e\textsuperscript{-} ORR. a Without phosphate. b With phosphate. Hydrogen, platinum, oxygen and phosphor atoms have been color-coded white, gray, red and purple, respectively. Courtesy Prof. Jakob Kibsgaard.](image)

From figure 4.1 one may conceive that the following effects influence the ORR activity of the surface independently or through combinatorial effects:

1. The oxygen reduction reaction is impeded since phosphoric acid anions adsorb strongly to the platinum catalyst surface and act as poisons.\cite{125, 132, 135}
2. Anion adsorbates may decrease the solubility and diffusivity of oxygen species in the double-layer region of the catalyst\cite{134, 136} and solubility of O\textsubscript{2} in H\textsubscript{3}PO\textsubscript{4} electrolytes is lower than in HClO\textsubscript{4},\cite{132, 175} both interpretations will introduce increased mass-transport limitations.
3. Interface modification through adsorbates may also alter the contact resistance of the catalyst-electrolyte interface, thus lowering the overall efficiency.\cite{170, 244}
4. Interface sensitivity to spectator species may be different in the presence of strong adsorbates. Such spectator species may additionally block active sites and/or influence the double-layer kinetics.\cite{68, 130}
5. Anions may affect the local pH at the interface.\cite{241}
Investigation of the effect of phosphate has been elucidated using standard RDE techniques, presented in section 2.1, on well-ordered extended surfaces.

4.1.1 Phosphate Poisoning on Polycrystalline Platinum

To assess the fundamental effect(s) of phosphate on Pt based catalysts polycrystalline Pt samples (Mateck, 99.999%, h×Ø = 4 × 5 mm), were prepared by the usual method\textsuperscript{[144]} of flame-annealing and Ar cooling and mounting in a RDE setup containing 0.1 M HClO$_4$, see chapter 2.

Experiments concerning the effect of the series resistance and the RHE evaluation, when the electrolyte were dosed with low level amounts of (otho-)phosphoric acid (Merck, Suprapur\textsuperscript{®}, 85%) were then conducted at room-temperature using the cell presented in figure 2.1. Figure 4.2 exemplifies the results of such an experiment, in which a Pt$_{\text{Poly}}$ sample had an initial CV obtained prior ORR, EIS and HOR/HER evaluation. Consequently, the sample was removed from the cell and a 10 μL droplet of 1.0 M H$_3$PO$_4$ was placed on the crystal and rinsed off with Millipore water before being re-immersed under potential control into the electrolyte and ORR, EIS and HER/HOR evaluation was repeated. Following this the a total concentration $c_{H_3PO_4}$ of approximately 10 mM H$_3$PO$_4$ was added to the HClO$_4$ electrolyte and ORR, EIS and HER/HOR evaluation was re-obtained again. Figure 4.2 summarizes the electrochemical impedance and HOR/HER results for this Pt$_{\text{Poly}}$ sample.

\textbf{Figure 4.2:} Electrochemical data at 23°C of Pt$_{\text{Poly}}$ samples in 0.1 M HClO$_4$ electrolyte in following conditions: Pristine (blue), surface subjected to H$_3$PO$_4$ and rinsed (red), and after 10 mM H$_3$PO$_4$ was added to the electrolyte (black). \textit{a} Nyquist plot of impedance. \textit{b} CVs in H$_2$-saturated electrolyte at 50 mV/s and 1600 rpm with insert of diffusion limited HOR current divided with average cathodic and anodic sweep current.
From figure 4.2a it is evident that the limited phosphate ($\leq 10$ mM) poisoning has very little effect on the systems’ series resistance. Although it appears that removing the electrode from the electrolyte and re-immersing it, may have caused some micro-bubbles to form increasing the contact resistance slightly. However, while adding additional $\text{H}_3\text{PO}_4$ to the electrolyte it became clear that any phosphate effect on the Ohmic-drop compensation can be disregarded at these low concentrations. Nor does the HOR/HER equilibrium potential changes substantially when adding phosphate, i.e. RHE remains more or less constant as $\delta \Delta U_{\text{RHE}} \approx 1.2$ mV for the three instances shown in figure 4.2b.

From figure 4.2b it is evident that $\text{H}_3\text{PO}_4$ poisoning has an slight impact on the HOR as well as a substantial influence in the ORR region. The latter is apparent from the $j/j_{\text{diff}} - 1$ insert, here $j_{\text{diff}}$ designates the diffusion limited HOR current density and $j$ the average cathodic and anodic current density. Hence, the drop in $j/j_{\text{diff}} - 1$ in figure 4.2b indicates that the ORR onset potential is lowered, i.e. oxygen (co-)adsorption begins earlier than for pristine PtPoly in $\text{HClO}_4$. Since it is known [81] that PtPoly binds OH too strongly, the now even higher ORR overpotential indicates a decrease of ORR activity, which is verified in figure 4.3 summarizing the gathered electrochemical ORR data.

![Figure 4.3](image)

**Figure 4.3:** RDE data of a PtPoly sample in $\text{O}_2$-saturated 0.1 M $\text{HClO}_4$ electrolyte (23°C, 50 mV/s and 1600 rpm) in following conditions: Pristine (blue), surface subjected to $\text{H}_3\text{PO}_4$ and rinsed (red) and after 10 mM $\text{H}_3\text{PO}_4$ had been added (black).  
\(a\) Anodic sweeps.  
\(b\) Tafel plots.

From the phosphate induced decrease of the ORR activity in figure 4.3a it is noticed that $\text{H}_3\text{PO}_4$ poisoning is an extremely surface sensitive phenomenon, as specific activity at 0.9 V vs. RHE drops from 2.0 mA/cm² (in agreement with earlier reported values [171]) to 0.7 mA/cm² after the surface has been treated with phosphoric acid and rinsed, i.e. virtually no $\text{H}_3\text{PO}_4$ concentration is present in the electrolyte. It is also noted that although the Pt sample is very sensitive to the initial surface dosage of $\text{H}_3\text{PO}_4$ it is still possible to decrease the activity even further by adding $\text{H}_3\text{PO}_4$ to the electrolyte as also
seen in figure 4.3. This may be due to the fact that steady state phosphate adsorption conditions\cite{132, 134} have not occurred for the electrode that were only surface treated with H$_3$PO$_4$. The specific activity is observed to drop to 0.3 mA/cm$^2$ in 0.1 M HClO$_4$ electrolyte containing 10 mM H$_3$PO$_4$. From the anodic sweeps in figure 4.3a a decrease in the diffusion limited current magnitude is observed, *i.e.* mass-transport limitations are likely affected by both the surface adsorption of H$_3$PO$_4$, but also by the H$_3$PO$_4$ concentration in the double-layer, in accordance with literature.\cite{136, 175}

From the results of figure 4.3a\textsuperscript{1} a framework for conducting H$_3$PO$_4$ poisoning experiments were established. In this framework re-evaluation of Δ$U_{ref.-RHE}$ and $R_{sol}$ after poisoning with low amounts (< 10 mM) H$_3$PO$_4$ could be omitted with reasonable accuracy. Having established this, the effects of temperature were investigated for PtPoly.

From equation (1.17) it is clear that temperature will have a profound effect on adsorption.\cite{67, 245, 246} Moreover, both adsorption coverage and desorption rates, O$_2$-solubility and diffusion rates are expected to be dependent on temperature. Hence, a simple experiment on a PtPoly sample was conducted for which EIS, ORR and HOR/HER evaluations were undertaken at 20, 40, 60 and 80°C. Once at 80°C the 0.1 M HClO$_4$ electrolyte was dosed with a total concentration of 4 mM H$_3$PO$_4$, before the the electrochemical procedure was repeated in reverse order at 80, 60, 40 and 20°C (see figure 4.4 and 4.5). An initial and final base CV in N$_2$- and Ar-saturated electrolyte and a CO-strip was also obtained. The base CVs and CO-strip can be seen in figure 4.4.

![Figure 4.4](image_url)

**Figure 4.4:** RDE data of PtPoly sample at 20°C in 0.1 M HClO$_4$ electrolyte (blue) and with 4 mM H$_3$PO$_4$ (black) added. *a* Initial and final base CVs in Ar-saturated electrolyte at 400 rpm and 50 mV/s. Effect of H$_3$PO$_4$ has been sketched. *b* Initial and final CO-strips taken at 200 rpm and 10 mV/s.

\textsuperscript{1}And others not presented here.
The base CV and CO-strip data for PtPoly before and after phosphate poisoning reveals little in terms of the effect of phosphate poisoning (figure 4.4). Albeit, it appears that CO oxidation on extended surfaces are severely influenced by either contaminants from the rather prolonged electrochemical experiment or the phosphate, as charge areas of 327.9 μC/cm² and 448.7 μC/cm² have been estimated for the same sample before and after introduction of H₃PO₄ and at elevated temperatures (figures 4.4a and b). The initial CO charge area of 327.7 μC/cm² is comparable to earlier established values for polycrystalline Pt of 349 ± 9 μC/cm².[171] Moreover, the base CV in figure 4.4a reveals general trends from adding low levels H₃PO₄ to the electrolyte, such as the general suppression of the H UPD region. Most noticeably the features at 0.12V vs. RHE associated with (110)-steps[247] are seen to diminish. Similarly the (100)-steps[247] peak position is observed to shift to lower potentials. The (110) and (100)-peak magnitudes were generally both observed to diminish and although instances did occur where the (100) was seen to elevate slightly. This discrepancy in the H₃PO₄ effect on the (100)-step peak magnitude likely reflects small variations when preparing the PtPoly sample, but according to Chen and co-workers[125] this behavior is not unexpected and the general decrease of the hydrogen adsorption onset potential is clearly observed. Figure 4.4a also reveals a noticeable suppression in the oxygen adsorption region as expected,[125] as well as a slight reversible feature in the double-layer region (0.45 to 0.6 V vs. RHE), which likely corresponds to phosphate desorption and adsorption.

The ORR results of the PtPoly samples when subjected to heating and H₃PO₄ have been summarized in figure 4.5.

**Figure 4.5:** RDE data of PtPoly at in 0.1 M HClO₄ electrolyte (full lines) and with 4 mM H₃PO₄ (dashed lines) at various temperatures. **a** Anodic sweeps taken at 1600 rpm with 50 mV/s in O₂-saturated electrolyte. **b** Tafel plots of the **a** data.

The ORR data in figure 4.5a fits very well with reports by others.[248,249] Meaning, that
the increased temperature may initially improve the kinetics, e.g. up to 60°C, which is in agreement with the results by Markovic and co-workers, but at higher temperatures, such as 80°C, there is a clear decrease in activity. The most likely reason for this surprising drop in activity at 80°C concerns contaminants from the glassware may desorb at these temperatures. Moreover, mixing through the electrolyte interface and solubility of contaminants are also likely increased when elevating the temperature sufficiently. Interestingly it appears that some of the lost activity at 80°C is relatively preserved after H₃PO₄ poisoning, indicating that higher temperature ORR kinetics are improved, but that such beneficiary effects may be hidden in RDE experiments due to adverse effects from increased electrolyte contamination. *Koutecky-Levich* plots of the same PtPoly sample as in figure 4.4 and 4.6 at 20°C both before and after the H₃PO₄ poisoning can be seen in figure 4.6.

**Figure 4.6:** RDE data at 20°C of PtPoly in O₂-saturated 0.1 M HClO₄ at 400, 900, 1600, and 2500 rpm at 50 mV/s. a Anodic sweeps without (blue) and with 4 mM H₃PO₄ (black). b Koutecky-Levich analysis in clean electrolyte. c Koutecky-Levich analysis in electrolyte with H₃PO₄.
Figure 4.6 indicates that the electron transfer number, which has been calculated as an average of every 0.05 V potential step from 0.3 to 0.8 V vs. RHE, is independent of the introduction of H$_3$PO$_4$ as a value in both instances of $\bar{n}_e \approx 3.8$ have been found. The electron transfer number has been calculated using the values by Y"in et al.$^{[174]}$ for aqueous 0.1 M HClO$_4$ at 23°C. In context to the Pt$_{Poly}$ experiments relevant electrochemical reference parameters have been obtained throughout this thesis work, these have been included in table 4.1.

| Table 4.1: Electrochemical parameters for Pt$_{Poly}$ gathered in 0.1 M HClO$_4$ at 23°C from 34 distinct measurements. *At 0.9 V vs. RHE. |
|-----------------|-----------------|
| Parameter       | Value           |
| $\sigma_{PtPoly}$ | 341.0 ± 15.6 μC/cm$^2$ |
| $\sigma_{PtPoly}$ | 190.1 ± 10.4 μC/cm$^2$ |
| $j_k(0.9 V)$     | 1.96 ± 0.25 mA/cm$^2$ |
| $\beta$         | 65.8 ± 4.1 mV/dec. |
| $U_{onset}$      | 869 ± 5 mV       |
| $U_{half-wave}$  | 864 ± 4 mV       |

Figure 4.5 and similar studies revealed that ORR kinetics, seen both through the Tafel slopes and half-wave potentials, change drastically when subjected to heating and poisoning. Interestingly the ORR onset potentials was to a wide degree seen to be independent of temperature and anions as no clear effect was on this parameter during these experiments. From the preceding experiments on Pt$_{Poly}$, and the results presented in figures 4.2 to 4.6 the following framework for investigating the propensity of Pt based surfaces towards phosphate poisoning have been established:

- Prolonged temperatures and/or prolonged electrochemical testing may mask catalyst sensitivity to the effect of H$_3$PO$_4$ anions on Pt catalyst surfaces.
- Pt ORR selectivity towards the 4e$^-$ pathway seems to be independent of phosphate anion adsorption.
- Pt ORR kinetics are influenced severely both from initial irreversible phosphate adsorption and by the concentration of H$_3$PO$_4$ in the catalyst double-layer.
- Using CO charge areas to evaluate catalyst area in instances with strongly varying H$_3$PO$_4$ concentration is indicated to introduce severe errors.
- RHE potential and series resistance $R_{sol}$ evaluation in 0.1 M HClO$_4$ electrolyte appear independent to low ($\leq$ 10 mM) H$_3$PO$_4$ contamination levels.

Following what has been learned a more in-depth analysis of the effect of H$_3$PO$_4$ poisoning on Pt$_{Poly}$ was undertaken.
To accommodate the observance of the effect of phosphate on the ORR, low concentration H$_3$PO$_4$ poisoning experiments were conducted. For all these studies RHE equilibrium
potential and $R_{sol}$ determination were conducted prior to any H$_3$PO$_4$ dosage. The studies were conducted on flame-annealed polycrystalline Pt, but only at room-temperature (23°C) to maintain that any effects observed as changes in ORR activity could only be attributed to phosphate and not other sources of contamination. Figure 4.7 shows an example of phosphates effect on the ORR.

![Graph a](image1)

**Figure 4.7:** RDE data at 23°C of a PtPoly sample in O$_2$-saturated 0.1 M HClO$_4$ electrolyte that has had increasing amounts of H$_3$PO$_4$ added (color-coded) taken at 1600 rpm at 50 mV/s. **a** Anodic sweeps. **b** Tafel plot of the kinetic current density.
Figure 4.7 gives a good overview of the detrimental effects\textsuperscript{[125,127,134,193]} that phosphate has on Pt. Multiple poisoning experiments were undertaken using three different Pt\textsubscript{Poly} crystals. The results from these studies have been summarized in figure 4.8.

![Graphs](image)

**Figure 4.8:** Electrochemical parameters and fits (blue lines) of Pt\textsubscript{Poly} samples measured in O\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} (23 °C, 1600 rpm and 50 mV/s). All parameters have been plotted as function of the relevant H\textsubscript{3}PO\textsubscript{4} concentration.  

- **a** Double-logarithmic plot of the specific activity at 0.9 V vs. RHE.  
- **b** Tafel slope at 0.9 V vs. RHE with logarithmic 1st axis.  
- **c** ORR onset potential.  
- **d** Half-wave potential of the ORR reaction with logarithmic 1st axis.

From the ORR specific activity data in figure 4.8a it is evident (\textit{e.g.} from the fits) that something changes fundamentally with the activity at the surface whenever trace amounts of H\textsubscript{3}PO\textsubscript{4} are present. The effect of the H\textsubscript{3}PO\textsubscript{4} after initial poisoning is also shown, in-
indicating that $\text{H}_3\text{PO}_4$ poisoning is a two component effect: 1) Initial blockage of surface sites from irreversible and steady-state anion adsorption. 2) Oxygen solubility lowering and thus mass-transport limitations on activity. The initial effect of phosphate is also observed in the Tafel slopes (see figure 4.8b). In which an increase from $\sim 65 \text{mV/dec.}$ to $85 \text{mV/dec.}$ is observed for even the slightest concentrations of phosphoric acid, in agreement with literature observations.$^{[134, 193, 245]}$ Thus, from figure 4.8a and b it is evident that $\text{H}_3\text{PO}_4$ has an immediate and irreversible effect on the kinetics of the ORR reactions, which have been attempted quantified from both the $U_{\text{onset}}$ and $U_{\text{half-wave}}$ potentials, as seen in figure 4.8c and d, respectively. From figure 4.8d it is clear that the half-wave potential follows the expected trend, albeit with a more gradual influence from the immediate poisoning. However, from figure 4.8c it is also evident that, as the method of identifying the ORR onset is very dependent on the transport limitations, this method (explained in figure 2.11) is of limited use.

From the ORR data in figure 4.8 some variance are observed e.g. in specific activities $\text{etc.}$ Possible reasons for this may be the uncertainties built into the experimental approach. For example, initially a known amount of $\text{HClO}_4$ electrolyte were poured into the three-electrode cell and it was assumed that this volume would be constant throughout the experiment. However, even at $23^\circ\text{C}$ a substantial amount of electrolyte is transported from the cell by gas bubbling. Furthermore, utilizing a graduated beaker for the initial volume determination may increase the chances of introducing contaminants into the cell. Based on these experiences it was decided that electrolyte amounts would be measured after the electrochemical measurements had proceeded.

The method of dosing the electrolyte was also investigated, in which a pipette (Alpha Laboratories Ltd.) were utilized. The pipette tips cleanliness were verified by adding $0.1\text{M HClO}_4$ by pipette to an already running three-electrode cell with a Pt$_{\text{Poly}}$ crystal revealing no changes in ORR activity or CVs. The main source for uncertainties from the $\text{H}_3\text{PO}_4$ dosing experiments was thus thought to concern cleanliness, crystal mounting errors and the success of the Pt$_{\text{Poly}}$ flame-annealing procedures.

From the experiments on bulk polycrystalline Pt samples insight into the effects of phosphates on ORR on extended Pt surfaces have been established and some fundamental observations concerning poisoning phenomena of the ORR have been derived.

### 4.1.2 Phosphate Poisoning on Pt(111)

Following the experiences for polycrystalline Pt and the surface’s propensity towards severe poisoning by phosphate, studies of single-crystalline platinum were conducted as Pt(111) as a model systems gives a vast range of possibilities in terms of surface modification techniques and its behavior has been well reported.$^{[68, 125]}$ Using the preparation techniques of section 2.3 the electrochemical data seen in table 4.2 was collected for flame-annealed Pt(111) in 0.1 M $\text{HClO}_4$. 


Table 4.2: Electrochemical parameters for Pt(111) in 0.1 M HClO$_4$ and 23°C from 7 distinct measurements. *At 0.9 V vs. RHE.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{Pt(111)} \text{CO}}$</td>
<td>$332.8 \pm 10.2 \mu\text{C/cm}^2$</td>
</tr>
<tr>
<td>$\sigma_{\text{Pt(111) H UPD}}$</td>
<td>$176.1 \pm 12.7 \mu\text{C/cm}^2$</td>
</tr>
<tr>
<td>$j_k^*$</td>
<td>$2.0 \pm 0.25 \text{mA/cm}^2$</td>
</tr>
<tr>
<td>$\beta^*$</td>
<td>$61.9 \pm 1.7 \text{mV/dec.}$</td>
</tr>
<tr>
<td>$U_{\text{onset}}$</td>
<td>$948 \pm 1 \text{mV}$</td>
</tr>
<tr>
<td>$U_{\text{half-wave}}$</td>
<td>$873 \pm 6 \text{mV}$</td>
</tr>
</tbody>
</table>

From table 4.2 the specific current density at 0.9 V vs. RHE is slightly higher than the earlier reported 1.73 mA/cm$^2$[157]. Moreover, lower values of $\sim 1.6$ mA/cm$^2$[1,93] are often encountered in literature. This discrepancy is likely due to whether Ohmic-drop compensation has been utilized or not in the studies. According to table 4.2 one also notices that surface charge densities evaluated from CO oxidation and from the H UPD area are both roughly 5% smaller than for polycrystalline Pt, which is surprising in the case of the CO charge. $\sigma_{\text{Ptpoly}}$ and $\sigma_{\text{Pt poly CO}}$ are often in literature$^{[168,171,181,192]}$ expected to be 190 $\mu\text{C/cm}^2$ and 340 $\mu\text{C/cm}^2$, respectively, while for Pt(111) $\sigma_{\text{Pt(111) H UPD}}$ and $\sigma_{\text{Pt(111) CO}}$ were expected$^{[146,192]}$ to be on the order of 157 $\mu\text{C/cm}^2$ and $\sim 489$ $\mu\text{C/cm}^2$, respectively. The differences in CO charges are not readily explainable but a provisional explanation can be given by considering hydrogen co-desorption when evaluating CO charge as discussed by others.$^{[146,192]}

Phosphate Poisoning on Pt(111)

Similarly to the polycrystalline Pt, a range of experiments investigated the Pt(111) phosphate sensitivity. Using the established lessons from Pt$\text{Poly}$, samples of Pt(111) were prepared, electrochemically tested and dosed with varying amounts of H$_3$PO$_4$. As most of the changes from H$_3$PO$_4$ on Pt$\text{Poly}$ were observed at low concentrations ($< 2$ mM) lower dosing were utilized for Pt(111) (see figure 4.9).

**Figure 4.9:** RDE data of Pt(111) in 0.1 M HClO$_4$ (23°C, 50 mV/s). a Base CVs in N$_2$-saturated electrolyte at 400 rpm without (blue) and with 0.98 mM H$_3$PO$_4$ added (black). b Tafel plots and anodic sweeps in O$_2$-saturated electrolyte at 1600 rpm where H$_3$PO$_4$ have been dosed.
Figure 4.9 reveals similar trends for Pt(111) activity as seen for PtPoly when poisoning electrolyte with H₃PO₄. However, the influence on the base CV when adding H₃PO₄ is fundamentally different as seen in figure 4.9a wherein “little” change is seen in the HUPD region, likely as a result of the features from (110) and (100)-steps are missing. A broad emerging and quite domineering feature in the Pt(111) double-layer region is clearly observed when adding H₃PO₄ to the electrolyte, while the oxygen adsorption region has completely been suppressed (see figure 4.9a).

A range of poisoning experiments on Pt(111) electrodes were conducted and the results summarized in figure 4.10 and 4.11. Due to the lower poisoning doses better insight, into the transition from a non-poisoned Pt(111) surface to one suffering from severe H₃PO₄ poisoning, could be established. Again no insight was gained from the ORR onset potential, which for both poisoned and non-poisoned cases attained average values of 943 ± 3 mV.

Exponential decrease in half-wave potential as a function of poisoning is clearly observed from figure 4.10a, indicating that there is decreased mass-transport from the Pt(111) surface, thus showing an increase in the ORR overpotential.

Moreover, the fundamental kinetics of the ORR reaction also changes as Tafel slopes are seen to change from ~ 61 mV/dec. to ~ 90 mV/dec. which is in agreement other reports, [193] suggesting highly concentrated phosphoric acid 15.2 M should exhibit slopes of 117 mV/dec. (85 % H₃PO₄ at 25°C). In the case of the Tafel slope an exponential relationship to phosphate concentration was also found. Furthermore, by plotting the specific kinetic current density at 0.9 V vs. RHE as a function of the H₃PO₄ a polynomial relationship was uncovered (see figure 4.11).
Figure 4.11: Double-logarithmic plot of the specific activities of Pt(111) with fit (blue line) at 0.9 V vs. RHE as function of H$_3$PO$_4$ concentration in O$_2$-saturated 0.1 M HClO$_4$ at 1600 rpm, 50 mV/s and 23°C.

Figure 4.11 shows the severe effect of H$_3$PO$_4$ poisoning revealing a clear trend in ORR activity drop after the initial poisoning, thus indicating a mechanistic framework for describing Pt based catalyst sensitivity towards low level poisoning.

Chlorate Poisoning on Pt(111)

From a purely experimental point of view it should be noted that in real PEMFC systems poisoning from phosphates and sulphates only represents a sub-set of anions which may disrupt the activity. Issues with salts from the halides may also prove problematic. A good example of this is chloride, which similarly to the case of H$_3$PO$_4$, severely decreases the ORR activity. An example of the effect of KCl (Merck, Suprapur®, 99.999%) poisoning can be seen in figure 4.12.

Figure 4.12a shows a noticeable suppression of the hydrogen adsorption region and complete suppression of the oxygen adsorption region by Cl$. The oxygen suppression is also observable from figure 4.12b, in which the activity decrease is seen to follow the KCl content of the electrolyte, although the poisoning does not follow the same steadily increasing mechanism as seen for phosphoric acid. KCl poisoning seems to be a more delicate effect as seen from the O$_2$-saturated CVs of figure 4.12c.

In figure 4.12c subtle changes in the anodic and the cathodic sweeps are observed when poisoning with KCl, as such the ORR activity seems to increase first followed by a severe retardation. Whether the initial, small increase in activity is a real increase in ORR or reduction of minute Cl$^-$ adsorbate species is unknown. This initial increase also seems to follow the presence of some oxidation, seen as an "bump", in the cathodic sweep.

Data from a very preliminary chloride investigation seen in figure 4.12 has been included.
Figure 4.12: RDE data at 23°C of a Pt(111) sample in 0.1 M HClO₄ taken at 50 mV/s.  

a Base CV in N₂-saturated electrolyte at 400 rpm before and after 0.85 mM KCl had been added to the electrolyte.  

b Tafel plots with anodic sweeps insert in O₂-saturated electrolyte at 1600 rpm, wherein increasing amounts KCl were added.  

c Select CVs corresponding to the insert of b.

for posterity, as ORR efficiency may be impeded by other poisoning effects than just those from the chosen PEM proton carrying phosphoric or sulfuric groups. Hence, solving one ORR poisoning effect for a catalyst may not necessarily account for overall performance issues related to poisoning in a real MEA system, as many adsorption issues may arise. The figure 4.12 data reveals that when fabricating PEMFC stacks the possibilities of salt incorporation should be carefully avoided.
4.2 Anion Tolerance by Available Site Engineering

As indicated in section 1.4.2 it is natural to consider atomic ensemble effects in context to phosphate adsorption. Blocking of Pt sites by cyanide revealed that exceptional tolerance towards phosphate adsorption\cite{68,117,118} could be obtained. Hence, we decided to utilize the knowledge accumulated in our group concerning the Pt-Hg system, as this surface modified alloy should preferentially allow single Pt sites for ORR.\cite{57} Even-though it has been established that Pt-Hg alloys are selective towards peroxide rather than water and thus would generate additional issues in real-life PEMFC applications.

4.2.1 Phosphate Poisoning of the Pt-Hg System

Earlier work in our group\cite{57} was relied upon to investigate whether site engineering using the Pt-Hg system would have any advantageous effects with regard to platinum’s surface sensitivity towards phosphates. Thus, a polycrystalline Pt sample (Mateck, 99.995%), which was flame-annealed in the usual fashion (see section 2.3) was characterized and found to perform electrochemically as expected. This crystal was then submerged in an electrode-position cell with 0.1 M HClO$_4$ solution containing 1.0 mM HgClO$_4$ under OC conditions and swept at 50 mV/s to 0.2 V vs. RHE (−0.52 V vs. Hg|HgSO$_4$) and kept at that potential for 2 minutes before the electrode was allowed to sweep to 0.65 V vs. RHE (−0.07 V vs. Hg|HgSO$_4$) and maintained while the electrode was removed from the electrolyte. The deposition of Hg and subsequent formation of a Pt-Hg surface alloy were investigated in a standard three-electrode RDE setup for base CVs (see figure 4.13). Again there was a special focus on the ORR activity, this were investigated at both 23 and 63°C and compared to pristine PtPoly with and without H$_3$PO$_4$ present. From the ORR results from figure 4.14a and b the notion that Pt-Hg alloying would have any beneficiary effect towards ORR catalysis was completely decimated as a considerable overpotential was generated from alloying with Pt with Hg. Furthermore, it is evident that the Pt-Hg surface alloys seems equally prone to phosphate poisoning. Although unsuccessful in optimizing phosphate resilient Pt-Hg based surfaces, using an "available site approach", the result did push us towards a more mechanistic investigative approach for understanding how to optimize ORR catalysts in terms of phosphate tolerance.

![Figure 4.13: RDE base CVs of Pt-Hg surface alloy in N$_2$-saturated 0.1 M HClO$_4$ (23°C, 50 mV/s and 400 rpm) before (blue) and after 10 mM H$_3$PO$_4$ had been added to the electrolyte (black).]
Figure 4.14: RDE data of PtPoly and Pt-Hg surface alloys in O₂-saturated 0.1 M HClO₄ electrolyte taken at 50 mV/s and at rotations of 1600 rpm. a Anodic sweeps at 23 °C with and without 10 mM H₃PO₄. b Anodic sweeps at 23 °C and 63 °C with and without 10 mM H₃PO₄.

4.3 Anion Tolerance by Electronic Structure Engineering

As discussed in this work and reported in literature[1] (see section 2.3.3 and chapter 3) a flame-annealed Pt(111) crystal can be modified to contain Cu in the 2nd atomic layer as illustrated in figure 4.15. From the results of chapter 3 and earlier reports in our group[1] it has been thoroughly established that the average potential shift in OH binding relative to Pt(111) describes ORR activity in both acid and alkaline media.[183] Considering this OH adsorbate dependency towards activity it is adjacent to consider the effect of phosphate adsorbates when tuning OH adsorption on Cu/Pt(111) NSAs surfaces. However, this was not straight forward as the experiments were time consuming and prone to mishaps, as discussed in chapter 3. Moreover, the stability of Cu/Pt(111) NSAs has been reported to be fairly poor.[1,154] Hence, the experiments were carried out at 23 °C in 0.1 M HClO₄ wherein H₃PO₄ were dosed in various amounts during electrochemical ORR experiments. Concentrations, were calculated by measuring the final electrolyte volume post electrochemical experiments and correlating with the known H₃PO₄ dosages used.

The ORR experiments on non-H₃PO₄ poisoned Cu/Pt(111) surfaces revealed a volcano-like relationship as reported earlier by our group,[1] as seen in figure 4.16.
Figure 4.16: Cu/Pt(111) data from RDE measurements in 0.1 M HClO₄ compared to earlier work,[¹] showing the activity enhancement at 0.9 V vs. RHE relative to pure Pt(111) plotted against shift in OH potentials.

From figure 4.16 both, reasonable agreement between ORR activity and the potential shift associated with 1/6 *OH ML coverage on Pt(111) and similar activity enhancement as a function of initial Cu deposition, was observed as seen in figure 4.17b.

Figure 4.17: Electrochemical Cu/Pt(111) data from measurements in 0.1 M HClO₄ compared to earlier work.[¹] a Initial Cu coverage plotted as function of shift in OH potentials relative to pure Pt(111). b Activity enhancement at 0.9 V vs. RHE for Cu/Pt(111) NSAs plotted as function of initial Cu deposition coverage.
However, there appear to be slight discrepancies between the initial $\theta_{\text{Cu}}$ and the OH potential shift in figure 4.17a, as also observed for the same relationship in figure 3.11 of chapter 3. Note that the measurements in figure 4.16 of the initial specific current density at 0.9 V vs. RHE, represent the initial activity of the Cu/Pt(111) NSAs investigated prior phosphate poisoning.

4.3.1 Phosphate Poisoning on Cu/Pt(111) Near-Surface Alloys

For each fabricated NSA the Cu deposition charge $\theta_{\text{Cu}}$, initial base CVs, EIS and RHE evaluation and ORR measurements were collected (for examples see figure 4.18).

Figure 4.18: Examples of electrochemical data of a Cu/Pt(111)($\theta_{\text{Cu}} \approx 0.92$ ML) NSA at 23°C in 0.1 M HClO$_4$, with varying amounts of H$_3$PO$_4$ added. 

a Hanging meniscus configuration of Cu oxidation peak at 20 mV/s in Ar-saturated 3 mM Cu$^{II}$ electrolyte. 
b RDE base CVs in N$_2$-saturated electrolyte at 400 rpm and 50 mV/s compared to Pt(111). 
c Anodic sweeps in O$_2$-saturated electrolyte at 1600 rpm and 50 mV/s. 
d Tafel plots.
Given the example of figure 4.18 relevant parameters, such as OH potentials shifts, specific activities, *Tafel* slopes and initial Cu deposition coverages could be found and when relevant plotted as a function of the phosphate concentration (see figure 4.19).

![Graph of specific parameters](image)

**Figure 4.19:** Examples of specific parameters derived from figure 4.18 for a Cu/Pt(111)($\theta_{Cu} \approx 0.92$ ML) NSA plotted as a function of phosphate concentration with accompanying fits (blue lines).

- **a.** Double-logarithmic plot of specific activity at 0.9 V vs. RHE.
- **b.** *Tafel* slopes at 0.9 V vs. RHE with logarithmic 1st axis.
- **c.** Half-wave potentials plotted with logarithmic 1st axis.

Figure 4.19 exemplifies relevant trends relative to ORR poisoning from H$_3$PO$_4$, same trends seen from pure Pt$_{Poly}$ and Pt(111) in figures 4.8, 4.10 and 4.11. Both the *Tafel*
slopes and half-wave potentials were found to change as a logarithm to the poisoning levels and quite surprisingly the activity seemed to follow a double-logarithmic trend. For now no deeper meaning will be assigned to the format of the fitted trends of activity, half-wave potential, or the Tafel slopes seen in the representative example of figure 4.19. It should instead be stressed that each measurement for a single Cu/Pt(111) NSA was very time consuming and that there are extensive issues pertaining to the predictive nature of the Cu/Pt(111) system. Interpretation of data from experiment to experiment proved difficult. As a consequence samples of specifically selected Cu coverages were fabricated and electrochemically analyzed through poisoning experiments, thus minimizing the complexity of the data analysis. Moreover, as Cu amounts in the 2nd atomic layer[1,183] (see chapter 3) have been revealed to tune the potential shift of OH adsorption and thus the OH binding which is an universal catalytic descriptor, the formed Cu/Pt(111) alloys were indexed by their OH potential shifts relative to Pt(111). Moreover, parameter fits rather than the actual data points were utilized when comparing the effect of the H₃PO₄ poison. The work by Wang, Markovic and Adzic[126] suggests that the changes observed in the ORR kinetics of Pt(111) in H₂SO₄ compared to HClO₄ are strongly dependent on the site availability which (bi-)sulphates are known to block. It is exceedingly likely that similar considerations is true for phosphates. Moreover, potential governed OH coverage has been seen to yield different responses in the kinetics,[126,250] as also suggested by considering Tempkin[251] adsorption isotherms². From these implications[126] it is straightforward to assume that similar issues will arise when considering the difference of Pt(111) in HClO₄ with and without H₃PO₄. By contemplating the kinetic current from available site considerations the following crude first order approximation of the reduction part of the Butler-Volmer[126,142] equation can be formed in which phosphate blocking has been exemplified by PO₄³⁻ anions

\[ j_k(U) = -j_0 \left[ 1 - \gamma_{OH}\theta_{OH}(U) - \gamma_{PO_4^{3-}}\theta_{PO_4^{3-}}(U) \right]^{\chi} \]
\[ \times \exp \left( \frac{2.303}{\beta} \frac{U - U_0}{\epsilon_{OH}\theta_{OH}(U) + \epsilon_{PO_4^{3-}}\theta_{PO_4^{3-}}(U)} \right) \]  
(4.1)

, where \( j_0 \) is the intrinsic exchange-current density, the pre-exponential term \( (1 - \sum \gamma_i \theta_i(U)) \) denotes site availability, \( \chi \) the sites required for ORR and the exponent \( -\sum \epsilon_i \theta_i(U) \) term is associated with the ORR onset perturbation by coverage. Equation (4.1) gives qualitatively insights into why the Tafel slope follows an logarithmic trend when changing the coverage e.g. from phosphate poisoning. Further, as \( U_{\text{half-wave}} \propto \ln (j_k) \) the logarithmic trend found for the half-wave potential as a function of the now obvious H₃PO₄ induced potential shift makes sense as \( j_k \propto \theta_i \) of equation (4.1). From equation (4.1) the specific activities exemplified with \( j_k \) at 0.9 V vs. RHE were found to follow a polynomial rather than exponential form, hence the straight fitted line on the double-logarithmic plot of the given example in figure 4.18d. Given the pre-exponential coverage dependent term of

²Or other isotherms resulting in coverage dependent adsorption energies
equation (4.1) which is exactly a potential dependent polynomial function \(^{252}\) (raised to the power of \(\chi\)) this is hardly surprising.

A framework for the relevant parameters and the origin for the fits in figure 4.19 on Cu/Pt(111) NSA systems (and for Pt\(_{\text{Poly}}\) and pure Pt(111)) have been qualitatively established. Following this the relevant results for the Cu/Pt(111) NSAs will be presented. Kinetic analysis of selected Cu/Pt(111) alloys were conducted for 14 different samples and the OH potential shifts in clean 0.1 M HClO\(_4\) were used as descriptor for the observed changes in kinetic parameters. Firstly, the specific kinetic current at 0.9 V \(\text{vs.} \) RHE were considered as shown in figure 4.20.

![Figure 4.20: Cu/Pt(111) NSAs specific ORR activities at 0.9 V \(\text{vs.} \) RHE measured at 23 °C at 1600 rpm and at 50 mV/s in O\(_2\)-saturated 0.1 M HClO\(_4\) electrolyte with varying amounts of H\(_3\)PO\(_4\) plotted with double-logarithmic axis.](image)

Figure 4.20 reveals some fundamentally very important points when considering the effects phosphates on the activity. For low levels (<0.25 mM H\(_3\)PO\(_4\)) of phosphate poisoning the inherent best initial activity observed for Cu/Pt(111) samples in pure HClO\(_4\) also corresponds to the samples which exhibited the overall highest activity when subjected to phosphate poisoning.

As established earlier \(^{1,81}\) Pt(111) binds OH approximately 0.1 eV too strongly for ideal ORR, but interestingly from figure 4.20 it seems that tuning ligand effects to OH will also optimize to best ORR performance also in H\(_3\)PO\(_4\). This (unsurprisingly) suggests that
phosphate anion adsorption energies scales with oxygen intermediates. Whether the exact OH adsorption weakening will result in the best phosphate resilience is as of yet unknown, but when fabricating real catalyst for PBI membranes (and likely also Nafion®) it appears that catalyst designers should aim at optimizing the OH binding, i.e. the activity for best ORR performance. This is a huge relief, from an engineering point of view, as catalyst versatility and optimization do not have to be tailored specifically to the anion containing acidic electrolyte in which it will be used.

Besides the specific activity the half-wave potential were also plotted for the Cu/Pt(111) systems in HClO₄ when subjected to phosphate poisoning as shown in figure 4.21.

**Figure 4.21:** Cu/Pt(111) NSAs half-wave potential vs. RHE measured at 23°C at 1600 rpm and at 50 mV/s in O₂-saturated 0.1 M HClO₄ electrolyte with varying amounts of H₃PO₄.

Similarly to the specific activity of figure 4.20 the Cu/Pt(111) half-wave potentials of figure 4.21 revealed what appears to be superior (i.e. lowest overpotentials at half diffusion limited current) for the Cu/Pt(111) surfaces exhibiting shifts in OH potential in the order of 0.1 V. Which incidentally correlates with the ideal potential shift for ORR activity as seen in figure 4.16. This and the results of figure 4.20 suggests that by optimizing the OH binding for ORR of the catalyst resilience to the adverse effects of phosphate poisoning is also optimized.
From the trends in Tafel slopes somewhat curious observations are made for the Cu/Pt(111) system when poisoning the surface/electrolyte with phosphate (as shown in figure 4.22). It seems that for most instances the Cu/Pt(111) attains values in the vicinity of 60 mV/dec. in clean HClO$_4$ electrolyte as predicted$^{[125, 133]}$ for a system with constant mass-transport conditions that follows an one electron rate determining step. From figure 4.22 there are a few instances with only small OH shifts $0.1 \leq \Delta U_{1/6}^{*}$OH ML (pure Pt(111) excluded) where the Tafel slopes maintains these values near $\sim 60$ mV/dec. even during H$_3$PO$_4$ poisoning, indicating limited changes in rate determining mechanisms.$^{[130, 253]}$ Conversely, for instances where $0.1 < \Delta U_{1/6}^{*}$OH ML the Tafel slopes are generally seen to increase during poisoning (see figure 4.22).

![Figure 4.22](image)

*Figure 4.22: Tafel slopes evaluated at 0.9 V vs. RHE for Cu/Pt(111) NSAs measured at 23°C at 1600 rpm and at 50 mV/s in O$_2$-saturated 0.1 M HClO$_4$ electrolyte with varying amounts of H$_3$PO$_4$."

The increase in Tafel slopes for Cu/Pt(111) samples, where $0.1 < \Delta U_{1/6}^{*}$OH ML, the slopes are seen to change from $\sim 60$ mV/dec. up to $\sim 90$ mV/dec. suggesting a strong dependence on the OH adsorbate availability, i.e. the apparent transfer coefficient of the system is clearly dependent on available adsorption sites and further the adsorbate coverage is dependent on OH binding energy. From figure 4.22 one may speculate that the rate deter-
mining step of the Cu/Pt(111) changes dependent on OH binding. Others groups working on Pt(111) and PtSn(111) systems have shown that when poisoning with 100 mM H$_3$PO$_4$ Tafel slopes are seen to vary from 64.4 mV/dec. to 80.6 mV/dec. for the Pt(111) case and from 64.5 mV/dec. to 73.4 mV/dec. for PtSn(111)\cite{125}. These results indicate, as for the Cu/Pt(111) in figure 4.22, that kinetics at the catalyst surface is less affected when OH binding is weakened relative to Pt(111). By considering OH binding as a variable which changes the coverage of both OH and phosphate it was speculated that the Cu induced OH weakening may result in varying rate determining steps\cite{253} on the Cu/Pt(111) at 0.9 V vs. RHE. However, too many assumptions, regarding fixed pH, exceedingly similar OH coverages for the various Cu/Pt(111) NSAs at 0.9 V vs. RHE and identical symmetry factors $\chi$, would have to be made for such analysis to bear any conclusions.

It should be stressed that the results for the various Cu/Pt(111) NSAs were not easily reproduced. These noticeable experimental shortcomings of the Cu/Pt(111) NSAs limit the quantitative predictions one may infer, e.g. from the Tafel slopes and indeed the overall kinetics of the ORR reaction. Rather, the experimental data qualitatively suggest that both OH coverage and OH binding are strongly interrelated entities and complex interactions between adsorption of spectator species,\cite{130} such as phosphate anions, will modulate the ORR kinetics substantial by altering the number of available sites for OH and the OH binding itself. Moreover, variations in mass-transport from temperature\cite{134} and oxygen solubility in the electrolyte are expected to play a role, thus masking some of the more subtle details of the ORR kinetics during anion poisoning. In short, a comprehensive investigation of the kinetics of the exceedingly complex Cu/Pt(111) NSA system in the presence of phosphate has been attempted and revealed that in terms of tuning electronic structures of the catalysts, for PBI (and likely also Nafion®) based PEMFCs, developers should apply catalysts of optimum OH binding as these appear to offer the best performance in terms of both ORR activity and anion resilience.

### 4.3.2 Carbon-Monoxide Poisoning of Cu/Pt(111)

Given earlier work in our group\cite{1,156,171} an incipient study of the CO oxidation of a few Cu/Pt(111) NSAs was conducted. CO oxidation is of profound importance in DMFCs as such devices suffer from issues pertaining to CO poisoning.\cite{33,254–256} CO-stripping experiments conducted on Cu/Pt(111) NSAs\cite{257} indicates that CO adsorption on Cu/Pt(111) is decreased compared to Pt(111) and thus perhaps performed better in terms of CO resilience. It was thus attractive to probe Cu/Pt(111) NSAs CO tolerance. This was done using a fixed procedure\cite{171,258,259} that was set to mimic methanol poisoning of the cathode.\cite{254} The procedure relied on chronoamperometric measurements at 0.1 V vs. RHE in a system with optimized kinetics, i.e. subjected to minimal transport limitations. This was done by RDE measurements rotating at 2500 rpm in a 60 °C heated clean three-electrode cell containing HClO$_4$. Hence, Cu/Pt(111) NSAs were fabricated, immersed in three-electrode cells under potential control and base CVs were obtained ensuring expected features.\cite{1,183} The cell was then heated to 60 °C and EIS and
RHE evaluation were conducted ensuring appropriate chronoamperometric potentials were used. The samples were then fixed at 0.1 V vs. RHE and rotated at the aforementioned 2500 rpm. Once the signal was stable (a fixed wait time of 300 seconds was employed) gas entering the cell (figure 2.1) was changed from H$_2$ to a H$_2$/CO(2\%) containing one using a fixed 2 bar line pressure. Varying line pressures were directly observed to influence the CO tolerance profile.

![Figure 4.23: RDE Ohmic-drop corrected CA measurements on Pt(111) and select Cu/Pt(111) NSAs showing CO tolerance curves obtained at 2500 rpm, 60 MyC, 0.1 V vs. RHE in H$_2$/CO(2\%) bubbled 0.1 M HClO$_4$ electrolyte.](image)

CO tolerance curves, as shown in figure 4.23, revealed that alloying Cu in the 2$^{nd}$ atomic layer of Pt(111) definitely had an effect. However, quantification was troublesome and there appeared to be a big discrepancy in initial CO adsorption onset. Whether this onset was due to the experimental procedure or due to the Cu alloying is unknown. From figure 4.23 it appears that although initial CO poisoning on the pure Pt(111) seems to happen later than on the Cu/Pt(111) NSAs, these have a propensity to maintain higher HOR currents than pure Pt(111). I.e. electronic structure effects are indicated to have an impact on the CO tolerance on Pt based systems such as the Cu/Pt(111) NSAs.
4.4 Conclusion

In the preceding poisoning of Pt based catalysts model systems have been investigated. In relation to anion poisoning a framework for investigating phosphate poisoning on Pt alloys has been presented. This was developed through fundamental studies on first polycrystalline Pt and consequently Pt(111) surfaces. The framework developed for investigating Pt based catalyst effects revealed that utilizing low level poisoning concentrations at room-temperatures in clean RDE three-electrode setups allowed elucidation of subtle changes to the surface kinetics of the catalysts. For example, changes in specific activities, *Tafel* slopes and half-wave potential were identified as relevant ORR parameters, which changes could be tracked as a function of phosphate poisoning.

Considerations pertaining to the development of poisoning tolerant catalysts have been presented by employing both atomic ensemble effects using the Pt-Hg system and tuning electronic structure (ligand) effects using the Cu/Pt(111) NSA system. The results of the Pt-Hg system indicated that employing surfaces with single site Pt surrounded by Hg did not block phosphate anion adsorption. Moreover, a considerable increase in ORR overpotential is associated with alloying Pt with Hg. From the studies of Cu/Pt(111) NSAs it was possible, by capitalizing on the Cu induced weakening of the OH binding energies, to identify that the NSAs that exhibited the highest tolerance toward phosphate were the ones that exhibited OH bindings similar to those associated with optimum ORR activity. This was ascertained through careful analysis of specific activities, half-wave potentials, *Tafel* slopes and OH potential shifts relative to Pt(111). This analysis indicates scaling between phosphate anions and OH adsorption energies. From a research and development point of view when optimizing ORR catalysts in terms of electronic structure for PEMFC applications relying on anion rich membranes, it appears that optimizing the catalyst through weakening the OH binding toward ideal ORR conditions (ca. 0.1 eV weaker binding compared to pure Pt(111)) is sufficient to ensure optimum catalysts performance.

Preliminary CO poisoning experiments on Cu/Pt(111) NSAs were also performed. These results revealed that some HOR current retention could be observed when investigating the CO tolerance of the system compared to that of pure Pt(111).
Pt(111) and Gd/Pt(111) Single Crystals

In the following electrochemical and structural characterization of Pt(111) and Gd/Pt(111) will be presented. These studies, conducted in collaboration with PhD Anders Filsøe Pedersen, PhD Elisabeth Therese Ulrikkeholm and Prof. María Escudero-Escribano, were aimed at characterizing the Pt overlayer formation on Pt alloys and effect of the overlayers on ORR activities. The studies utilized Pt(111) extended model surface as a reference and a highly ordered Pt-Gd surface alloyed on Pt(111), thus denoted Gd/Pt(111). Surface fabrication and X-ray techniques were combined with electrochemical results and theoretical models in order to get insight into Pt based ORR catalysis.

5.1 Gd/Pt(111) Fabrication

The fabrication of Gd/Pt(111) was based upon evaporation of Gd on a clean Pt(111) single crystal (Mateck, 99.999 %, h×Ø = 4 × 5 mm) in a UHV system. In here deposition of approximately 200±50 Å Gd (Alfa Aesar, 99.99 %) on Pt(111) samples which were heated to 800°C formed the stable Pt-Gd surface alloy (figure 5.1), which thickness were indirectly controlled using the deposition rate measured using a QCM.

ISS, LEED, CO-TPD and AR-XPS were all utilized to ensure the formation of a Pt-Gd alloy surface on top of a Pt(111) crystal, this and the fabrication was adapted from PhD Paolo Malacrida.
done by *PhD Elisabeth Therese Ulrikkeholm*. The alloy was from XRD and LEED, found to correspond to a Cu$_5$Ca structure\cite{261-263} indicative of that of a Pt$_5$Gd surface alloy had been formed. From the characterization of the two Gd/Pt(111) samples it was seen that a Pt$_5$Gd structure on top of a Pt(111) substrate had been produced, whereupon a Pt-skin\cite{264} layer had formed terminating the surface, see figure 5.1. From later GI-XRD measurements it was found that in some instances the Pt$_5$Gd alloying layer was rotated 30° compared to the Pt(111) substrate, whereas the structure orientation was maintained for the others. This rotation was expected to influence the Pt$_5$Gd unit-cell size and thus the in-plane strain imposed when leaching out the secondary alloying metal.\cite{2} The fabrication of Gd/Pt(111) was done multiple times on the same Pt(111) substrate crystals. This required sputtering off the top Pt-Gd surface alloys using Ar sputtering and was verified using XPS, ISS and LEED. To distinguish the two rotation instances the nomenclature Gd/Pt(111) R0 and Gd/Pt(111) R30 has been utilized.

### 5.2 Gd/Pt(111) Oxygen Reduction Studies

A range of studies using X-ray and electrochemical techniques have been utilized to verify what was assumed to be a highly ORR active Gd/Pt(111) catalyst surface.\cite{2,109} The study was conducted in three sub-parts: A study where a Gd/Pt(111) R30 sample was investigated using GI-XRD before and after electrochemical characterization.\cite{157} An *in-situ* electrochemical GI-XRD study of a Gd/Pt(111) R0 sample.\cite{198} Followed by an electrochemical study using RDE techniques of the same Gd/Pt(111) R0* sample (R0* denotes its been subjected to extensive cycling).

From the experiments on the well-ordered alloy catalyst surfaces a clear indication of thick overlayer formation when subjected to acid leaching was observed. Moreover, this overlayer was found to be under compressive strain, thus capable of reaching close to 5-fold improvement in ORR activity compared to Pt(111) while seemingly maintaining most of its activity after accelerated degradation tests.

#### 5.2.1 Electrochemical Gd/Pt(111) R30 Studies

RDE measurements on Gd/Pt(111) R30 were conducted by *PhD Anders Filsøe Pedersen, PhD Elisabeth Therese Ulrikkeholm* and *Prof. María Escudero-Escribano*, on the as-prepared Gd/Pt(111) R30 samples using standard electrochemical methods.\cite{261} The Gd/Pt(111) R30 electrode catalysts was immersed in N$_2$-saturated 0.1M HClO$_4$ (Merck, Suprapur®, 70%) electrolyte under potential control at ca. 0.1 V vs. RHE to avoid excessive surface oxidation. Once the electrode had been immersed it was conditioned by performing extensive CVs between -0.1 and 0.8 V vs. RHE for 1461 cycles followed by additional CVs from 0.0 and 1.2 V vs. RHE until a stable CV could be observed. The prolonged CV conditioning of the Gd/Pt(111) R30 samples were employed due to contamination issues from ambient transport of the UHV prepared samples.\cite{260} Base CVs in N$_2$-saturated 0.1M HClO$_4$ at 50 mV/s and 400 rpm at room-temperature
have been presented in figure 5.2a.\textsuperscript{[157]} The CVs facilitated removal of advantageous adsorbed contaminants from the sample may, besides forming the Pt-skeleton\textsuperscript{[264]} by acid leaching\textsuperscript{[2,109]} of gadolinium from the surface, also induce increased roughness and strain relaxation of the surface. Further the considerable cycling may raise questions about the interpretation of the ensuing XRD and ORR results, however the Gd/Pt(111) R30 surface was considered representative of a stable Gd/Pt(111) R30 surface.

After the electrochemical conditioning the Gd/Pt(111) R30 sample was subjected to CV in O\(_2\)-saturated electrolyte from 0.05 and 1.00 V vs. RHE at 1600 rpm, see figure 5.2.

![Electrochemical RDE data obtained at 23 °C in 0.1 M HClO\(_4\) electrolyte at 50 mV/s. a Base CVs in N\(_2\)-saturated electrolyte at 400 rpm. b Tafel slope with anodic sweep insert, data obtained at 1600 rpm in O\(_2\)-saturated electrolyte.](image)

**Figure 5.2:** Electrochemical RDE data obtained at 23 °C in 0.1 M HClO\(_4\) electrolyte at 50 mV/s.  
\(a\) Base CVs in N\(_2\)-saturated electrolyte at 400 rpm.  
\(b\) Tafel slope with anodic sweep insert, data obtained at 1600 rpm in O\(_2\)-saturated electrolyte.

Electrochemical measurements, in figure 5.2, show a resulting ORR activity of 7.3 ± 1.4 mA/cm\(^2\) was found. This was approximately a 4-fold improvement of the 1.73 ± 0.07 mA/cm\(^2\) measured for Pt(111) prepared by flame-annealing.\textsuperscript{[144,157]} It should be noted that the reported 7.3 ± 1.4 mA/cm\(^2\) ORR activity of Gd/Pt(111) R30 may be a convolution of a R30 alloy and a Gd/Pt(111) sample of unknown orientation as at the time of the ORR experiments\textsuperscript{[157]} the exact discrepancy in Pt\(_5\)Gd alloy orientation (R0 and R30) had not been fully realized.

Fundamentally, the oxygen electroreduction results from the Gd/Pt(111) R30 study\textsuperscript{[157]} indicated that Pt overlayers forms when exposing the highly ordered Pt-Gd surface to acidic conditions, e.g. such as an acidic HClO\(_4\) electrolyte. This results in increased Pt-Pt compressive strain. Such claim were supported by ex-situ synchrotron GI-XRD measurements of an as-prepared Gd/Pt(111) R30 sample prior and after electrochemical characterization, see figure 5.3a and b. Figure 5.3a and b indicates the formation of a thin 3 to 4 atom thick Pt overlayer and that the Pt overlayer rotation matches that of the Pt\(_5\)Gd alloy. The overlayer formation of figure 5.3b was further investigated and
strains (relative to Pt films) and the correlation lengths were identified, see figure 5.3c.

Figure 5.3: GI-XRD diffraction patterns of Gd/Pt(111) R30 sample in reciprocal $Q$-space. The absence and formation of a thin overlayer structure have been circled. a As-prepared sample, no overlayer visible. b After electrochemistry, a thin overlayer has clearly formed. c Overlayer in- and out-of-plane strains and correlation lengths. Courtesy PhD Anders Filsoe Pedersen.[157,206]

5.2.2 Electrochemical Gd/Pt(111) R0 In-Situ Studies

A Gd/Pt(111) sample was fabricated and sent to SSRL where PhD Anders Filsoe Pedersen, PhD Elisabeth Therese Ulrikeholm and Prof. María Escudero-Escribano utilizing the Beam Line 7-2 with a Pilatus 300K detector and laser aided surface-normal alignment system to the $\phi$ rotation axis, see figure 2.22, conducted electrochemical in-situ GI-XRD experiments.[157,198,206]

The sample identified as a Gd/Pt(111) R0 type was placed in the figure 2.22 electrochemical three-electrode setup at Open Circuit (OC) potential using 0.1 M HClO$_4$ electrolyte in a N$_2$-saturated environment under ambient pressure and temperature conditions. Diffraction patterns were then obtained at 0.1, 0.5 V and $U_{\text{max}}$ vs. RHE holding potentials. This was done after a sequence of:

- 62 cycles at 20 mV/s from 0.0 to $U_{\text{max}} = 0.6$ V vs. RHE.
- 92 cycles 20 mV/s from 0.0 to $U_{\text{max}} = 0.8$ V vs. RHE.
- 71 cycles 20 mV/s from 0.0 to $U_{\text{max}} = 1.0$ V vs. RHE.
- Every 1000 cycles at 20 mV/s from 0.6 to 1.0 V vs. RHE up to 8000 cycles.
Diffraction patterns while cycling were obtained. After the 8000 cycles, the electrolyte was changed (air exposure) and an additional measurement was taken on the crystal. From the GI-XRD measurements it was possible to correlate electrochemical in-situ potentials to in- and out-of-plane strains relative to Pt(111) and also the correlation lengths associated with the overlayer structure relative to Pt(111) (see figure 5.4).

**Figure 5.4:** Pt-Pt overlayer strain where errorbars arises from uncertainties from the overlayer and Pt(111) substrate peak positions, also plotted are correlation lengths calculated by fitting of the FWHM using a pseudo-Voigt profile and Scherrer’s equation, herein errorbars correspond to the fitting error and variety of the FWHM during the measurement.  

- **a** In-plane strain.  
- **b** Out-of-plane strain.  
- **c** In-plane correlation length.  
- **d** Out-of-plane correlation length.
From figure 5.4 it can be concluded that the Gd/Pt(111) R0 seems to form a fairly stable overlayer after the first exposure to acid electrolyte. In-fact this is a common phenomenon when dealing with Pt based alloys, wherein all major restructuring from leaching seems to happen almost instantaneously after acidic electrolyte contact. Figure 5.4 also reveals that the overlayer seems to be completely stable after ca. 3000 cycles indicating that after initial overlayer formation Pt$_5$Gd any ORR activity enhancement from in-plane compressive Pt-Pt surface strain is maintained during operation. Figure 5.4b showing the out-of-plane strain, furthermore suggests a constant strain, at least after the initial Gd dissolution from immersion of the sample into electrolyte. This is strongly indicative of a stable surface with minimum Pt dissolution, as such dissolution will typically manifest in a surface roughening resulting in additional degrees of freedom which Pt atom would be able to relax in.

Exceptionally small out-of-plane correlation lengths on the order of $\sim 8.2$ Å and in-plane lengths of $\sim 55.7$ Å are seen in figure 5.4c and b. As correlation lengths relate strongly to the minimum crystalline size, it seems that the top layer of the Gd/Pt(111) R0 system consists of relatively small crystal domains which are all oriented according to that of the Pt(111) substrate. These very small crystal domain sizes, may indicate a high degree of stepped interfaces and stacking faults etc. all structural phenomena known to influence catalytic activity. Moreover, from figure 5.4a and c, any surface restructuring from changes of in-plane crystalline size seem to stop after 3000 cycles and the out-of-plane structure seem to remain constant throughout the experiment. Both cooperating the fact that a very stable overlayer has been established.

From figure 5.4 it is possible to illustrate the Gd/Pt(111) R0 surface post 8000 cycles in the same manner as seen in figure 5.3c. This has been done in figure 5.5.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5_5.png}
\caption{Overlayer in-plane and out-of-plane strain and correlation lengths after 3000 cycles from 0.6 to 1.0 V vs. RHE in 0.1 M HClO$_4$ electrolyte. Adapted from PhD Paolo Malacrida.\cite{106}}
\end{figure}

By comparing figure 5.5 to figure 5.3c it is clear that although the out-of-plane correla-
tion lengths are quite similar, substantial discrepancy is observed when considering the overlayer out-of-plane and in-plane strain and correlation length. The in- and out-of-plane strain discrepancy reported for the Gd/Pt(111) R30 sample of $-0.31\%$ and $0.2\%$ compared to that of the Gd/Pt(111) R0 sample of $-0.78\%$ and $-2.6\%$. To make sense of these strain discrepancies, Density Functional Theory (DFT) calculations by Dr. Martin Hangaard Hansen were employed. He showed that replacing the 2\textsuperscript{nd} or 3\textsuperscript{rd} atomic layer from the sample surface by a 30° rotated Kagomé layer and allowing a six atom layer thick $2 \times 2$ super-cell top three layers to relax would lead to varying in-plane and out-of-plane compression relations, see figure 5.6.\textsuperscript{[263]}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.6.png}
\caption{DFT calculated out-of-plane strain as a function of the in-plane strain for relaxed Pt(111) (blue) and overlayers containing a Kagomé layer in the 2\textsuperscript{nd} (green), 3\textsuperscript{rd} (red), and 4\textsuperscript{th} (black) layer. Courtesy PhD Martin Hangaard Hansen.\textsuperscript{[198,263]}}
\end{figure}

The DFT results of figure 5.6 reveal that a Kagomé layer in the 3\textsuperscript{rd} atomic layer is consistent with our measurements on a Gd/Pt(111) R0 sample and Kagomé layer in the 4\textsuperscript{th} is consistent with the Gd/Pt(111) R30 sample. Unfortunately, the structural changes of the top most atomic layers which have been proposed to be responsible for the substantial changes in strain were insufficiently captured by the utilized GI-XRD.\textsuperscript{[198,206]} Furthermore, it is unknown whether the proposed explanation sufficiently captures the inherent ensemble differences between a well-ordered DFT model surface and a real surface with finite domain sizes, faults and affinities towards relaxation when subjected to electrocatalytic measurements. It does however appear to be the case that surface termination of the overlayer with respect to the underlying Kagomé layers and/or the Pt\textsubscript{5}Gd alloy orientation induce significant surface strain variations, which are again expected to result in significant differences in electrochemical ORR responses as expected from the $d$-band model.
5.2.3 Electrochemical Gd/Pt(111) R0* Stability Studies

After the *in-situ* synchrotron measurements the Gd/Pt(111) R0* sample, having experienced 8000 cycles, was shipped to DTU for further RDE measurements. *I.e.* post the 8000 cycles going from 0.6 to 1.0 V *vs.* RHE, conditions, reminiscent of the catalysts benchmarking conditions\[199,200]\ generally utilized in the literature.

As the Gd/Pt(111) R0* sample could not be re-annealed\[157\] or electropolished for cleaning the surface\[267\] without ruining the GI-XRD evaluated overlayer the sample was electrochemically cleaned after the transport from SSRL to DTU. This cleaning was completed in clean glassware by immersing the electrode in 0.1 M HClO4 under potential control at ∼0.1 V *vs.* RHE and cycling between 0.05 and 1.00 V for 1216 cycles. The first 158 cycles were conducted at 50 mV/s, followed by 1056 cycles mostly obtained at 200 mV/s, although a few CVs were obtained at the 400, 1100 and the 1200 cycle mark at 50 mV/s to trace the evolution of the base CVs, see figure 5.7.

![Figure 5.7: CVs taken at 23 °C in N2-saturated 0.1 M HClO4 electrolyte at 50 mV/s showing the evolution of Gd/Pt(111) R0* base CVs rotating at 400 rpm.](image)

From figure 5.7 the evolution of the surface can be seen to change dramatically after the 8000 cycles at SSRL and the cleaning procedure. Fortuitously, the CVs appeared extremely stable after the accelerated cycling in N2-saturated electrolyte at 400 rpm.

The now clean Gd/Pt(111) R0* electrode was then subject to ORR evaluation at 1600 rpm in O2-saturated electrolyte, see figure 5.8b. This was followed by RHE and EIS evaluation. Before, between, and after these steps base CVs in N2- or Ar-saturated electrolyte were obtained, thereby ensuring that neither the increased mass-transport at 1600 rpm nor the O2 and H2 gasses did anything to alter the surface structure seen as changes in the base CV features (see figure 5.8).
Figure 5.8: Electrochemical data obtained at 23°C in 0.1 M HClO₄ taken at 50 mV/s. a Base CVs of Pt(111) and Gd/Pt(111) R0* and before and after 10000 cycles accelerated stability test in fresh electrolyte. All CVs in N₂-saturated electrolyte and rotating at 400 rpm. Sketched regions denote charge areas used to evaluate $Q_{\text{UPD}}$ and $\Delta U_{1/6} \ast \text{OH ML}$. b Tafel plots derived from the anodic sweep (insert) in O₂-saturated electrolyte taken at 1600 rpm. An accelerated test at 0 rpm in O₂-saturated electrolyte from 0.6 to 1.0 V for 10000 cycles at 100 mV/s was then conducted, see section 2.1. Post this accelerated stability test ORR activity and a base CV were re-obtained in both old and fresh electrolyte. New RHE and EIS evaluation were conducted in both instances. CV and ORR measurement on the samples after 8000 cycles and after the additional 10000 cycles gives good insight into the durability of a strained overlayer. Assuming that the geometric crystal area corresponds to the actual ECSA of the sample it is extremely promising, as the Gd/Pt(111) R0* shows a specific activity at 0.9 V vs. RHE on the order of 8.53 mA/cm² representing a 4.9-fold improvement over pristine Pt(111) (1.73 mA/cm²). Furthermore, the retention of specific activity seems to be maintained even after an additional 10000 cycles (i.e. a total of more than 18000 cycles) with an astounding specific activity of 8.33 mA/cm², representing an activity retention of $\sim 97.6\%$. The earlier Gd/Pt(111) R30 activity of 7.3 ± 1.4 mA/cm²[157] which is somewhat lower can qualitatively be explained by the DFT model of figure 5.6. However, as potential driven relaxation may also be a key factor and noting that the Gd/Pt(111) R30 samples were subjected to potentials up to 1.2 V whereas the Gd/Pt(111) R0 sample was subjected to no more than 1.0 V vs. RHE. However, both the retention and the heightened activity give rise to suspicion in terms of ECSA constancy. If the Gd/Pt(111) R0 surface area increase as a result of dissolution induced roughening the ECSA will be underestimated and the activity consequently overestimated. Evaluation of the cathodic and anodic sweep $H_{\text{UPD}}$ regions as seen on figure 5.8a, as well as the potential OH shift
associated with the adsorption of 1/6 OH ML$^1$ relative to Pt(111), were conducted and compared to results from earlier studies.$^{[157]}$ These evaluated parameters can be seen in table 5.1.

**Table 5.1:** Electrochemical data for Pt(111) and Gd/Pt(111) samples.$^{[157, 198]}$ The ORR data for the Gd/Pt(111) R30 sample may in-fact be a convolution of both R30$^{[157]}$ and R0 activities. Activities and Tafel slopes were evaluated at 0.9 V vs. RHE.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>$j_k$ in mA/cm$^2$</th>
<th>$\beta$ in mV/dec.</th>
<th>$\Delta U_{1/6 \text{OH ML}}$ in [V]</th>
<th>$Q_{H_{UPD}}$ in [$\mu$C]</th>
<th>$Q_{H_{UPD}}^{\text{Pt(111)}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>1.7 ± 0.7</td>
<td>57.6</td>
<td>0.000</td>
<td>175.9</td>
<td>1.00</td>
</tr>
<tr>
<td>Gd/Pt(111) R30</td>
<td>7.3 ± 1.4</td>
<td>61.4</td>
<td>0.104</td>
<td>124.8</td>
<td>0.71</td>
</tr>
<tr>
<td>Gd/Pt(111) R0*</td>
<td>8.5</td>
<td>66.6</td>
<td>0.081</td>
<td>105.1</td>
<td>0.60</td>
</tr>
<tr>
<td>Gd/Pt(111) R0* 10k</td>
<td>8.3</td>
<td>68.5</td>
<td>0.034</td>
<td>140.4</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Table 5.1 reveals that the relative change in $H_{UPD}$ charge to Pt(111) is a poor metric for estimating any area change. This is due to the effect of the $d$-band change has on the hydrogen adsorption isotherm and has been reported extensively by others.$^{[100, 179, 182]}$ Comparison of key electrochemical parameters with earlier Gd/Pt(111) experiments$^{[157]}$ was attempted, as seen table 5.1. The comparison of $H_{UPD}$ charge area of the as-prepared Gd/Pt(111) R30 or Pt(111) to the Gd/Pt(111) R0* sample gives little indication of roughening. It is therefore unlikely that roughening is a principal source of the increased activity of the Gd/Pt(111) R0* sample. Rather, the in-plane strain of the Gd/Pt(111) R0* sample compared to that of the Gd/Pt(111) R30 can sufficiently explain the activity increase. From table 5.1 it can also be ascertained that the OH potential shift evaluation procedure may be compromised due to the combined effect of surface strain relaxation and roughening as substantial difference between the Gd/Pt(111) R0* sample before and after stability is observed. Furthermore, for good measure the Tafel slopes have been evaluated at 0.9 V vs. RHE (close to the half-way potential). The slopes all ranges from 57.6 to 68.5 mV/dec. and correspond well with those reported in literature,$^{[125, 127, 175]}$ indicative of similar kinetic limitations. Using the relative shift in $H_{UPD}$ charge before and after stability test for the Gd/Pt(111) R0* sample in conjunction with the specific activities, it appears the Gd/Pt(111) R0* sample conservatively are able to retain 75% of its activity.

After this extensive investigation of the Gd/Pt(111) R0* sample it was further studied using (AR-)XPS, figure 5.9. For specifics of the XPS procedure see section 2.6. The Pt4f and Gd4d peak coincided with earlier Pt-Gd studies,$^{[106, 109]}$ as shown on figure 5.9a and b. It was also observed that the Gd4d peak of figure 5.9b closely resembled that reported for pure Gd foils by Lademan et al.$^{[268]}$ The reference data$^{[268]}$ of figure 5.9b has been constructed by superposition of spin-up and spin-down XPS spectra which has then been arbitrarily rescaled with an appropriate background.

Importantly, figure 5.9b reveals that there is little signal from Gd$_2$O$_3$ or other oxide/carbide species, indicating a stable passivating Pt overlayer has been formed.
Figure 5.9: XPS data of Gd/Pt(111) R0* after stability test. 

a) Pt4f peak with the 7/2 and 5/2 at 71.2 eV and 74.6 eV highlighted.

b) Gd4d peak with the 5/2 and 3/2 multiplets at 141.2 eV and 147.8 eV highlighted. With rescaled Gd4d reference peak from Lademan et al.[268] inserted.

c) Gd/Pt(111) surface profile[157] as-prepared and after ORR test.

d) Gd/Pt(111) R0* surface profile after stability test.
Figure 5.9c and d show AR-XPS profiles of the Gd/Pt(111) of unknown overlayer orientation and Gd/Pt(111) R0* sample after electrochemical stability measurements, respectively. From these two profiles it seems that the Gd/Pt(111) R0* profile fits nicely with the earlier AR-XPS investigations.\textsuperscript{[157]} The overlayer has been thickened slightly after the more than 18,000 cycles to a thickness of approximately 3 to 5 atom layers.

5.3 Conclusions

Direct observation of Pt overlayer formation using \textit{ex-situ} and \textit{in-situ} GI-XRD experiments has been presented for the Gd/Pt(111) model alloy system. These Pt overlayers’ characteristics have been coupled to existing DFT models and the samples’ electrochemical performances.

In the preceding a scheme for fabricating well-ordered extended \(\text{Pt}_5\text{Gd}\) layers on Pt(111) substrate has been outlined and samples have been characterized.\textsuperscript{[157, 260, 269]} It was found that \(\text{Pt}_5\text{Gd}\) and surface terminating Pt overlayers tend to be either 0 or 30° rotated compared to the Pt(111) substrate.

A Gd/Pt(111) R0 sample cycled at increasing potential initially forms a thin Pt overlayer, which skeleton structure allows for compressive strained Pt overlayer. For such a sample in-plane strain and correlation length is indicated to be stabilized after the first 3000 CVs from 0.6 to 1.0 V vs. RHE. Moreover, out-of-plane strain and correlation length seems unaffected by electrochemical cycling.

From electrochemical study of the sample there is clear evidence of increased Gd/Pt(111) R0* ORR activity due to the increased in-plane overlayer strain compared to that observed for the Gd/Pt(111) R30 sample. However, slight surface roughening could account for some of this increased activity, although there is insufficient data available suggesting this and H\textsubscript{UPD} evaluation do not support it. Conservatively the Gd/Pt(111) R0* system is able to retain at least 75% of its initial activity after accelerated test. However, the Gd/Pt(111) activity seems to be ascribed to in-plane surface strain as indicated by the activity difference observed for Gd/Pt(111) R30 and R0* samples, 7.33 ± 1.4 mA/cm\textsuperscript{2} and 8.53 mA/cm\textsuperscript{2}, respectively.

DFT calculations propose surface strain is heavily dependent on rotated Kagomé layers position from the surface and gives a good qualitative explanation for the strain variety between R0 and R30 samples, but gives little insight into the mechanism allowing the specific overlayer to be favored.

(AR-)XPS of the Gd/Pt(111) R0* sample revealed a surface profile with metallic Gd in the bulk. By comparison to earlier studies\textsuperscript{[157]} it appears that prolonged cycling results in an overlayer thickness 3 to 5 atom layer compared to the initial 3 to 4 atom layer observed after short periods of ORR testing. Thus, hinting at the prospects of strained overlayers viability in real NP ORR catalyst designs for PEMFC applications.
As discussed in chapter 1, increased Pt ORR activity and thus lower Pt loading requirements for PEMFCs\cite{75,76} can be facilitated by alloying Pt with a secondary metal.\cite{110} For instance, alloying Pt with Rare Earths\cite{106,108,109} such as the Lanthanides,\cite{2} or transition metals\cite{75,93,95,122,163,270–275} has proven that great improvements in ORR activity are possible. Assessing stability and activities\cite{2,109} and overall viability associated with Pt Rare Earth catalyst alloys are problematic. This is due to the fact that (large scale) chemical synthesis of Pt Rare Earth NP alloys has proven extremely challenging\cite{34,204} and bulk crystal analysis\cite{2,109} of macroscopic samples of fixed elemental compositions are costly and inflexible in terms of alloying composition. Hence, studies rarely allow investigators to tune Pt:M compositions, as each model catalyst represents a substantial investment. In recent years the emergence of DFT has allowed screening of materials prior to any experimental verification.\cite{54,271} However, DFT operates for very idealized systems and although impressive and often every complex models exist for screening for good ORR catalysts, these models are severely struggling to satisfactory account for the full range of complex behavior at the electrocatalytic interfaces.

Sputter deposition is a versatile technique used extensively in the semiconductor industry.\cite{276} It allows relatively easy fabrication of a long range of elemental compositions. Hence, besides being able to form Pt_xM alloys it is also possible to produce films through reactive sputtering such as RuO_x\cite{277} and MnO_x\cite{278} or even ternary thin films.

In the following the investigations, made in collaboration with PhD Eleonora Zamburlini, on Pt_xGd thin films will be presented. This work was undertaken as these catalyst systems are of particular interest due to their desirable catalytic performances\cite{2,109,161} and the reported difficulty of synthesizing them in a scalable fashion.\cite{279–281} Other types of thin films, such as high surface area Pt\cite{282} and Pt-Ni\cite{283,284} have been successfully fab-
Platinum Based Thin Films

ricated and tested in literature in terms of ORR activity and stability. Moreover, it has been speculated if thin film deposition techniques could have a prominent role in future PEMFC fabrication schemes. Some clear benefits of thin films exist, for instance thin films utilize no surfactants, dispersion is generally uniform and ultra low loadings can be employed. Some drawbacks of thin film deposition are that it is widely considered a vacuum technique and optimization of thin films with PEM is notoriously difficult. Hence, the following Pt$_x$Gd study should be viewed as a study in the versatility of catalyst fabrication and testing using thin film deposition as a platform tool for rapid experimental screening.

6.1 Thin Film Fabrication

Some of the most challenging issues with Pt$_x$Gd and Pt$_x$Y NP synthesis concern the extremely oxyphilic nature of both Gd and Y.\cite{204} Hence, similar concerns must be kept in mind when producing thin films of these elements. Extensive optimization of the thin film fabrication procedure were required before reproducible results could be obtained. In that context it should be mentioned that all depositions were conducted by PhD Eleonora Zamburlini. Besides, the extensive sputter cleaning of glassy carbon substrates, Gd and Pt targets and Ti sublimation through sputtering, a wide range of considerations were made, some of these have been covered in section 2.4 or will be covered in the following. Pt-Gd layers that were too thick (> 100nm) had a tendency to result in delamination, this were likely due to build-up of stress\cite{285} between the glassy carbon substrate and the Pt-Gd interface. Moreover, thin film layers that were too thin (< 27nm) allowed in pin-hole formation, something which were also observed if the thin films were subjected to oxygen during fabrication, as seen in figure 6.1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.1.png}
\caption{SEM at 15 kV of two Pt$_5$Gd thin films after electrochemistry. \textit{a} Dealloyment due to the presence of oxygen in the film. \textit{b} Intact film. Courtesy PhD Eleonora Zamburlini.\cite{202}}
\end{figure}
Circumvention of the thickness constraints were also attempted using Ti adhesion layers on the glassy carbon substrates. But as it was found that operating within a narrow (sub-100 nm) thickness range and adhering to the procedures designed to minimize the oxygen pressure in the UHV system during sputter deposition would allow reproducible thin films to be produced this method was chosen as a Ti adhesion layer ultimately would introduce an added variable in the sputtering and consequent electrochemical testing procedure.

Besides the thickness constraints, the sputter deposition and consequent annealing temperatures presented with a range of challenges. There appeared to be a tendency for thin films annealed at higher temperatures $< 400 \, ^\circ$C to suffer delamination or present with very rough surfaces. Thermal stresses may have played a part, as degassing of the glassy carbon at elevated temperatures could potentially cause issues at the carbon/thin film interface. Moreover, from earlier works on Gd/Pt(111)\cite{157, 260} it was found that some segregation of Gd and Pt elements are possible above 400 $^\circ$C. It was also known from that pure glassy carbon stubs have a tendency to roughen when heated above 400 $^\circ$C. In conclusion, rather narrow deposition parameters were found to result in reproducible thin films, hence in the following only two types of thin films will be presented:

- Pure Pt sample of a thickness of 40nm deposited at 300 $^\circ$C.
- Pt$_5$Gd sample of a thickness of 50nm deposited at 300 $^\circ$C.

For specific details of the thin film fabrication see section 2.4. After sputter deposition the samples were kept at their annealing temperature for 10 minutes, before being allowed to cool (2 to 3 h in the UHV system). QCM was calibrated prior to each deposition and used to quantify deposition amounts.

### 6.2 X-ray Characterization of Thin Films

As indicated extensive, issues pertained to maintaining Gd sputter deposition under sufficiently oxygen deprived conditions. Hence, a range of experiments using as-prepared Pt$_5$Gd thin films were undertaken. For example AR-XPS of as-prepared thin film samples were attempted and compared to the same thin film after it had been subjected to electrochemistry (CVs in 0.1 M HClO$_4$). These results showed nothing conclusive as the AR-XPS profile seemed to indicate that as-prepared Pt$_5$Gd thin films suffered from severe oxidation when transferred through ambient conditions and this oxide layer (likely Gd$_2$O$_3$) was removed when subjected to acidic conditions (see figure 6.1).

The AR-XPS of figure 6.2 gives no indication of the actual surface profile of an as-prepared and consequently electrochemically cycled Pt$_5$Gd thin film. Figure 6.2 instead indicates that as-prepared thin film samples contain substantial amounts of oxygen in the outermost surface layers and that these oxides likely dissolve when subjected to acid treatment. Moreover, it seems that, due to the difficulty of obtaining usable AR-XPS profiles, thin film surfaces may be somewhat roughened or consist of small Pt$_5$Gd domains terminated by any oxide species available during the UHV fabrications. The (AR-)XPS also reveals...
that any such possible oxygen surface termination disappears when treated with acid.

Brief EXAFS studies conducted by PhD Anders Filsøe Pedersen at SSRL on an as-prepared Pt\textsubscript{5}Gd thin film sample revealed clear surface Gd-O coordination prior electrochemistry but hardly any afterward. This strongly suggests that after Pt\textsubscript{5}Gd sputter deposition, while samples are being annealed, any oxygen (albeit minute) will oxidize the thin film surface. This unfortunate oxide top layer is then dissolved when electrochemically treated in acid, rendering the surface metallic and resembling with a thick Pt overlayer.\cite{2,108,109,286} One may speculate that this surface oxide dissolution can potentially result in some roughening of the thin film surface, thus increasing the surface area and/or allowing some surface relaxation of the overlayer.

To verify that minimal amounts of oxygen had been trapped inside the thin films a sput-
tering experiment was conducted, in which C1s, O1s, Gd4d and Pt4f peaks were monitored after sequential Ar sputter etching procedures. This was done in the Theta Probe (figure 2.25) using an Ar sputter area of $6 \times 6 \text{mm}^2$, a power of 0.5 μA and 0.5 keV in $1.11 \times 10^{-7}$ mbar Ar (AGA N5). Various etch times were used, but fundamentally the experiment relied on earlier studies by PhD Paolo Malacrida which indicated that this ”soft” Ar sputtering should result in a ca. 9 nm etching depth of pure Pt after 20 minutes. However, the actual sputter rate for Pt$_5$Gd has not been investigated here.

Results of the quantitative XPS of the sputtered Pt$_5$Gd surface are shown in figure 6.3 as a function of the total etching time $\sum t_s$.

![Figure 6.3](image)

**Figure 6.3:** XPS sputter profile of as-prepared Pt$_5$Gd thin film transferred through air to the Theta Probe. Profile quantification was conducted utilizing the Pt4f, Gd4d, C1s and C1s peaks.

Figure 6.3 revealed, as similarly observed from the electrochemically treated thin films, that after the initial surface etching most of the carbon and oxygen signals dissipate. However, the O1s signal never completely disappears during Ar sputtering.

Combining the knowledge from the AR-XPS in figure 6.2 and earlier reports,$^{[106]}$ system limitations of the Theta Probe UHV chamber seemed plausible rather than actual oxygen incorporation in the bulk of the thin film. Hence, as Gd is extremely oxyphilic and the pressure in the Theta Probe UHV chamber was typically on the order of $5 \times 10^{-8}$ mbar and the thin film electrode area was $0.1847 \text{cm}^2$, one may evaluate the maximum oxygen flux $F_{O_2} = P/\sqrt{(2mO_2k_BT)}$ and thus find the number of $O_2$ molecules hitting the entire thin film surface per second. Such estimates indicate that the surface may experience such events at a rate of $\sim 0.29 \times 10^6$ molecules/s. This number is relatively small but considering the combined XPS data acquisition times of ca. 3 hours for sufficiently resolved C1s, O1s, Pt4f and Gd4d peaks together with the oxyphilicity suggests that oxygen contami-
nation from the XPS chamber is as likely a source as the sputtering deposition procedure. This, combined with the EXAFS data, suggests that oxygen predominantly comes from surface contamination and not the fabrication.

It is worth mentioning that earlier XPS studies on bulk Pt$_5$Gd polycrystalline samples\cite{109} of the Gd4 peak were attempted by *PhD Paolo Malacrida*,\cite{106} in which XPS spectra were obtained while Ar sputtering, such spectrum has been used for reference, but due to the thin film thickness a similar approach were not opted for. XPS Pt4f and Gd4d peaks from Pt$_5$Gd thin films and bulk polycrystalline reference sample have been compared in figure 6.4.\cite{168}

![Figure 6.4: XPS of Pt$_5$Gd thin film (blue) and polycrystalline sample (red), the latter was Ar sputtered during XPS measurement (courtesy PhD Paolo Malacrida) and both were sputter cleaned prior.\cite{109,168} a Pt4f peaks. b Gd4d peaks.](image)

Figure 6.4 shows Pt4f and Gd4d peaks of a Pt$_5$Gd thin film plotted with the same peaks of a polycrystalline Pt$_5$Gd reference sample. In order to ensure minimum signal from advantageous adsorbates such as oxygen and carbon after the transfer from the thin film deposition chamber the samples in figure 6.4 were subjected to Ar sputter cleaning. According to figure 6.4 the peak position of the thin film appears to match those of the bulk reference sample, indicating an alloy with good resemblance to the polycrystalline bulk Pt$_5$Gd reference had formed.\cite{109} A shift in the Gd4d peak was however observed in figure 6.4b on the order of 0.5 eV. This shift was interpreted as minor Gd-O coordination in the surface as discussed in the preceding.\cite{168}

Besides, the rather "qualitative" XPS studies considered above, standard XPS of Pt$_5$Gd thin films were also conducted. It is important here to mention that XPS was extensively utilized ensuring no unknown elemental species had been incorporated into the sample during fabrication (see figure 6.5).\cite{168}
**Figure 6.5:** XPS survey of as-prepared Pt<sub>5</sub>Gd thin film (red) transferred through air and the same film after 10,000 cycles electrochemical stability test in 0.1 M HClO<sub>4</sub> (black).\textsuperscript{[168]}

*Ex-situ* XPS, as that presented in figure 6.5, revealed little or no contamination signals from unexpected elements, *i.e.* besides signals from Pt and Gd, only signals from advantageous adsorbates such as C and O from the ambient sample transfer were observed. Besides the broad XPS survey in figure 6.5 high resolution zoom-ins of the Gd<sup>4d</sup>, Pt<sup>4f</sup>, O<sup>1s</sup> and C<sup>1s</sup> peaks were obtained before and after electrochemical stability tests, as shown in figure 6.6.\textsuperscript{[168]}

XPS zoom-ins, as those of figure 6.6, of the Pt<sup>4f</sup>, Gd<sup>4d</sup>, C<sup>1s</sup> and O<sup>1s</sup> peaks were also used to co-establish metallic ratios of the thin films. However, as XPS is a surface sensitive technique and the as-prepared thin films were expected to energetically favor Pt termination of the surface,\textsuperscript{[264,287]} XPS could overestimate the metallic ratio of Pt vs. Gd signal. It was possible however to establish a rough elemental composition of the as-prepared Pt<sub>5</sub>Gd thin films. The composition in Pt:Gd:C:O percentages were 40.0, 8.4, 28.6, and 23.0\% for the as-prepared sample, corresponding to a Pt:Gd ratio 4.9:1.0, close to the stoichiometric 5:1 ratio. Similarly, the Pt:Gd:C:O percentages of the Pt<sub>5</sub>Gd thin film subjected to electrochemical stability test were 68.5, 2.6, 25.0 and 3.9\%. For the instance of the Pt<sub>5</sub>Gd thin film after stability test the Pt:Gd ratio increased to 26.3:1.0, likely due to the formation of the thick Pt overlayer, which would be in agreement with previous observations on polycrystalline Pt Lanthanide alloys.\textsuperscript{[2,108,109]}

The peak associated with carbon in an oxidized state, seen in figure 6.6c denoted as "A",
Figure 6.6: XPS of non-sputter cleaned Pt₅Gd thin films as-prepared (red) and after 10000 cycles electrochemical stability test (black), both times transferred through ambient conditions.⁷¹⁸  
a Pt4f peaks.  
b Gd4d peaks.  
c C1s peaks.  
d O1s peaks.

is seen to disappear after electrochemistry, indicating that the carbon-oxide were removed from the surface of the thin film sample when exposed to acid. Figure 6.6d further indicates that at least some oxygen, from the peak denoted ”B”, is likely in a metal-oxide state and this metal oxide is similarly dissolved in acid.

From the XPS data of the Pt₅Gd thin films one may surmise that the top-most layer of the as-prepared thin film consists of Pt, Gd, C and O mixture with something that resembles a native gadolinium oxide layer,⁷¹⁸ which can be removed in acid, i.e. the surface of the thin film is oxidized but the thin film bulk is not.
Besides XPS, XRD were utilized to evaluate the Pt$_5$Gd thin films, as shown in figure 6.7.

![XRD of thin film and polycrystalline references.](image)

**Figure 6.7:** XRD of thin film and polycrystalline references. *a* Pure Pt 40 nm thin film (black) and Pt powder reference (blue). *b* Pt$_5$Gd thin film (black) and bulk polycrystalline reference (red) sample, with insert showing a schematic of the obtained crystal structure. Courtesy PhD Eleonora Zamburlini.\(^{168}\)

According to the XRD data of figure 6.7a comparing Pt spectra of Pt thin films with a Pt powder reference it is noticed that the peaks match, indicating that something resembling a standard polycrystalline Pt structure has formed. The peak broadening around 43° is assigned to interference from the glassy carbon support.

Figure 6.7b exhibits the XRD profile of a Pt$_5$Gd bulk polycrystalline reference and a thin film. The Pt$_5$Gd thin film samples present with a crystal structure similar to that observed for polycrystalline Pt$_5$Gd\(^{109}\) and with a hexagonal Cu$_5$Ca-type structure in accordance with literature.\(^{260,288}\)

### 6.3 Electrochemical Thin Film Characterization

Extensive electrochemical analysis of the thin films were also conducted with special attention towards the ORR activity. Pure Pt and Pt$_5$Gd thin films were fabricated and transferred under ambient conditions to clean\(^{171}\) RDE setups, wherein samples were mounted and immersed in 0.1 M HClO$_4$ under potential control. The mounting procedure assimilated that of polycrystalline Pt discussed in section 2.1.1. In the following, electrochemical results collected in collaboration with PhD Eleonora Zamburlini will be presented.

Electrochemical conditioning of the thin films were required prior to the actual data col-
lection. Hence, after thin film immersion the thin film electrodes were cycled extensively in N₂-saturated electrolyte until the CVs appeared stable, as seen in figure 6.8.

![Figure 6.8: RDE base CVs conditioning the thin film samples. The CVs were taken at room-temperature in N₂-saturated 0.1 M HClO₄ 400 rpm. a Pure Pt thin film taken at 200 mV/s. b Pt₅Gd thin film taken at 50 mV/s.][168]

The immediate conditioning of the Pt₅Gd thin film surface when cycled can be observed in figure 6.8, it is noted that the shape of the CVs changes with cycling, especially during the first 50 cycles, due in part to leaching out of secondary metal and partly to removal of surface impurities.[168] Observing the evolution of the CVs is important as it is an indication of both the formation of the right catalyst surface and the cleanliness of the RDE three-electrode setup. As indicated in figure 6.8 scan-rates of both 50 mV/s and 200 mV/s were utilized. Initial activation cycles for any new catalyst were usually performed at 50 mV/s in order to properly monitor the evolution CVs. However, once a set behavior of the evolution of the thin film samples was established, it was preferred to perform accelerated activation cycling (e.g. at 200 mV/s) as this decreases the overall duration of the experiment, thus minimizing contamination issues associated with prolonged electrochemical exposure.[168] Examples of stable Pt and Pt₅Gd thin films are shown in figure 6.9a. The base CVs of figure 6.9a show a Pt thin film compared with a flame-annealed bulk polycrystalline Pt sample. The differences observed in the CVs indicates that the two have different surface structures. Such variation of CV features correlates to differences in distinct adsorption/desorption energies for H, OH and O.[179] Utilizing the H_{UPD} area, see section 2.2.3, revealed $A_{ECSA}$ differences of less than 10% for both the Pt thin films and the Pt₅Gd thin films (see table 6.1). In accordance with the CVs in figure 6.9a it is worth noticing that the distinct (110)- and (100)-step features[289] of the PtPoly at ~ 0.12 V and 0.28 V vs. RHE respectively are unevenly represented for the thin film samples, i.e. it
Electrochemical Thin Film Characterization

Figure 6.9: Base CVs of thin film samples. The CVs were taken at room-temperature in N$_2$-saturated 0.1 M HClO$_4$ 400 rpm. 

(a) Pt thin film sample (green) compared to a Pt$_{\text{Poly}}$ sample.

(b) Pt$_{\text{Thin film}}$ (green), Pt$_{\text{Poly}}$ (black), Pt$_5$Gd$_{\text{Poly}}$ (red) and Pt$_5$Gd$_{\text{Thin film}}$ (blue) samples.\[168\]

appears as if the thin films (at least for the pure Pt ones) favor (110)-step surfaces when comparing to the polycrystalline reference. This may have a significant impact on ECSA evaluation as differences in step distribution can have a significant impact on hydrogen coverages.\[179\] Moreover, the fact that the thin films are seen to have a preference towards the more ORR active (110) surface\[98\] suggests that sputter deposition may favorably produce morphologies excelling in ORR. It is also worth stressing that the presence of the (110) and (100) features in the polycrystalline Pt CVs in figure 6.9a are indicators of good system cleanliness and that the flame-annealing procedure has been conducted appropriately.\[144,171\]

Figure 6.9b combines polycrystalline bulk reference CVs with the corresponding Pt and Pt$_5$Gd thin film counterparts. As can be observed from figure 6.9b, the CVs of both Pt$_5$Gd thin films and polycrystalline Pt$_5$Gd presents with similar characteristic features. The similar hydrogen adsorption regions suggests comparable surface areas. Assuming that the hydrogen charge area for Pt$_5$Gd thin films takes on the same values as for polycrystalline Pt, it is expected that the roughness of the Pt$_5$Gd thin films calculated from the ECSAs will be slightly larger compared to Pt thin films and polycrystalline Pt. Besides the use of the H$_{\text{UPD}}$ method the roughness of the thin films were also evaluated using the CO-stripping method, see table 6.1 and figure 6.10 for CO-stripping examples.\[168\]

Figure 6.10 shows that the CO-stripping occurs at lower potentials on both Pt$_5$Gd and Pt$_{\text{Thin films}}$ compared to Pt$_{\text{Poly}}$. This might be related to the (110)-like defects\[146\] observed in the base CVs (figure 6.9b and 6.10).\[187\] Furthermore, the pre-peak on Pt$_{\text{Poly}}$ can be assigned to oxidation of step sites as proposed by Cuesta et al.\[184,185\]
Platinum Based Thin Films

Figure 6.10: CO-stripping $\text{Pt}_{\text{Thin film}}$ (green), $\text{Pt}_{\text{Poly}}$ (black), and $\text{Pt}_5\text{Gd}_{\text{Thin film}}$ (blue). Taken at room-temperature in Ar-saturated 0.1 M HClO$_4$ at 200 rpm and 10 mV/s.\textsuperscript{168}

From extensive ECSA evaluations using either the H$_{\text{UPD}}$ or CO-stripping charge, see section 2.2.3, table 6.1 could be constructed which shows the roughness factors (calculated as the ratio $A_{\text{ECSA}}/A_{\text{geo}}$) as well as the average electrochemical surface area for the thin films and bulk polycrystalline samples.\textsuperscript{168}

Table 6.1: Roughness factors and ECSAs for the different thin film and bulk polycrystalline samples.\textsuperscript{168} *For extended surfaces the geometric electrode areas was used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Roughness factor (H$_{\text{UPD}}$)</th>
<th>Roughness factor (CO-stripping)</th>
<th>$A_{\text{ECSA}}^{\text{H_{UPD}}}$</th>
<th>$A_{\text{ECSA}}^{\text{CO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pt}_{\text{Poly}}^*$</td>
<td>1.0</td>
<td>1.0</td>
<td>0.196</td>
<td>0.196</td>
</tr>
<tr>
<td>$\text{Pt}<em>5\text{Gd}</em>{\text{Poly}}^*$</td>
<td>1.0</td>
<td>1.0</td>
<td>0.196</td>
<td>0.196</td>
</tr>
<tr>
<td>$\text{Pt}_{\text{Thin films}}$</td>
<td>0.9 ± 0.1</td>
<td>1.0 ± 0.1</td>
<td>0.182±0.01</td>
<td>0.188±0.02</td>
</tr>
<tr>
<td>$\text{Pt}<em>5\text{Gd}</em>{\text{Thin films}}$</td>
<td>1.6 ± 0.4</td>
<td>1.4 ± 0.2</td>
<td>0.253±0.03</td>
<td>0.260±0.15</td>
</tr>
</tbody>
</table>

Table 6.1 shows that the roughness of the sputter deposited thin films is comparable to those of the polycrystalline samples, suggesting similar surface morphology, \textit{i.e.} polycrystallinity.\textsuperscript{109} The $<1$ roughness factor for the $\text{Pt}_{\text{Thin films}}$ is likely a result of the difference in surface morphology and the preferential (110)-step structures.\textsuperscript{179} ORR activities were also evaluated for the thin film samples compared to polycrystalline bulk reference measurements, as shown in figure 6.11.
From figure 6.11a a considerable positive shift in the electrocatalytic ORR activity of both Pt and Pt$_5$Gd thin films, as compared to polycrystalline Pt is evident. Hence, the overpotential for the Pt$_5$Gd thin films has been substantially decreased when compared to Pt$_{\text{Poly}}$, in agreement with our previous results on sputter-cleaned polycrystalline Pt$_5$Gd.\cite{2,109} The kinetic currents have also been extrapolated from the Koutecky-Levich relation,\cite{142} see equation (2.5) and figure 6.11b. The ECSA values from the CO charge areas have been used for identifying the kinetic current densities. Specific activities at 0.9 V vs. RHE, which have been evaluated from Tafel plots similar to those in figure 6.11b. These results show that Pt$_5$Gd thin films exhibits a 4.5-fold improvement in specific ORR activity compared to polycrystalline Pt, with a specific activity of 9.0 ± 0.6 mA/cm$^2$. This result is comparable with that obtained for polycrystalline Pt$_5$Gd bulk samples\cite{109} exhibiting specific activities of 10.6 ± 0.5 mA/cm$^2$ (as seen in table 6.2).

**Table 6.2:** Specific activities and specific mass activities at 0.9 V vs. RHE for Pt and Pt$_5$Gd thin film and bulk polycrystalline samples, all thin film values given with respect to the CO charge evaluated ECSA.\cite{2,168} *Geometric electrode area was used.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$j_k$ in [mA/cm$^2$]</th>
<th>$j_{k,m}$ in [A/mgPt]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_{\text{Poly}}$*</td>
<td>1.9±0.2</td>
<td>-</td>
</tr>
<tr>
<td>Pt$<em>5$Gd$</em>{\text{Poly}}$*</td>
<td>10.6±0.5</td>
<td>-</td>
</tr>
<tr>
<td>Pt$_{\text{Thin films}}$</td>
<td>4.7±0.8</td>
<td>0.07±0.02</td>
</tr>
<tr>
<td>Pt$<em>5$Gd$</em>{\text{Thin films}}$</td>
<td>9.0±0.6</td>
<td>0.12±0.01</td>
</tr>
</tbody>
</table>

Besides the results for the Pt$_5$Gd alloys, a substantial activity enhancement of Pt$_{\text{Thin film}}$ is observed compared to that of Pt$_{\text{Poly}}$, as seen in figure 6.11 and table 6.2. This appears
to be consistent with the (110)-like base CV features of figure 6.9a as (110)-steps are expected to enhance the activity towards ORR. However, from this thin film study it is evident that further surface studies are required in order to unequivocally assign preferential (110)-step and/or surface terminations as the sole cause of the increased ORR activity of the pure Pt\textsubscript{Thin film} compared to the Pt\textsubscript{Poly} samples. Consequently, the impact of the apparent (110) preference of thin films towards the ORR activity is at present only a working hypothesis, although one which correlates well with other literature reports.

As expressed in table 6.2 the specific mass activities for the thin films were also reported, these were evaluated by considering a cylindrical pure Pt layer of volume $V_{Thin film}$

$$j_{k,m} = \frac{j_k \times A_{ECSA}}{\rho_{Pt} V_{Thin film}}$$  (6.1)

, where $\rho_{Pt}$ is the density of pure Pt. The evaluation of equation (6.1) is inherently incorrect at it do not take into account the Gd, but as a conservative estimate it is appropriate. According to table 6.2 it is obvious that Pt\textsubscript{5}Gd thin films’ mass activities have to be significantly improved to $> 0.44 \text{ A/mg}_{Pt}$ for real PEMFC applications. This indicates that extensive reduction of film thickness and general system optimization would be required for thin films to have a role in real PEMFC production.

Besides the immediate ORR activity measurements, the thin films were also subjected to accelerated stability tests. These tests were carried out after initial ORR evaluation and consisted of 10000 cycles between 0.6 and 1.0 V vs. RHE in O\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4}, these results have been summarized in specific activities before and after stability test in figure 6.12.

**Figure 6.12:** Specific activities at 0.9 V vs. RHE for pure Pt and Pt\textsubscript{5}Gd thin films and bulk polycrystalline samples prior to and post accelerated stability tests.

According to figure 6.12, it is seen that the Pt\textsubscript{5}Gd thin films maintained around 83% of
their initial activities which is comparable to the instabilities reported for polycrystalline samples of ca. 87%. Consequently, the overall Pt₅Gd thin film activity is more than 4.5 times higher than that of polycrystalline Pt and more than twice that of pure Pt thin films, all the while still exhibiting a > 3-fold improvement over that of polycrystalline Pt after accelerated stability test.\textsuperscript{[168]}

### 6.4 Conclusion

In this chapter collaborative results concerning Pt based thin film fabrication and their characterization have been presented and discussed. UHV sputter deposition has been shown to be a viable technique for forming Pt based alloys exhibiting similar electrocatalytic performance, as their rather costly and fabrication-wise time consuming bulk crystal counterparts. From extensive trials the underlying importance of an oxygen-free environment, when dealing with Lanthanides during sputter depositing, have been experienced and accounted for. In that context, extensive X-ray techniques were utilized and revealed that, although UHV conditions were maintained during fabrication the oxyphilicity of Gd the samples termination would resemble a native gadolinium-oxide layer. Only after acid treatment did a passivating Pt overlayer of sufficient thickness form, thereby protecting the bulk alloy. EXAFS, (AR-)XPS and XPS sputter profiling support this claim when combined with the electrochemical performances of the films.\textsuperscript{[168, 203]} Minimal amounts of oxygen appears to have been embedded in the thin films and would have an affinity to oxidize the surface after deposition.

XRD investigations (coupled with XPS) of the thin films revealed that Pt₅Gd thin films with a hexagonal Cu₅Ca-type structure were produced from the sputter deposition, in good agreement with previous reports on polycrystalline Pt₅Gd.\textsuperscript{[2, 109]} Moreover, Pt thin films showed similar crystallinity as that of a P-XRD reference spectra indicating something resembling polycrystalline Pt had been formed.

Benchmarking protocols for testing the electrochemical performance of Pt-Gd thin films were established and adhered to using basic RDE setups and clean three-electrode cells. The thin film ORR activity and stability were evaluated and compared with appropriate bulk crystalline samples in HClO₄. Pt₅Gd thin films show a 4.5-fold improvement compared to polycrystalline Pt and a 2.5-fold improvement when compared to pure Pt thin films. Furthermore, Pt₅Gd thin films presented with similar stability as reported for bulk polycrystalline Pt₅Gd,\textsuperscript{[109]} thereby retaining approximately 83% of the initial activity. Generally, thin film fabrication seemed to favor (110)-step morphologies as seen from the pure Pt\textsubscript{Thin films} CVs. This preferential morphology was speculated to have a substantial effect as indicated from the observed ORR activity enhancement on Pt\textsubscript{Thin films} compared to Pt\textsubscript{Poly}, although further studies is needed to verify this hypothesis.

It is the hope that the presented methods facilitates a framework for future fabrication and characterization for electrocatalytic ORR active thin films and a general basis for further investigation of Pt based Lanthanide alloys.
Considering the preceding presentations spanning from extended model systems of Pt, Gd/Pt(111) and Cu/Pt(111) NSAs to systems with broader perspectives towards actual PEMFC applications such as sputter deposited Pt-Gd thin films, it is natural to also consider actual nanoparticulate catalyst. Which would be the actual catalyst type operating in a FCEV. Herein, interim work and results pertaining to nanoparticles of Pt-Y will be presented and discussed.

Recent years have shown an elevated interest in Pt-Y based catalysts as both DFT,\(^{[54]}\) extended surface\(^{[286]}\) and mass-selected NP\(^{[162]}\) studies have revealed such systems to be promising catalysts materials with good ORR activities and excellent stability. However, years of research within our group\(^{[34, 204, 293]}\) and others\(^{[279–281]}\) have found that a chemical synthesis route for producing metallic Pt\(_x\)Y nanoparticles is paved with difficulties. These difficulties arises mainly from yttrium’s oxyphilic\(^{[204]}\) nature and issues with size control of the nanoparticles.

In the following the electrochemical characterization of in-house synthesized particles, prepared by PhD Brian Peter Knudsen at DTU will be presented and discussed. It should be mentioned that as part of this PhD work an external research visit to KAIST was completed, at which extensive electrochemical characterization of NPs were conducted in collaboration with JeongHoon Lim and Hoin Lee under supervision of Prof. EunAe Cho.

### 7.1 Pt-Y Synthesis and Physical Characterization

The catalysts investigated in this project part were based on commercial Pt/C (49.8 wt%) nanoparticles of ca. 6.8 nm, see figure 2.21b, which were modified using an yttrium pre-
cursor\textsuperscript{[293]} and an oxygen free reactor. The synthesis was performed by Ph.D Brian Peter Knudsen\textsuperscript{[293]} and was based on mixing of commercial Pt/C NPs with an appropriate yttrium precursor; in this study YCl$_3$ (Sigma-Aldrich, anhydrous, 99.999\%) dissolved in acetonitrile (Sigma-Aldrich, anhydrous, 99.8\%) under oxygen free conditions in an Ar filled glove box. The stoichiometric Pt:Y ratio was 1.5:1 as excess yttrium was expected to have little influence on the final Pt$_x$Y/C alloy stoichiometry. This was assumed as any alloying were expected to go through Pt$_5$Y phases, followed by Pt$_3$Y and finally Pt$_2$Y phases. However, the latter was not expected to be stable and of interest as an ORR catalyst.\textsuperscript{[286]} After mortaring and uniformly mixing Pt/C and the YCl$_3$ powders the mixture was placed in a carbon lined steel reactor\textsuperscript{[293]} and mounted in a gas-line setup with an iron oxygen trap. The setup was flushed with first N$_2$ Ar followed by N$_2$ H$_2$. A quadrupole mass-spectrometer was mounted down-stream from the reactor and used to monitor the masses associated with HCl formation, oxygen products, carbohydrates, argon and hydrogen.

By monitoring the oxygen species relative to the HCl partial pressure some measure of alloy formation and phase control appears to be maintained and by tuning the temperature for appropriate alloying conditions NPs resembling Pt-Y alloys could be obtained.\textsuperscript{[293]} For the NPs synthesized in this study the temperature was ramped to ca. 400$^\circ$C in an Ar atmosphere at 10 mL/minute for 10 minutes before switching to H$_2$ at 20 mL/minute removing all in-line oxygen species. The reactor temperature was then increased to 800$^\circ$C for 360 minutes before cooling, see figure 7.1.

Extensive studies within our group\textsuperscript{[34, 204, 293]} have gone into optimizing the reaction conditions, however as the focus in this work is on the ORR performance rather than the synthesis these have been excluded in this work.

The produced Pt$_x$Y/C NPs were evaluated using ICP-MS, EDS, XRD and XPS after acid washing. Acid washing was of paramount importance as excess yttrium oxides were dissolved, something which is omitted in most reports on Pt-Y.\textsuperscript{[279, 280]} The acid wash also allows removal of unwanted contaminants from the synthesis while forming the protective Pt overlayer on the Pt$_x$Y/C NPs. XPS revealed that after acid washing the Pt$_x$Y/C NPs stopped exhibiting a yttrium-oxide signal (e.g. from Y$_2$O$_3$).\textsuperscript{[106]} Hence, the Y3d signal from the XPS exhibited clear Y3d$_{5/2}$ and Y3d$_{3/2}$ peaks at 156.0 eV and 158.0 eV as indicated in figure 7.2.

XPS was also utilized to ensure that no contamination was introduced from the synthesis,
Figure 7.2: XPS of Pt<sub>x</sub>Y/C NPs. a Broad survey spectrum. b Pt4f peaks. c Y3d peaks.

as indicated in figure 7.2a. From figure 7.2b and c a Pt:Y stoichiometry of roughly 6.5:1 was identified. However, as XPS is a very surface sensitive technique and a 3 to 4 atom thick overlayer is expected to have formed after the acid washing, the content Pt is stoichiometrically expected to be overestimated by XPS. As XPS is likely to overestimate the Pt:Y ratio EDS were also performed by Cristiano Spiga. These results conducted on a range of earlier synthesized Pt<sub>x</sub>Y/C NPs, revealed a Pt:Y ratio of 5.3:1, which is in reasonable agreement with the XPS data.

Besides EDS, TGA was also employed to evaluate the stoichiometry. For this TGA experiments on both acid washed commercial Pt/C NPs and the acid washed Pt<sub>x</sub>Y/C NPs were conducted to ensure no dissolution of other than Y could be observed. The TGA
procedure simply consisted of weighing catalyst powder (ca. 10 mg), which were loaded into a TGA (Netzsch TG209F Libra) crucible and heated in a synthetic air stream. The samples were heated at 10 °C/minute from room-temperature to 1000 °C. For both the Pt/C and Pt$_x$Y/C NPs most of the mass is seen to dissipate from carbon oxidation from 400 to 500 °C. Assuming only carbon dissipated from the TGA experiment and that no mass was added from yttrium oxidation\(^1\) it was possible to make a very rough estimate of the Pt:Y. The Pt:C ratio of the commercial Pt/C catalyst was found to be 50.8:49.2, which is close to the 49.8 wt% from the manufacturer specification. Similarly the Pt$_x$Y:C ratios of the synthesized NPs were found to be 52.3:47.7 indicating an yttrium mass percentage of 1.3 wt% and thus a rough Pt:Y stoichiometry of 14:1 could be derived. The crude TGA analysis suggested a lower Y stoichiometry than that expected from both XPS and EDS. Hence, ICP-MS were also employed, by dissolution of acid washed Pt$_x$Y/C NPs in nitric acid (OCI, 60%, Extra pure) and heating at 80 °C for 2 h. ICP-MS suggested a 4.7 wt% Y versus Pt ratio, i.e. a Pt:Y ratio of 3.5:1.

XRD was also utilized to evaluate the Pt$_x$Y/C NPs structure and give some insights into stoichiometry and crystal structure of the nanoparticles, see figure 7.3 of Pt$_x$Y/C NPs XRD spectrum obtained by PhD Brian Peter Knudsen.

![XRD spectrum of Pt$_x$Y/C NPs with reference Pt, Pt$_2$Y, Pt$_3$Y and Pt$_5$Y reference peaks.](image)

**Figure 7.3:** XRD spectrum of Pt$_x$Y/C NPs with reference Pt, Pt$_2$Y, Pt$_3$Y and Pt$_5$Y reference peaks. Courtesy PhD Brian Peter Knudsen

Although correct background subtraction of the sample holder failed in the XRD spectra seen in figure 7.3 it is evident that at least partial phase changes from the pure Pt structure can be observed for the Pt$_x$Y/C NPs. Changes in observed structures using XRD of

\(^1\)Though Pt-Y alloys are know to oxidize at 500 to 600 °C.
Pt₃Y/C NPs were expected when compared to pure Pt/C, as similar changes has been observed between bulk Pt and Pt₃Y polycrystalline samples.\cite{286} The spectra also reveals that the NPs are unlikely to be in a single phase, but rather in a mixed phase structure. Besides the XRD in figure 7.3, a range of samples and XRD analysis were conducted supporting the picture of a mixed phase Pt-Y structure of the NPs. Moreover, detailed Rietveld analysis from XRD data by PhD Brian Peter Knudsen indicated the average NP size after synthesis had grown from ca. 6.8 to 7.7 ± 2.1 nm, suggesting that some NP sintering had occurred during the thermal synthesis.\cite{204}

### 7.2 Half-Cell Electrochemical Characterization

Extensive RDE experiments on Pt based nanocatalysts were conducted. For this an optimized ink deposition procedure on glassy carbon electrodes was used. The general recipe was based on 5 mg carbon supported catalyst mixed with 1.4 mL H₂O-mQ, 3.6 mL isopropanol, 2.0 mL ethanol and 2 μL Nafion® 5 wt% all sonicated and mixed approximately 20 minutes. Each element added to the ink(s) was weighed, hence Pt mass-fractions could be used by weighing the deposition of ink on the RDE glassy carbon samples. Moreover, within the field of NP ORR evaluation the increased double-layer capacitance inherent to the large NP surface area background correction of the current signal had to be considered. This can either be done by utilizing lower scan-rates or employing background subtraction,\cite{171} thereby minimizing background induced signal contributions. Background subtraction was opted for in this work and relies on the subtraction of an anodic sweep from the base CV from the anodic sweep of the ORR CV, as indicated in figure 7.4.\cite{295,296} The electrochemical characterization of PtₓY/C NPs was conducted both at DTU and KAIST as inconsistent activities were evaluated, likely due to the fact that different cleaning procedures, than what has been presented in chapter 2, were available at KAIST. Hence, both procedures and results collected at KAIST and DTU will be presented below, denoted Evaluation I and II, respectively.

![Figure 7.4: PtₓY/C NPs in 0.1 M HClO₄ (23°C, 1600 rpm and 50 mV/s). Base CV (blue) in N₂-saturated and ORR CVs in O₂-saturated electrolyte (red) are shown and the capacity subtracted anodic ORR scan (black) derived from the two.](image-url)
7.2.1 Evaluation I

In this section the electrochemical evaluation of Pt$_x$Y/C NPs conducted at KAIST will be presented. Contrary to earlier described methodology (see section 2.1) limited cleaning options were available in this instance. The cleaning procedure consisted of rinsing glassware with Millipore water. However, piranha cleaning and cell heating were not possible. Moreover no Luggin capillary was available and the bubblers available consisted of PTFE lines, which were difficult to keep clean.

The inks were mixed in glass vials using Millipore water, isopropanol (J.Baker, 2-propanol, Analyzed®), ethanol (Samchun, Ethyl Alcohol, 99.5 wt%, Extra Pure), Nafion® (Sigma-Aldrich, 5 wt% with 15-20% H$_2$O) and catalyst in the earlier mentioned amounts, in figure 7.5 a photo of an electrode with and without uniform ink deposition of ca. 10 μL have been shown.

The samples were loaded into a three-electrode RDE setup (no potential or temperature control was available) and an optimized RDE procedure as follows were conducted:

1. Sample conditioning for 300 cycles from 0.00 to 1.00 V vs. RHE at 400 rpm and 200 mV/s in N$_2$-saturated electrolyte.
2. Measurements of base CVs in N$_2$-saturated electrolyte from 0.00 to 1.00 V vs. RHE at 400 rpm and 50 mV/s.
3. EIS evaluation.
4. Measurements of CV in O$_2$-saturated electrolyte from 0.00 to 1.00 V vs. RHE at 1600 rpm and 50 mV/s.

RHE evaluations were done externally in H$_2$-saturated electrolyte.

It was decided upon to investigate the Pt$_x$Y/C NPs in both 0.1 M HClO$_4$ (Samchun, 70.0 wt%, Special grade), H$_2$SO$_4$ (Samchun, 95.0 wt%, Extra pure), and H$_3$PO$_4$ (Samchun, 85.0 wt%, Extra pure), the results of the base CVs and ORR activity have been exemplified in figure 7.6.

In accordance with the results of figure 7.6 it was noted that overall the Pt$_x$Y/C performed better than the Pt/C NPs which the synthesized was based upon. However, the activity was subpar to what was expected from other studies$^{[162,204]}$ concerning Pt$_x$Y/C NPs. This have been exemplified in figure 7.7 revealing the specific mass activity at 0.9 V vs. RHE.

Figure 7.7 reveals that the apparent commercial Pt/C NPs exhibits a specific mass activity in 0.1 M HClO$_4$ of $0.13 \pm 0.05$ A/mgPt, which is approximately half of that expected from studies within our group$^{[297]}$ of $0.21 \pm 0.03$ A/mgPt. Similarly, the Pt$_x$Y/C showed a specific mass activity of $0.24 \pm 0.09$ A/mgPt in HClO$_4$, which again was lower than
Figure 7.6: RDE room-temperature data for Pt/C and Pt$_x$Y/C NPs taken at 50 mV/s in 0.1 M HClO$_4$ (top), H$_2$SO$_4$ (middle) and H$_3$PO$_4$ (bottom). a Base CVs in N$_2$-saturated electrolytes at 400 rpm. b Tafel plots in O$_2$-saturated electrolytes at 1600 rpm.
Figure 7.7: Specific mass activities at 0.9 V vs. RHE in various electrolyte solutions for the Pt\textsubscript{x}Y/C and commercial Pt/C NPs measured at KAIST.

expected\textsuperscript{[162]} Theses discrepancies in expected activity for both reference and Pt\textsubscript{x}Y/C NPs were extremely worrying and various cleaning and ink recipe changes were attempted at KAIST without any substantial changes to the obtained activities. By analysis of the H\textsubscript{UPD} area it was found that the ECSA of the NPs again was roughly half of that expected\textsuperscript{[297]} from earlier studies, see table 7.1.

Table 7.1: Characteristic electrochemical parameters of commercial Pt/C and the thereof synthesized Pt\textsubscript{x} Y/C NPs. Specific activities were evaluated at 0.9 V vs. RHE.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(j_k) in [mA/cm\textsuperscript{2}]</th>
<th>(j_{k,m}) in [A/mg\textsubscript{Pt}]</th>
<th>ECSA in [m\textsuperscript{2}/g\textsubscript{Pt}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expected\textsuperscript{[297]} Pt/C</td>
<td>1.5</td>
<td>0.21</td>
<td>26±3.32</td>
</tr>
<tr>
<td>Found Pt/C</td>
<td>1.14±0.48</td>
<td>0.13±0.05</td>
<td>12.5±2.38</td>
</tr>
<tr>
<td>Found Pt\textsubscript{x}Y/C</td>
<td>2.79±1.08</td>
<td>0.24±0.09</td>
<td>8.3±2.57</td>
</tr>
</tbody>
</table>

The results in table 7.1 strongly suggests activity issues regarding the limited cleaning possibilities available and as a consequence the electrochemical characterization procedure were re-conducted at DTU, where the cleaning procedures presented in chapter 2 were followed.
7.2.2 Evaluation II

Following the already optimized ink recipe at DTU Millipore water, isopropanol (Honey-Well, Puriss, 99.8%), ethanol (Merck, Emsure®), Nafion® (Sigma-Aldrich, 5 wt% with 15-20% H₂O), catalyst inks were prepared through extensive sonication in glass vials. Consequently, the produced ink were dispersed on polished and cleaned glassy carbon stubs for RDE experiments,[296] these experiments were executed using the following procedure:

1. Conditioning for 300 cycles 0.00 to 1.00 V vs. RHE at 400 rpm and 200 mV/s in N₂-saturated electrolyte at 23°C.
2. Collection of base CVs in N₂-saturated electrolyte from 0.00 to 1.00 V vs. RHE at 400 rpm, 50 mV/s and at 23°C.
3. Collection of ORR CVs in O₂-saturated electrolyte from 0.00 to 1.00 V vs. RHE at 1600 rpm, 50 mV/s and at 23°C.
4. EIS evaluation at 23°C.
5. CO-stripping as discussed in section 2.2.3 by cycling from 0.1 to 1.00 V vs. RHE at 200 rpm, 10 mV/s and at 23°C.
6. RHE evaluation through identification of HER/HOR equilibrium potential -0.02 to 1.00 V vs. RHE at 1600 rpm, 50 mV/s and at 23°C.
7. Heating of cell from 23°C to 70°C.
8. RHE evaluation at 70°C.
9. Collection of base CV in N₂-saturated electrolyte from 0.00 to 1.00 V vs. RHE at 400 rpm, 50 mV/s and at 70°C.
10. Collection of ORR CVs in O₂-saturated electrolyte from 0.00 to 1.00 V vs. RHE at 1600 rpm, 50 mV/s and at 70°C.
11. EIS evaluation at 70°C.

From this procedure any effect of elevated temperature kinetics was hoped to be investigated for the various electrolytes in which the NP catalysts were tested, i.e. 0.1 M HClO₄ (Merck, Suprapur®, 70%), H₂SO₄ (Merck, Suprapur®, 96%), and H₃PO₄ (Merck, Suprapur®, 85%).

From the found H_UDP and CO-stripping charges (see figure 7.8) estimates of the ECSA were attempted. However, as indicated in table 7.1 it seemed that both charge from CO[146] and H_UDP[128] region is influenced by the anion adsorption.[129,181]

From the CO-stripping peaks of figure 7.8 nothing concrete can be said, except that some features in the CO-stripping peaks and background CVs changes as function of the electrolyte type. It also appears that both H_UDP and CO charge areas are dependent on the electrolyte type, as the samples Pt loading, shown in figure 7.8, were expected to vary less than 10%, which were evaluated from the inks’ Pt mass-fraction and weighing of the RDE electrodes after ink deposition (see table 7.2 for overview of key parameters).

Table 7.2 reveals that for experiments on Pt/C and PtₓY/C NPs the use of charge areas from CO oxidation or H_UDP to evaluate catalyst ECSA might present with issues. Hence, ECSA evaluation in H₃PO₄ and H₂SO₄ electrolytes was omitted as in-sufficient
Figure 7.8: CO-stripping CVs taken at 23 °C, 200 rpm and 10 mV/s in 0.1 M Ar-saturated HClO₄ (black), H₂SO₄ (blue), and H₃PO₄ (red) electrolytes. a Commercial Pt/C NPs. b PtₓY/C NPs. Pt mass loading varied ≤ 10%.

Table 7.2: Electrochemical data measured at DTU on commercial Pt/C and synthesized PtₓY/C. All potentials given vs. RHE and all electrolytes are 0.1 M concentrations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
<th>T</th>
<th>jₘₙ (0.90 V)</th>
<th>jₘₙ (0.85 V)</th>
<th>Q_{UPD}/M_{Pt}</th>
<th>Q_{CO}/M_{Pt}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>in</td>
<td>[A/mg_{Pt}]</td>
<td>[A/mg_{Pt}]</td>
<td>[mC/g_{Pt}]</td>
<td>[mC/g_{Pt}]</td>
</tr>
<tr>
<td>Pt/C</td>
<td>HClO₄</td>
<td>23</td>
<td>0.23±0.01</td>
<td>0.61±0.05</td>
<td>70.4±4.3</td>
<td>127.3±4.5</td>
</tr>
<tr>
<td>Pt/C</td>
<td>HClO₄</td>
<td>70</td>
<td>0.20±0.01</td>
<td>0.61±0.04</td>
<td>60.0±2.1</td>
<td>-</td>
</tr>
<tr>
<td>Pt/C</td>
<td>H₂SO₄</td>
<td>23</td>
<td>0.04±0.01</td>
<td>0.15±0.01</td>
<td>50.3±5.2</td>
<td>58.2±2.8</td>
</tr>
<tr>
<td>Pt/C</td>
<td>H₂SO₄</td>
<td>70</td>
<td>0.07±0.01</td>
<td>0.29±0.01</td>
<td>52.4±5.8</td>
<td>-</td>
</tr>
<tr>
<td>Pt/C</td>
<td>H₃PO₄</td>
<td>23</td>
<td>0.02±0.01</td>
<td>0.06±0.01</td>
<td>43.1±3.9</td>
<td>75.8±16.9</td>
</tr>
<tr>
<td>Pt/C</td>
<td>H₃PO₄</td>
<td>70</td>
<td>0.03±0.01</td>
<td>0.10±0.01</td>
<td>55.1±0.9</td>
<td>-</td>
</tr>
<tr>
<td>PtₓY/C</td>
<td>HClO₄</td>
<td>23</td>
<td>0.30±0.08</td>
<td>1.06±0.40</td>
<td>51.7±9.9</td>
<td>82.6±12.6</td>
</tr>
<tr>
<td>PtₓY/C</td>
<td>HClO₄</td>
<td>70</td>
<td>0.30±0.11</td>
<td>1.22±0.63</td>
<td>63.3±15.6</td>
<td>-</td>
</tr>
<tr>
<td>PtₓY/C</td>
<td>H₂SO₄</td>
<td>23</td>
<td>0.10±0.04</td>
<td>0.41±0.16</td>
<td>57.9±10.5</td>
<td>86.6±11.3</td>
</tr>
<tr>
<td>PtₓY/C</td>
<td>H₂SO₄</td>
<td>70</td>
<td>0.11±0.01</td>
<td>0.50±0.07</td>
<td>68.7±3.0</td>
<td>-</td>
</tr>
<tr>
<td>PtₓY/C</td>
<td>H₃PO₄</td>
<td>23</td>
<td>0.04±0.01</td>
<td>0.12±0.01</td>
<td>44.4±6.6</td>
<td>70.1±8.0</td>
</tr>
<tr>
<td>PtₓY/C</td>
<td>H₃PO₄</td>
<td>70</td>
<td>0.04±0.01</td>
<td>0.16±0.03</td>
<td>47.6±3.5</td>
<td>-</td>
</tr>
</tbody>
</table>

corroborating evidence of the above observations could be found, although the electrolyte dependence of CO charge area is likely a result form CO desorption combined with simultaneous strong anion adsorption. [298]
The discrepancies of the CO-charge area between the different electrolytes aside, by using the formerly found polycrystalline sample values in HClO$_4$ at 23°C, $\sigma_{\text{PtPoly}}^{\text{CO}} = 349 \mu\text{C/cm}^2$\textsuperscript{[171]} and $\sigma_{\text{H}_{\text{UPD}}}^{\text{PtPoly}} = 190 \mu\text{C/cm}^2$,\textsuperscript{[168]} the expected ECSAs of the commercial seed Pt/C and the synthesized Pt$_x$Y/C catalyst were evaluated. ECSAs for the Pt/C were thus evaluated and ECSA$_{\text{CO}}$ found to be $36.5 \pm 1.3 \text{m}^2/\text{gPt}$ and similarly ECSA$_{\text{H}_{\text{UPD}}}$ to $37.0 \pm 2.3 \text{m}^2/\text{gPt}$, in reasonable agreement with earlier investigations.\textsuperscript{[297]} For the synthesized Pt$_x$Y/C NPs ECSA$_{\text{CO}}$ were found to be $23.7 \pm 3.6 \text{m}^2/\text{gPt}$ and ECSA$_{\text{H}_{\text{UPD}}}$ to $27.2 \pm 5.2 \text{m}^2/\text{gPt}$, indicating a roughly 26 to 35% drop in Pt mass to catalyst surface area ratio. From the ECSA evaluation it seems likely that the thermal treatment may impose issues with sintering and thus Pt usage.\textsuperscript{[299]}

In context to the ECSA evaluation it is very encouraging that although the ECSA of the synthesized Pt$_x$Y/C indicated a roughly 30% poorer Pt utilization they still exhibited a roughly 29% specific mass activity improvement over the commercial Pt/C from which they initially was synthesized, calculated from both H$_{\text{UPD}}$ and CO-stripping values in HClO$_4$ at 23°C, see table 7.1 or figure 7.9.

![Figure 7.9: Specific mass activities at 0.9 V vs. RHE in various 0.1 M electrolyte solutions for the Pt$_x$Y/C and commercial Pt/C NPs.](image)

Utilizing the ECSA$_{\text{H}_{\text{UPD}}}$ and ECSA$_{\text{CO}}$ it was possible to estimate the specific activity at 0.9 V vs. RHE in HClO$_4$ and 23°C. For the commercial Pt/C NPs such values were found to be $j_k \sim 0.6 \text{mA/cm}^2$ (both from CO and H$_{\text{UPD}}$ ECSAs). Similarly, the Pt$_x$Y/C NPs specific activity were evaluated to be $j_k = 1.2 \text{mA/cm}^2$ using ECSA$_{\text{CO}}$ and $j_k = 1.1 \text{mA/cm}^2$ using ECSA$_{\text{H}_{\text{UPD}}}$. These specific activity and specific mass activity values are insufficiently low for real PEMFC applications.\textsuperscript{[76]}

Table 7.1 reveals that at both 0.90 V and perhaps more prominently at higher overpotentials, such as 0.85 V vs. RHE, the catalysts performs better at elevated temperatures espe-
Platinum Based Nanoparticles

cially in the instances where sulphates and phosphates anions are present. This strongly supports the notion of using PBI and Nafion® membranes at elevated operation temperatures for optimum performance in PEMFCs.

Figure 7.9 reveals that approximately 20% higher specific mass activity could be obtained for the same PtₓY NPs when employing the cleaning procedures described in section 2.1. This in combination with the evaluated ECSA suggests that insufficient cleanliness of the experiments in section 7.2.1 was a major component for the subpar activity evaluation, i.e. Pt based NPs catalyst are clearly sensitive to contamination.

Evidence of substantial ECSA lowering of the already relatively large (∼ 6.8 nm) seed Pt/C NPs used in the synthesis have been electrochemically derived. From the electrochemical results it appears the PtₓY/C NPs, though certainly more active than similar sized Pt/C NPs, suffers from effects related to sintering. Something which undoubtedly is a result from the elevated synthesis temperature and long synthesis time, i.e. the ”thermal budget” from diffusion transport ∝ \sqrt{D(T)t} is relatively high, where t is time and the diffusion can be approximated by D(T) = D₀ exp (-E_{a,\text{diff}}/k_BT). From further extensive Small-Angle X-ray Scattering (SAXS) investigation conducted by PhD Christoffer Mølleskov Pedersen on the commercial seed Pt/C NPs indicated that volumetric particle distributions were broader and slightly larger than expected from XRD. SAXS data suggested that of the as-received seed Pt/C NPs 20% were ≤ 6.94 nm, 50% were ≤ 8.60 nm and 80% were ≤ 11.26 nm. As earlier reports suggests that particles < 6 nm will not experience any benefit from alloying as all secondary metal will leach out, combined with the fact that exceedingly large particles will lower the ECSA. This suggests that a narrower seed particle size distribution together with optimization of the thermal budget could improve the particle properties further.

From the electrochemical analysis and XRD data (figure 7.3) it is reasonable to suspect that non-uniformity in PtₓY structure and the phase variety may also inadvertently lower the activity compared to that reported for PtₓY cluster source NPs. Although promising evidence suggest PtₓY/C NPs superiority towards ORR electrocatalysis compared to Pt/C exist, further system comparison of commercially available state-of-the-art Pt₃Co particles and Pt/C of sizes specifically optimized for PEMFC applications should also be investigated. Moreover, size and dispersion analysis using TEM/SEM could be of interest as possible sintering issues could be identified and perhaps alleviated.

7.3 Single Cell Electrochemical Characterization

Up until now only RDE based electrochemical catalyst characterization have been presented for the commercial Pt/C and PtₓY/C NPs, in the following a range of experiments done in collaboration with and executed by JeongHoon Lim and Hoin Lee will be presented. The motivation for this was to investigate the effect of the commercial Pt/C NPs in a MEA setup and how these compare to the synthesized PtₓY/C. These results were also compared with a high area commercial Pt/C NPs from TKK of same Pt loading as
the ones used for the synthesis (50 wt%). These Pt/C TKK particles had an average size of 3.5 nm corresponding to roughly half that of the particle used for the Pt\textsubscript{x}Y/C synthesis. The MEA experiments were conceived to be done both low temperature settings 65 °C using a Nafion\textsuperscript{®} (211 type) membranes and at high temperature settings 160 °C using a PBI membrane (Danish Power Systems, Dapozol\textsuperscript{®}).

The principle behind the MEA tests basically relies on ink deposition on membranes, which are then placed on GDLs (JNTG-20-A3). Ink deposition is achieved by careful spray coating. For illustration and photo of MEA setup see figure 2.12 and 1.6.

The ink for the LT-MEA test consisted of catalyst material mixed with isopropanol and liquid Nafion\textsuperscript{®} resin (30 wt% on the cathode and 23 wt% on the anode). An optimized recipe by the group of Prof. EunAe Cho were utilized,\cite{300} however due to the elevated temperatures required for the HT-MEA tests another ink recipe were attempted utilizing PTFE solution instead (Sigma-Aldrich, 60 wt%), as Nafion\textsuperscript{®} is known to decompose above 120 °C. Unfortunately extensive problems persisted with the dispersion\cite{301} of Pt/C NPs in the PTFE containing ink. Hence, as of now no good solutions have been obtained for this dispersion type and as a consequence only low temperature MEA performances will be presented, see figure 7.10.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure7_10.png}
\caption{MEA test measurements taken at 65 °C and 1 bar at a relative humidity of 100 % (H\textsubscript{2}/air) and at H\textsubscript{2} and air flows of 209 and 663 mL/minutes, respectively. Standard Pt loadings of the anode and cathode were utilized of 0.15 and 0.4 mgPt/cm\textsuperscript{2}. Two measurements each of the commercial seed Pt/C and the synthesized Pt\textsubscript{x}Y/C are presented, as well as a single representative measurement of the Pt/C TKK (50 wt%) high area catalyst.}
\end{figure}

According to figure 7.10 it is evident that the relative large particles ≥ 6.8 nm of the
commercial Pt/C and Pt\textsubscript{x}Y/C is a strong inhibitor of the systems activity compared the highly optimized Pt/C TKK (50 wt\%, 3.5 nm) NP system. Furthermore, it is also evident that no substantial difference between the Pt\textsubscript{x}Y/C NPs and the seed Pt/C NPs could be derived. In terms of trends it seems that, although higher ORR onset potential for the commercial Pt/C than Pt\textsubscript{x}Y/C, at low current densities the Pt\textsubscript{x}Y/C out-performed the commercial Pt/C NPs, all the while both were out-competed by the Pt/C TKK (50 wt\%, 3.5 nm) NPs.

A general result from the MEA tests is that substantial improvements of the mass activity and/or the ECSA is needed for the Pt\textsubscript{x}Y/C NPs to be able to compete with existing high area NPs, such as Pt/C TKK (50 wt\%, 3.5 nm), which usually exhibit ECSAs\textsuperscript{[297]} of the order of 70 m\textsuperscript{2}/g. From figure 7.10 one may speculate that as the particle sizes are larger for the commercial seed Pt/C NPs and Pt\textsubscript{x}Y/C, these are more sensitive to issues relating to dispersion. Further, obtaining good GDL/catalyst/PEM interfaces may be exceedingly difficult exactly due to the low ECSA. The overpotential \( U_{\text{ORR}} - U_0 \) dependence associated with MEA system has been extensively studied. Gasteiger et al.\textsuperscript{[302]} proposes a simple relationship

\[
|U_{\text{ORR}} - U_0| = \alpha \ln \left( \frac{j - j_0}{10 \frac{A_{\text{ECSA}}}{m_{\text{Pt}}} \times \upsilon \times j_0, T, P} \right)
\]  

(7.1)

, where \( A_{\text{ECSA}}/m_{\text{Pt}} \) denotes the ECSA (active surface area per Pt mass of the employed catalyst), \( \upsilon \) denotes the catalyst usage exemplified as the ratio between the inherent catalyst ECSA and that in a MEA and \( j_{0, T, P} \) is the temperature and pressure dependent exchange current density, for other variables see equation (4.1) and figure 1.9. Equation (7.1) has been presented as it give good qualitatively explanation to the poor MEA results of the seed Pt/C and synthesized Pt\textsubscript{x}Y/C NPs shown in figure 7.10, as the \( A_{\text{ECSA}}/m_{\text{Pt}} \) is clearly a size dependent entity. Moreover, the issues of GDL/catalyst/PEM interface discussed in section 1.3.1 may influence \( \upsilon \) in a negative way when using larger particles. From the MEA data in figure 7.10 it is unfortunate that if one is to benefit from the strain effect in Pt-Y alloyed NPs, there are clear indications from cluster source NPs\textsuperscript{[161,162]} and thin film studies\textsuperscript{[161,203]} that particle size should minimum be around 6 to 8 nm. However, as sintering studies\textsuperscript{[293]} have revealed that the particles grows from ca. 6.8 nm to 7.7 nm during synthesis, one could speculate that something might be gained in terms of ECSA from changing to a slightly smaller commercial seed Pt/C NP type. E.g. assuming spherical particles shifting from a 7.7 nm to a 6.2 nm size NP could result in almost a factor two difference in surface area per Pt mass and although mass activity from studies\textsuperscript{[161,162]} on cluster particles seems to indicate optimum of particles \( \geq 8 \) nm surface area may be of greater importance in actual MEA systems due to the added issues of Pt usage \( \upsilon \). Applying the same geometric consideration on the commercial Pt/C 6.8 nm seed NPs and that of the 7.7 nm Pt\textsubscript{x}Y/C NPs one would expect a 31% poorer ECSA for the Pt\textsubscript{x}Y/C NPs compared to that of the seed Pt/C, which was exactly that found from H\textsubscript{UPD} and CO charge area evaluation. In terms of synthesis optimization lowering the particle size
Conclusion

will likely result in increased sintering, which earlier stated may already be an issue, as a compromise\cite{74} it may be more appropriate to utilize seed NPs of narrower size distribution indicated to be an issue form SAXS. This is due to the fact that too small $< 6 \text{ nm}$ particles will be unaffected by alloying due to their small size and propensity to leaching out all of the secondary metal and too large particles (something that SAXS on average suggest there is 20% too many of) may unnecessarily lower the ECSA compared to that ideal for ORR catalysis.

Although low ECSA and the low activity exemplified in figure 7.10 the Pt$_x$Y/C still hold great promises in terms of extended life-time, especially in context to HT-MEAs, as stability issues often prove detrimental for small NP catalyst compared to larger ones. This is especially true for Pt alloyed particle e.g. Pt-Co and Pt-Ni.\cite{270} Hence, Pt$_x$Y/C NPs, when further optimized, may still be of great value for both LT-, but especially HT-PEMFC systems where Pt and secondary alloy metal dissolution is of great concern.

Lastly, one may speculate that as the XRD revealed varying crystal structures there may be multiple crystal domains within each NP allowing surface strain relaxation. From the slight Pt$_2$Y phases observed in the XRD pattern in figure 7.3 one may even propose that higher yttrium content is present at the synthesized NPs surface layer (yttrium impregnation from the outside and into the core). Both effects will result in lower compressive strain\cite{198,286} and represents possible optimization routes of the synthesis.

7.4 Conclusion

In the preceding a dry chemical synthesis route have been sketched and fundamental procedures for ascertaining metallic Pt-Y alloy formation have been presented. It was found that for any claim of Pt-Y NP alloying it is imperative that after acid washing of the synthesized particles exhibit the well-known metal Y states as shown by XPS and moreover that structural changes from XRD can be observed i.e. crystal structure signatures different than those of pure Pt. If either of these two methods does not support the Pt-Y alloying such claim is voided.

A batch of Pt$_x$Y/C NPs produced by PhD Brian Peter Knudsen has been in-depth investigated in terms of structure, chemical composition, electrocatalytic activity towards ORR. P-XRD revealed that the produced Pt$_x$Y/C NPs consists of multiphase structures formed to varying degrees.

XPS revealed that acid washed Pt$_x$Y/C exhibited metallic Y4d$_{5/2}$ at 156.0 eV and Y4d$_{3/2}$ at 158.1 eV peaks in accordance with earlier polycrystalline Pt$_5$Y bulk experiments.\cite{106,286} A range of stoichiometric tools have been utilized attempting to ascertain the Pt:Y alloying ratio. However, varying resulting ratios were found, most of which supports something resembling a 5:1 Pt:Y ratio. However, this value and all the utilized techniques evaluate average element ratios and not that specific of a single nanoparticle. Hence, further studies using TEM and EDS analysis on a small population of selected nanoparticles are certainly warranted.
Electrochemical investigations of Pt based nanocatalysts done at KAIST and DTU underlines the importance of maintaining high system cleanliness of electrolytes and electrochemical cells even when working NPs.

RDE experiments revealed that the Pt$_x$Y/C NPs specific mass activities were enhanced compared to that of the commercial seed Pt/C NPs in both 0.1 M HClO$_4$, H$_2$SO$_4$, and H$_3$PO$_4$. Moreover his activity enhancement was observed both at 23°C and 70°C. Specific mass activity of $\sim 0.30$ A/mgPt in HClO$_4$ for Pt$_x$Y/C was found compared to that of $\sim 0.23$ A/mgPt for the seed Pt/C NPs. From ECSA evaluation using CO oxidation charge and H$_{\text{UPD}}$ in various electrolytes inconsistencies was observed, indicating competitive co-adsorption of anions when evaluating desorption on nanoparticulate systems.

Both RDE and collaborative MEA experiments revealed that the synthesized Pt$_x$Y/C NPs did not perform substantially better than the commercial seed Pt/C particles they were created from. Reasons for this may pertain to phase segregation of the surface, surface relaxation from small crystal domain sizes, ECSA issues from sintering and the seed particles used may be too large for optimum synthesis and/or suffer form a too broad particle size distribution. Employing restrictions of the thermal budget on a Pt$_x$Y/C batch may allow phase preference and minimizing Pt2Y formation as-well-as stifling the effects from synthesis sintering. Moreover, further collaboration with a focus on catalyst and ink optimization are warranted, especially in context to the issues with PTFE containing ink dispersions for high temperature MEA test and stability investigation in actual single stack MEA systems.
Conclusions

Throughout this thesis a cornucopia of experimental knowledge concerning Pt-based ORR electrocatalysis have been presented and discussed. To do this in an proper manner, an initial outline of the relevant technological challenges were presented, followed by model systems investigations on well-defined surfaces and finally presentation of research on nanoparticulate catalysts, more technologically relevant for real-life PEMFCs.

*In-situ* surface-sensitive X-ray diffraction studies on Gd/Pt(111) single-crystals elucidated the formation of a thick Pt overlayer under compressive strain on the Pt-Gd alloy. These results suggest that that the strained overlayer is the governing metric describing the observed ORR activity enhancement relative to relaxed Pt. Moreover, the activity loss after 18 000 CVs is negligible.

From investigation of Cu/Pt(111) NSAs, clear observations of the universality of OH binding as ORR activity descriptor in both acidic and alkaline media has been presented for the first time. Thereby cementing the *Sabatier* principles’ correctness. Although the investigation did leave room for the inclusion of other descriptors and models treating synergistic effects of OH binding and non-covalent interactions between the electrolyte cations and the surface. Cu/Pt(111) NSAs revealed, to the to the best of our knowledge, the second highest specific ORR activity ever reported (100.7 ± 7.5 mA/cm$^2$ at 0.9 V vs. RHE) in 0.1 M KOH, only surpassed by Pt$_3$Ni(111) single-crystalline electrodes$^{[226]}$ (also in KOH). Cu/Pt(111) NSAs’ ability to tune the OH binding energy through sub-surface Cu alloying amounts was also utilized in the investigation of phosphate anion poisoning of Pt, as this holds relevance for the emerging field of PBI based HT-PEMFCs. From these studies, a framework for investigation was developed and employed in the analysis of polycrystalline Pt, Pt(111) and Cu/Pt(111) NSAs. It was found that phosphate adsorption both modifies the number of available sites for the ORR, but likely also the adsorption potential of OH,
seen as changes in both half-wave potentials, Tafel slopes and lowering of kinetic current densities for ORR. By tuning the OH binding by Cu in the 2nd atomic layer, a clear tendency towards minimum impacts from phosphate on these three metrics were observed near the optimum OH binding energy for ORR relative to Pt(111). This suggests that the catalyst system with the best tolerance towards phosphate is likely to be a system which electronic structure is closely optimized for ORR. These results suggests a possible scaling relation between ORR intermediates and phosphate and are in agreement with the Sabatier principle.

Pt and Pt-Gd thin film studies have been presented with a special focus on using appropriate X-ray techniques on the research of nanoparticle catalysts containing oxyphilic species such as Gd or Y. Sputter-deposited Pt thin films presents higher activity than polycrystalline Pt. These results could be explained by preferential Pt surface termination. The ability to produce oxygen-free Pt$_5$Gd thin films with exceedingly high activities (4.5-fold that of polycrystalline Pt) was demonstrated. Moreover, accelerated degradation tests show that the Pt$_5$Gd thin films retained up to 83% of their initial activity. The thin film system also enables a fabrication route for relatively quick and inexpensive screening studies of electrocatalysts for a wide range of applications.

Preliminary electrochemical characterization of in-house synthesized Pt$_x$Y/C nanoparticles have also been presented. From these results, the importance of working extremely clean, even when considering large surface area nanoparticles, was underlined by the apparent electrochemical discrepancies in catalysts performance when adhering to and not adhering to established cleaning procedures. The Pt$_x$Y/C exhibited promising specific mass activities (0.3 A/mg$_{Pt}$ at 0.9 V vs. RHE). However, since the Pt utilization due to the increased particle size remained low compared to high area commercial catalysts, both MEA and RDE measurements at low temperature were impeded.

### 8.1 Outlook

Perspectives concerning future investigations and shortcomings of the presented experimental work will be discussed below.

The limited sample availability of the Gd/Pt(111) systems severely limits the ability to make conclusive interpretations. Repeating the measurements on one to two additional samples for each of the Gd/Pt(111) R30 and R0 variants would be useful not only to get further insights into the overlayer orientation, but also in terms of strain evolution (as function of the rotation) and its influence on ORR activity. Moreover, STM studies of the Gd/Pt(111) overlayer before and during electrochemistry may be of vital importance when considering the apparent appealing stability performance exhibited for most Pt-Gd based ORR electrocatalysts. Finally, it would be interesting to see if favorable cation effects on the ORR can be observed both in alkaline and acidic electrolyte for the Gd/Pt(111) system.

Further studies on Cu/Pt(111) NSAs could easily be conceived. However, insights towards
the effect of the cations may instead be better investigated through careful modification of electrolytes rather than the Pt(111) surface. *E.g.* preparations are being made for dosing experiment with KClO$_4$ and similar cation perchlorates in HClO$_4$ electrolytes on pure Pt(111) as such experiments may elucidate the importance of pH dependence. From such studies it may be further chosen to conduct careful investigations of the cations possible interplay with the OH binding. Our data suggests the impact of the cation effect is somewhat tuned by the OH binding, though further systematic studies would be required to verify such claims. By use of the Cu/Pt(111) system it should be possible to see how the OH binding relative to the cation type behaves. Such studies could either be done using alkaline media with varying cation types or conceivable by using the cation perchlorate as suggested earlier. Moreover, theoretical models treating the subject of the cation induced ORR enhancement on Pt(111)-like surfaces should be explored through collaborative efforts with theoreticians. Such an extensive study may also benefit from EC-STM investigations of Pt(111) surfaces in KOH (or other alkaline media) as both cation adsorption, water structure changes on the surface and cation concentration in the double-layer could be conceived to be factors governing the activity enhancement.

Additional Pt based thin film work is warranted especially in terms of the increased pure Pt activity enhancement from sputter deposited samples. Moreover, the thin film study has opened up for a huge potential of sample screening through elemental binary or even ternary alloying *e.g.* Pt$_5$Gd$_{0.5}$Tb$_{0.5}$, which resulting overlayer contraction should be near optimum if the alloy can be formed.

Further electrochemical studies of Pt$_x$Y/C NPs would perhaps be the most relevant subject for further study in terms of both scientific and technological impact. This may also be the easiest investigation to continue as the preceding study strongly indicated that optimized process parameters in terms of thermal budget may allow phase pure Pt$_5$Y/C NPs to be synthesized. This, together with the synthesis methods applicability towards Pt$_5$Gd/C NP fabrication would allow interesting studies to be made. Such studies would also potentially allow fruitful continued collaboration with Prof. EunAe Cho and her group in terms of establishing good inks and gain fundamental insights into high temperature PBI based MEA testing. Such studies represents an operational range in need of reliable studies where the larger Pt$_5$Y/C and Pt$_5$Gd/C NPs are theorized to excel in terms of activity and stability. Beside the electrochemical testing TEM/SEM analysis is also warranted for these future studies both for the individual NPs, but SEM studies of MEAs with inks containing varying particle size may be of interest, as the effect of particle size in terms of MEA Pt usage is unknown.


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Experimental Elucidation of the Oxygen Reduction Volcano in Alkaline Media
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Experimental Elucidation of the Oxygen Reduction Volcano in Alkaline Media

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ABSTRACT: The ability to identify appropriate descriptors for oxygen electroreduction is of great importance for fuel cell development. In this work, Cu/Pt(111) near-surface alloys have been utilized to probe the complementarity of the activity enhancement observed from the weakening of OH by Cu alloying and the activity enhancement reported on Pt(111)-like surfaces in alkaline. Herein we report on these apparent synergistic effects of combining the right electrolyte and optimizing OH binding energies by near-surface alloying. This resulted in the first Sabatier volcano relationship in alkaline media exhibiting maximum specific activities of 100.7±7.5 mA/cm² at 0.9 V vs. RHE. We conclude that a total ORR enhancement exceeds the total product (58-fold improvement) observed individually by either moving Pt(111) from HClO₄ to KOH (4-fold improvement) or by sub-surface alloying (up to 8-fold improvement observed in HClO₄). Both OH binding and cation interaction is shown to be descriptors for the ORR activity in alkaline media, though the exact nature of the latter remains elusive.

Oxygen reduction is ubiquitous. In nature, it controls our respiration through the enzyme cytochrome c oxidase.1 It limits the efficiency of low temperature fuel cells and metal-air batteries for renewable energy conversion.2-3 A huge body of research has been devoted towards elucidating the factors controlling this all-important reaction;4-5 most studies focus on acidic media, where only Pt-based catalysts are able to provide the stability and activity required for technological applications.9 A theoretical model was developed to show that a Sabatier volcano relationship exists between the binding of the reaction intermediates and the catalytic activity.10-12 The most optimal metal catalyst should bind the key intermediate, *OH, 0.1 eV weaker than Pt(111). In an earlier work, we experimentally verified this in 0.1 M HClO₄, by modifying a Pt(111) single crystal with subsurface Cu to form a Cu/Pt(111) near-surface alloy13 (see Fig. 1). By lieu of the ligand effects14, we systematically tuned *OH adsorption and oxygen reduction activity. We subsequently showed that this relationship also holds for a wide range of Pt-based single-crystalline surfaces, as reported by others, including stepped single crystals and Pt₃Ni(111).15 Knowledge of the volcano has provided catalyst developers with a key design principle for the reaction and has led to the huge decrease in the amount of Pt required in commercial fuel cells today.16-20

The focus in oxygen reduction reaction (ORR) research is now extending beyond acidic media.21-25 State-of-the-art hydroxide conducting polymeric membranes26 allow alkaline fuel cells (AFCs) to be operated efficiently. At high pH, a much wider range of materials are stable, including Ag.27 and Fe-based28 electrodes. Nonetheless, there is little consensus regarding the factors that govern oxygen reduction in alkaline media. Model studies on Pt in alkaline reports among others on the effect of pH dependent adsorption29,30 and the surface morphology31,32 dependent shifts in water orientation due to cations33 and OH destabilization from cation induced water stabilization.24 Experimental observations suggest that the trends in activity in alkaline are somewhat different from those in acid. Bulk polycrystalline Pt and nanoparticulate Pt31 are a factor of ~2 less active in 0.1 M KOH than in 0.1 M HClO₄. Conversely, Pt₃Ni(111), exhibits an unprecedentedly high activity in 0.1 M KOH of ~300 mA/cm², >150-fold increase from in acid.24 Au(100), which is relatively inactive in 0.1 M HClO₄, exhibits activities equal to Pt(111) in 0.1 M KOH.24 Reports have even shown that the very same stepped Pt surfaces, which exhibit significant enhancements over Pt(111) in 0.1 HClO₄, show decreased oxygen reduction activity, relative to Pt(111), in 0.1 M NaOH.23

Aside from pH, non-covalent interactions induced by the electrolyte cation22-24 controls both the kinetics and thermodynamics of *O and *OH formation on Pt single crystal surfaces. Such interactions seem to play a strong role on catalytic activity, both for oxygen reduction and other electrochemical reactions.25-39 However, when changing the cation, there is no clear trend between the positions of the peaks for OH desorption and the oxygen reduction activity; this observation suggests that the cation changes the oxygen reduction activity by effects that go beyond simply adjusting the binding of the reaction intermediates. These seemingly discordant observations provide the motivation for our current work. In particular, we aim to determine whether the catalytic activity follows a Sabatier volcano in alkaline media. Moreover, we will also disentangle the effect of pH versus changing the electrolyte cation.

In brief, we prepared the Cu/Pt(111) near-surface alloy using our previously developed methodology,26 as follows: a Pt(111) single crystal was annealed and positioned in the headspace above the electrolyte in a custom electrochemical cell (see Fig. S1 and S2). Up to a monolayer (ML) of Cu was deposited on top of the crystal and inductively annealed in the headspace in Ar/H₂ (5 %), driving the Cu subsurface. By angle resolved X-ray photoelectron spec-
From Fig. 2 one notices a general trend from the CVs in alkaline solutions quantified by comparing the potential shift in adsorption charge of OH to 40 ± 0.3). Base CVs for various initial Cu coverages can be seen in Fig. 2.

From this one may plot the charge integral shown in Fig. 3 displays an increase in the shift in OH adsorption potential with respect to that of Pt(111) denoted \( \Delta U \). For an isotropic, non-adsorbate-adsorbate interacting surface, this \( \Delta U \) entity correspond to relative shifts in OH binding energy\(^{23}\) compared to that of pure Pt(111) \( \Delta E_{\text{OH}} = \Delta E_{\text{OH}}^{\text{Pt(111)}} \). By focusing on the potential shift for 1/6 *OH ML coverage (low coverage ensuring adsorbate interactions are minimal) for the NSAs with varying quantities of Cu in the 2nd atomic layer it is possible to exemplify the OH suppression and thus the weakening of the oxygen binding which earlier reports\(^{25}\) have estimated to be approximately 0.1 eV too strong for Pt(111) per OH molecule compared to an ideal ORR catalyst. The potential shifts were evaluated by\(^{13}\)

\[
\Delta U_{\theta_{\text{Cu}}=0.19 \text{ ML}} = \Delta U_{\theta_{\text{Cu}}=0.40 \text{ ML}} - \Delta U_{\theta_{\text{Cu}}=0.20 \text{ ML}} \approx \Delta E_{\text{OH}}
\]

From Fig. 3 two things are notable:

1) For low Cu subsurface amounts, \( \theta_{\text{Cu}}<0.19 \text{ ML} \), the OH adsorption charge as function of potential increases drastically compared to NSAs with higher degrees of Cu alloyed, \( \theta_{\text{Cu}}>0.40 \text{ ML} \). Coupling this with earlier observations\(^{13}\), suggests NSAs favors specific Cu:Pt ratios in the 2nd atomic layer, e.g. 2:3 Cu coverages is suspected to be much more stable than an 1/3 coverage.

2) For NSAs with low Cu amounts the OH adsorption potential dependence varies until \( \theta_{\text{Cu}}>0.20 \text{ ML} \), for higher Cu coverages the charge slopes converges. This suggest that any subsurface Cu drastically modifies the OH adsorption to a certain point, where after Cu induced weakening of the OH binding is shifted (similar trend is seen in 0.1 M HClO\(_4\).\(^{25}\) see Fig. S5c).

From Figs. 3 and S4b, it is clear that it is indeed the combined effect of NSA induced changes in the OH onset and adsorption potential which describes the apparent suppression of OH region. In this context, the apparent OH onset on Pt(111) in KOH vs. HClO\(_4\) is shifted ~47 ± 23 mV towards lower potentials. Although the high uncertainty, this corroborates the reported activity enhancement\(^{23,35}\) of Pt(111) in KOH compared to HClO\(_4\) as a product from weakening the OH binding.

A few measurements of selected NSA Cu coverages was also electrochemically measured in 0.1 M NaOH (pH=12.5±0.3), see Fig. S6). In that context it is worth noting the reasonable agreement between the features of the OH adsorption regions independently of the electrolyte cation at similar pH (Fig. S6). This suggests that the cations effect on the OH adsorption region is limited (LiOH excluded), in agreement with earlier reports\(^{13,22}\).
Fig. 4a shows shifts in OH potential relative to Pt(111) as function of initial Cu coverage in reasonable agreement with earlier results on Cu/Pt(111) NSAs. Fig. 4b shows the relative activity enhancement ($j_k/j_k(111)$) compared to Pt(111). The kinetic ORR activity is derived by the Koutecky-Levich relation $j_k=(j^d j_k)/(j^d j_k - j_k)$, where $j_k$ is the diffusion limited current density. From Fig. 4b it is seen that it is possible to directly modify ORR activity by means of NSA induced ligand effects, by controlling the initial Cu deposition. Fig. 4c shows the average AR-XPS intensity ratios calculated by the Cu2p3/2 and Pt4f peaks in the range 20 to 35°. These values are in line with earlier reports and indicates that some of the initial deposited Cu is lost into the Pt(111) bulk, which DFT studies corporate.

Fig. 4b shows that the optimum activity is obtained for a subsurface alloying with of $\theta_{Cu}=0.77$ ML, which is higher than that reported in acid ($\theta_{Cu}=0.55$ ML). Considering the ca. 47 mV shift in the OH onset potential for Pt(111) in KOH as compared to HClO4, this difference in optimum Cu coverage for the NSAs is a little surprising. This suggests that there is a difference in OH adsorption potential dependence, as can be observed in Fig. 4a as well. To elucidate this OH potential shift for various OH coverages were evaluated (Fig. 5).

Figure 4. Data from NSAs with guides for the eyes (full lines) plotted vs. $\theta_{Cu}$. (a) Potential shift in OH adsorption for 1/6 *OH ML in 0.1 M HClO4 and KOH. (b) Activity enhancement in KOH. (c) AR-XPS Cu:Pt ratios derived from angles from 20 to 35° with comparison to earlier reports and model (gray line).

Figure 5: Variations in OH potential shifts in KOH relative to Pt(111) for selected NSAs as function of the used OH coverage.

Figure 6: Volcano-plot showing shift in OH adsorption potential relative to Pt(111) vs. activity enhancement in 0.1 M NaOH (green) and KOH (red). Thermodynamic- (black) and kinetic volcano (grey) for 4e- ORR have been included together with single crystal values of Pt(775) and Pt(755) surfaces in NaOH evaluated from specific activities at 0.8 V vs. RHE.
From Fig. 5, it is evident that the shift OH adsorption potential will vary dependent on the isotherm and saturation coverage of the NSAs, i.e. the $\Delta U_{\text{OH}}$ evaluation is sensitive to the coverage. Hence, the optimal OH potential shift may vary from acid to alkaline. Moreover, activities and shifts in OH potentials were also collected for a few NSAs 0.1 M NaOH ($\theta_{\text{OH}}$=0.00, 0.79 and 0.99 ML) to elucidate the effect of the cation. Table S1 summarizes the specific activities derived from the Pt(111) and Cu/Pt(111) model systems.

The activity enhancement of the NSAs in KOH and NaOH has been plotted as a function of shifts in OH adsorption potential in Fig. 6. This revealed a clear volcano trend as seen in Fig. 6, which to the best of our knowledge, this is the first work showing the OH binding optimum of the model and that found in alkaline can be explained by: 1) Differences in OH coverage assumption in the model system compared to in alkaline, by proxy exemplified by Fig. 5. 2) Due to differences in rate limiting step in alkaline compared to the model $^i$OOH stabilization changing the rate constant of the system.

The maximum activity recorded for the NSAs was 107±7.5 mA/cm² which is a 13-fold improvement over Pt(111) in KOH (7.8±0.8 mA/cm²) and a 58-fold improvement over Pt(111) in HClO₄ (1.7±0.1 mA/cm²)$^{49}$. Moreover, the (111) surface morphology is of paramount importance for the activity enhancement$^{21,31}$, which is also evident from the literature reports on Au(100).$^{54}$ However, models for Au(100) assigning superoxide stabilization (and thus OH destabilization) as the principal mechanism behind the ORR enhancement in alkaline media$^{14}$, though we do see indications of this, the high activities observed at the modest shifts in OH binding in the volcano (Fig. 6), contradicts such an account. As the *OOH pathway would only dominate at the weak-binding side of the volcano$^{35}$ and ideally present with considerable changes in the Tafel slope (for Pt(111) seen to change from ~65.8 in HClO₄ to ~45.5 mV/dec. in KOH).

Any complete model describing ORR in alkaline media must take into account surface morphology and its intricate interplay between the cations. As such, a static model depending purely on cations properties is unlikely to successfully describe the enhancement on Pt(111). How such a model should look is still unknown, but it should incorporate both the OH binding and OH interplay with morphology combined with at least one additional unknown descriptor pertaining to the cation-surface morphology interplay, e.g. through static field considerations of entropy changes of adsorbed OH order in the presence of cations or water promoted OH destabilization$^{36}$, or even pH induced changes in reaction mechanisms$^{37}$, etc.

In summary, OH binding is a universal descriptor for ORR activity. In addition, non-covalent interactions between the electrode surface and the electrolyte cations play an important role in dictating the ORR activity in alkaline electrolyte.

**ACKNOWLEDGMENT**

The authors gratefully acknowledge funding from Innovation Fund Denmark for the KDFuelCell project and The Villum Center for the Science of Sustainable Fuels and Chemicals (SurfCat). M.E.-E. acknowledges funding from the Danish Council for Independent Research under the Sapere Aude – Research Talent Program.

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Notes: In preparation, 2017, abstract appended
Enhanced Oxygen Reduction in the Presence of anion poisons through subsurface alloying

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Keywords: Oxygen reduction, electrocatalysis, anion, Pt(111), adsorption, phosphate

Abstract

The adverse effects from phosphate anion poisoning for the oxygen reduction reaction (ORR) have been investigated on platinum-based well-defined electrode surfaces. Herein, we present rotating disk electrode (RDE) measurements on well-defined extended polycrystalline Pt, Pt(111) and Cu/Pt(111) near surface alloys (NSAs) in the presence of sub-25 mM amounts of H₃PO₄. ORR half-wave potential as well as kinetic current densities and Tafel slopes at fixed reference potential are suited metrics for tracking anion poisoning effects. We applied those metrics to study phosphate anions poisoning on Cu/Pt(111) NSAs. The varying degree to which Cu/Pt(111) NSAs were optimized to ORR were dependent on the OH binding to the surface following Sabatiers principle. Such changes in OH binding were evaluated by shifts in OH adsorption potential and controlled by the subsurface Cu amounts alloyed into the sample. Tuning ligand effects enabled the preparation of Pt electrode surfaces with better tolerance towards phosphate poisoning. Moreover, our results indicate direct scaling relation between adsorbed OH and phosphate. By contemplating this scaling, in context with the Sabatiers principle, the study strongly suggest that regardless whether H₃PO₄ is being present in the electrolyte or not, the ORR activity and mechanism will be governed by the OH binding and not the concentration of anions.
Benchmarking Pt and Pt-lanthanide sputtered thin films for oxygen electroreduction: fabrication and rotating disk electrode measurements
Benchmarking Pt and Pt-lanthanide sputtered thin films for oxygen electroreduction: fabrication and rotating disk electrode measurements

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Abstract

Platinum-lanthanide alloys are very promising as active and stable catalysts for the oxygen reduction reaction (ORR) in low-temperature fuel cells. We have fabricated Pt and Pt5Gd metallic thin films via (co-)sputtering deposition in an ultra-high vacuum (UHV) chamber. The electrochemical ORR activity, stability, as-well as chemical composition and crystallographic structure of Pt5Gd thin film catalysts have been investigated using a combination of electrochemical measurements, X-ray photoemission spectroscopy (XPS) and X-ray diffraction (XRD) techniques. We describe the measurement procedures, with the aim of benchmarking electrochemical characterization of Pt-based thin film catalysts for ORR. Pt5Gd thin films present an activity enhancement by a factor of 4.5 and 2.5 over polycrystalline Pt and Pt thin films, respectively.

Keywords:
Electrocatalysis, Oxygen Reduction Reaction, Rotating Disk Electrode, Pt-Alloys, Sputtering, Thin Films, Benchmarking
1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are one of the most promising technologies for potentially zero emission power conversion. They are suitable for both automotive and stationary applications, and will likely play an important role in future sustainable energy schemes. However, the high costs of PEMFCs, and specifically of the Pt-based electrocatalysts, constitute a major obstacle for a commercially competitive reality. Currently, a state-of-the-art PEMFC requires a Pt loading of 0.25 gPt/kW, of which 0.2 mgPt/cm² are required at the cathode, where the oxygen reduction reaction (ORR) takes place:

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]  

The slow kinetics of the ORR causes significant potential losses (overpotentials). As such, this is the limiting reaction in PEMFCs. Using current technologies, the amount of Pt available is too scarce to ensure a widespread implementation of PEMFCs. In order to reduce the Pt loading at the cathode, we need to develop new electrocatalysts with enhanced activity and improved long-term stability under realistic operating conditions. It is important to note that an order of magnitude decrease in the amount of Pt employed at the cathode of a PEMFC would result in a Pt group metal loading equal to that of advanced catalytic converters for automotive vehicles in terms of Pt usage.

The ORR on pure Pt surfaces has been studied extensively. In 0.1 M HClO₄, the ORR activity follows the order Pt(100)<Pt(111)<Pt(110). Moreover, defects such as steps and concave defects seem to enhance oxygen reduction. It is clear that the ORR is structure-sensitive. Therefore, modifying the surface structure can enhance the catalytic activity, selectivity and stability.

The OH binding energy governs the ORR activity on Pt-based catalysts. Other indirect descriptors influence the OH binding energy, such as the lattice parameter, d-band center and the generalized coordination number. The ORR activity of Pt can be enhanced by modification of the geometric structure (atomic ensemble effects) and/or alteration of the electronic properties of the surface atoms (electronic effects). The latter can be tuned by alloying Pt with other metals. The desired effect of alloying is to weaken the OH binding energy by means of strain and/or ligand effects.

During the last few decades, catalyst developers have intensively studied alloys of Pt and late transition metals for the ORR: Pt-Ni, Pt-Cu, Pt-Fe and Pt-Co alloys all present an enhanced activity over pure Pt. Several studies have shown that a Pt overlayer is formed after immersion in acidic
electrolyte. The composition and stoichiometry of the alloy influence the Pt overlayer structure, and therefore the activity and stability. Nonetheless, these catalysts often tend to degrade via dealloying under operating fuel cell conditions. Appropriate synthesis conditions can lead to exceptional stability during short-term accelerated degradation tests. Even so, it is an open question whether they can survive long-term stability tests and whether the impressive enhancement factors obtained during ideal rotating disk electrode (RDE) experiments can be translated to fuel cells.

Recent studies have demonstrated that it is possible to obtain a remarkable improvement in activity by alloying Pt with early transition metals and rare earths. Our studies on polycrystalline Pt-early transition metal and Pt-lanthanide alloys show up to a 6-fold improvement in activity at 0.9 V vs. RHE over polycrystalline Pt. Moreover, the lanthanide alloys have a very negative enthalpy of formation, which may stabilize them kinetically against degradation via dealloying. Nevertheless, rare earths such as Gd are thermodynamically unstable towards dissolution in acid; their kinetic stability is contingent on the robustness of the Pt overlayers ability to protect the alloys from further losses and increase their stability.

We synthesized mass-selected nanoparticles of Pt-rare earth alloys using a magnetron nanoparticle source, which demonstrated excellent catalytic properties towards ORR, with a mass activity for Pt,Gd nanoparticles of 3.6 A/mgPt. At the same time, our extended X-ray absorption fine structure (EXAFS) experiments showed that the nanoparticles are under compressive strain the ORR activity increasing as the bulk compressive strain decreased. In order to mass produce these catalysts and insert them in real PEMFCs, a chemical synthesis method has to be implemented. However, it is very challenging to synthesize Pt-lanthanide alloys chemically, to the most part due to the high oxygen affinity of lanthanides.

Pt and Pt-late transition metal catalysts in thin film form have been fabricated successfully. In the field of fuel cells, nanostructured thin films (NSTFs) and mesostructured thin films of Pt and Pt-Ni have been fabricated and successfully tested for activity and stability towards ORR. The Pt loading have been optimized, and these catalysts demonstrated higher activity of the alloys as compared to pure Pt films. Morimoto and co-workers showed that atomic layer deposition (ALD) can be successfully employed to produce Pt electrodes on SiO2 substrates for testing on MEAs. More recently, Schmidt and co-workers investigated the influence of the growth mechanism on the surface structure of thin films fabricated by pulsed laser deposition (PLD), demonstrating that strain can...
enhance the ORR activity.\textsuperscript{57,58} Kim and co-workers fabricated nanoparticulate thin films of alloys of Pt-late transition metals together with Pt-Y and Pt-La for ORR using magnetron sputtering.\textsuperscript{59–61} Their results show that Pt\textsubscript{3}Y thin films presented enhanced activity and stability in comparison to the rest of the Pt-alloy thin films tested.

Herein we present a method for fabrication of thin films of Pt and Pt-lanthanide alloys via co-sputtering, together with the detailed procedures to measure the electrochemical activity and stability towards ORR, using a rotating ring-disk electrode (RRDE) setup. This article reports, for the first time, the fabrication, characterization and electrochemical performance of thin films of Pt-Gd alloys for the ORR.

The sputtering technique consists of a beam of ionized Ar hitting the target and knocking out atoms. Some of the ejected material will then deposit on the designated substrate. This technique has already been used for the preparation of catalysts in electrochemistry.\textsuperscript{62–64} The main advantage of thin films is that they can cover large areas and can be inexpensively mass-produced at a reasonable rate. For a model study of the electrochemical properties, it is much easier to work on fabricated thin films samples compared to expensive polycrystalline samples, which require Ar sputter cleaning treatment in UHV before the electrochemical.\textsuperscript{8} Thin films make it easier to test different stoichiometry of Pt alloys, in order to optimize the ratio and minimize the Pt loading.

The focus of this paper is to investigate the ORR activity and stability of model sputtered Pt and Pt\textsubscript{5}Gd thin films. We aim to give key recommendations in order to be able to fabricate these Pt-based thin films and carry out the electrochemical measurements in a reliable way, relevant for PEMFC devices.

2. Experimental

2.1. Sample preparation

Pt\textsubscript{5}Gd and Pt thin films were prepared by sputter deposition in UHV compatible system from AJA. The chamber constitutes of a load lock that can be pumped down before transferring samples into the main chamber, a transferring arm, and the main chamber, which can be pumped down to a base pressure of 10\textsuperscript{–9} mTorr. The load lock can be vented by flushing with Ar (purity 5.0). The chamber can contain up to 9 targets of which three can be used simultaneously. The distance between substrate and target is approximately 10 to 15 cm. The substrate holder is cooled down by a water cooler.
The main chamber is equipped with a quartz crystal microbalance (QCM) to measure the deposition rate, a shutter that can be placed in front of the substrates to prevent deposition and a heating wire, for substrate heating up to 850 °C. A schematic of the co-sputtering process is provided in Figure 1. Additionally, oxygen can be leaked into the chamber to fabricate oxides thin films e.g. of MnOx catalysts for oxygen evolution. The substrate consisted of Ar sputter cleaned and polished glassy carbon (GC) disks of 5 mm diameter from HTW Hochtemperatur-Werkstoffe.

![Schematic of the co-sputtering process](image)

**Figure 1.** (a) Schematic of the sputter deposition process. Ar gas is ionized to plasma to form Ar⁺ (blue). A negative bias is applied on the target material (gray), which causes the Ar⁺ to bombard the surface and knock atoms loose. Some of the target atoms then deposit on the grounded substrate. Magnets confine the plasma near the targets; (b) Schematic representation of the Pt₅Gd thin film on top of the glassy carbon disk; (c) Scanning electron microscope (SEM) image of dealloyment due to the presence of oxygen in a Pt₅Gd thin film.

A GC square plate (1 cm²) with polished top side was also loaded in the chamber for each deposition, to be used for XRD and XPS testing. The polishing procedure included a polishing step using a
polishing disk and diamond paste from Struers and a sonicating step. The polishing step consisted of mounting the disk on a rotating support; the paste was spread on it and the glassy carbon surface was put in contact for 30 to 60 s. The sonicating step involved three cycles of sonication, where one “sonication cycle” constituted 10 min sonication in water and 10 min sonication in isopropanol. The glassy carbons were subsequently dried with Ar. The cleanliness of the surface is crucial for a good thin film deposition since it minimizes the contamination and lowers the roughness.

Because of the high oxygen affinity of the lanthanides, they will react with minimal amounts of oxygen present in the chamber and form oxides. Such oxide formation will compromise the electrochemical measurement, since the alloy will not form, and when immersed in the acidic environment for the electrochemical testing, the lanthanide-oxides will leach out of the film, which will dealloy (Figure 1c). Therefore, it is crucial to develop deposition routines that minimize the amount of oxygen in the UHV system. Herein we transcribe the procedure for removing the oxygen traces from the UHV chamber in an efficient and reproducible way:

1) The glassy carbon substrates were loaded in the load lock. When the load lock pressure was at least 10⁻⁷ mTorr, they were then transferred to the main chamber.
2) The substrates were heated up to 200 °C to make sure every water trace on them evaporated.
3) Ar sputtering on the substrates was performed for 45 min to eliminate all contamination from the surface.
4) The shutter was positioned in front of the substrates to prevent deposition, while Ti was sputtered in the chamber for 30 to 45 min, acting as a Ti sublimation pump, and leading to the removal of oxygen.
5) The chamber was then pumped down for 10 to 12 h until reaching a base pressure of 10⁻⁹ mTorr.

The samples were deposited at 4 mbar with a 50 sccm Ar flow. For the scope of this article all the reported results are related to our standard thin film samples:
- Pure Pt sample of 40 nm deposited at 300 °C.
- Pt₅Gd sample of 50 nm deposited at 300 °C.

The Pt power for this deposition was 180 W, while the Gd power was between 25 and 30 W, adjusted before every set of deposition accordingly with a measurement taken with the QCM. After deposition, the temperature was kept at 300 °C for 10 min. The samples were cooled in the chamber for 2 to 3 h.
2.2. Electrochemical characterisation

All electrochemical measurements were performed in a cell using an RRDE setup. The data have been Ohmic drop corrected and presented vs. the reversible hydrogen electrode (RHE). Before every set of electrochemical measurements, all the glassware was cleaned in piranha solution (98 % H₂SO₄ (Merck, Emsure) and 30 % H₂O₂ (Merck, Emsure), 3:1 V/V) for at least 24 h. Several different cleaning procedures can be found in the literature. We use the piranha cleaning as we find it is most effective in removing traces of organic contamination and ensure reproducible measurements on Pt-based well-defined electrodes. The glassware was then rinsed with 18.2 MΩ cm Millipore water at least 5 times and sonicated for 30 min at 70 °C to remove all traces of the cleaning solution. The electrochemical cell was rinsed from piranha 5 times and then heated using an heating jacket to 90 °C. The temperature was maintained for some hours, and the water inside the cell was changed 5 to 6 times.

The electrochemical cell is shown in Figure 2, and consists of:

- Two Pt wires (Chempur 99.9 %, 0.5 mm diameter). The Pt wires fit into the side holes, one of which is used as counter electrode.
- A Hg/HgSO₄ reference electrode (Schott Instruments), fitted in a separate compartment ending with a Luggin capillary, which terminates as close as possible to the sample surface, in order to minimize the Ohmic drop from the electrolyte resistance. All the potentials in this study all refer to that of the RHE.
- A gas inlet placed on the side of the cell, which allows saturating the cell with gasses without inserting tubes directly into the electrolyte.
- An external glass jacket, which can be connected to a water heater for temperature control.

The electrolyte consisted of 0.1 M HClO₄ prepared from 70 % HClO₄ (Merck Suprapur, 99.99 % purity) and 18.2 MΩ cm Millipore water. Prior to the measurements, the cell was heated repeatedly to 90 °C using the water heater and rinsed 5 times with Millipore water, letting 20 min passing between each rinse. During one of the rinsing, bubbling N₂ through the glass bubbler helps eliminate eventual residues (e.g. sulphate anions from the piranha solution).

The samples were mounted on a rotating disk Teflon tip using Teflon U-cups. The tips and the U-cups have been purchased from Pine Instruments and have also been previously cleaned in piranha solution. To make the mounting as clean as possible, the samples were placed face down on a polypropylene
film (from Chemoplex) previously sonicated for 20 min at 50 °C in Millipore water. Before mounting the sample on the rotator, the tip was rinsed with Millipore water.66,67

Figure 2. (a) Photo of the electrochemical cell and (b) schematic representation of the cell. The main parts are visible: the Pt wire (counter electrode), the Luggin capillary, the bubbler, the heating jackets and the rotator where the shaft holding the RDE tip is mounted.

The electrochemical measurements were performed using a VMP2 multi-channel potentiostat (BioLogic Instruments), controlled from a computer using EC-Lab software. All the gases used were supplied by AGA with instrument 5.0 purities for Ar, N₂ and O₂ gases, instrument 4.5 for the H₂ gas and instrument 3.7 for the CO gas.

All experiments were performed at room temperature (23 °C) and maintained with the heated water jacket of the cell (see Figure 2). Before measuring the sputtered Pt-based thin films, we performed a test measurement with polycrystalline Pt (purchased from Pine, purity 99.99 %), to check the cleanliness of the cell. Before the measurement, the polycrystalline Pt electrode was flame annealed for 5 min, using a LPG torch (Proxxon), then cooled down in a glass bell containing Ar-saturated
atmosphere for 3 min. Flame-annealing (or sputter cleaning) is crucial for benchmarking polycrystalline Pt, in order to obtain a clean, well-defined and reproducible Pt surface. After flame-annealing, the electrode was cooled in an Ar. Once at room temperature, the electrode surface was protected with a droplet of H$_2$-saturated Millipore water, in order to mount the sample without introducing any sources of contamination from the atmosphere. The polycrystalline Pt sample was then mounted on the rotating disk electrode tip, using a previously sonicated polypropylene film as mounting stage. Any residual hydrogenated water was carefully removed from the walls of the polycrystalline electrode using lens paper. Then, the RDE tip was inserted into the electrolyte under potential control (0.05 V vs. RHE). In this potential range, it is assumed that only H adsorption occurs and there is no oxidation of the surface. We check the cleanliness of the system, and confirm that the flame-annealing and cooling procedures has been carried out correctly, by examining the features on the base cyclic voltammograms on polycrystalline Pt in N$_2$-saturated electrolyte, as we describe below. The ORR activity measured on flame-annealed polycrystalline Pt at 0.9 V vs. RHE using 1600 rpm and 50 mV/s scan rate is 1.9 ± 0.2 mA/cm$^2$. The same mounting procedure (except the flame-annealing) was repeated for thin films. The potential was held at 0.05 V vs. RHE during immersion. Having potential control is crucial for thin films since potential spikes can cause damages to the sample surfaces and ultimately delamination. The sample was cycled between 0.05 and 1.00 V vs. RHE at 200 mV/s in N$_2$-saturated electrolyte for 200-300 cycles, rotating at 400 rpm. The exact number of cycles depends on the specific sample, since some thin films can have a bit rougher surfaces than others, or have been in contact with air longer and thus will require more cycling to obtain a stable CV.

The uncompensated Ohmic resistance in an electrochemical system derives from a sum of different resistance factors in the electrochemical circuit. In this case, it is dominated by the resistance of the electrolyte solution between the working electrode and the tip of the Luggin capillary. This resistance also depends on external factors such as temperature, current density and pH. Therefore it has to be evaluated for each measurement, in order to meaningfully compare the different samples. The Ohmic resistance was measured by means of electrochemical impedance spectroscopy (EIS). This method consists of measuring a Nyquist plot of the impedance. The real part of the impedance at high frequencies is largely due to the series resistance of the system, whereas the imaginary part of the impedance spectra relates to charge transfer and capacitive effects. The built-in series resistance is
evaluated from the intersection of the linear regression of the imaginary impedance to the axis of the real impedance, typical evaluated in the 400 to 60 Hz range where noise contributions are negligible. No rotation was applied to the working electrode during this measurement, and the electrolyte was N2-saturated. The measured Ohmic resistance $R$ typically ranges from 25 to 30 $\Omega$. The $IR$ compensation was subsequently taken into account during the data treatment.

The RHE potential has been measured experimentally by bubbling H2 while rotating the working electrode at 1600 rpm and cycling between -0.74 and -0.70 V vs. Hg(0)/HgSO4. The value of the RHE potential can be read as the intercept with the current axes as this value represent the reduction/oxidation potential for hydrogen i.e. the RHE zero. Typical values for RHE potentials are between -0.717 and -0.725 V vs. Hg(0)/HgSO4. Using the EIS and RHE technique explained, all data were thus corrected:

$$U_{RHE} = U_{Hg|HgSO_4} - \Delta U_{Hg|HgSO_4} - R$$  \hspace{1cm} (2)

The ORR activity has been measured in O2-saturated 0.1 M HClO4 while cycling the working electrode between 0.00 and 1.00 V vs. RHE and rotating at 1600 rpm. The scan rate used was 50 mV/s and the sample was cycled until a stable CV was reached (normally around 20 cycles). It is important to note that a variety of scan rates have been used in the literature for measuring the ORR, which makes it challenging to directly compare results from different laboratories. The ORR activity increases with increased scan rate, and it is unclear if this is due to some reconstruction of the surface or impurities. At low scan rates, however, the CVs in N2 and O2 are not reproducible and they do not stabilize, therefore 50 mV/s has been chosen for the measurements.

2.3. Evaluation of the electrochemically active surface area (ECSA)

To properly compare the ORR activity of the Pt-based thin films, it is necessary to evaluate the electrochemically active surface area (ECSA), which is the area involved in the electrocatalytic reaction. Two commonly used methods to determine the ECSA are underpotential deposition of hydrogen (H$_{UPD}$) and CO-stripping. Both methods rely on the adsorption of different species on the active site of the catalyst, and subsequently a total desorption of these species from the surface by applying an appropriate potential. This “release” of charge can be evaluated by integrating over the relevant onset/offset potential and dividing by the scan rate as:
\[ Q_{\text{ECSA}} = \frac{dI}{du} \int_{U_{\text{onset}}}^{U_{\text{offset}}} I - I_{\text{off}} \, dU \]  

(3)

Where \( \frac{dU}{dt} \) is the scan rate, \( U_{\text{onset/offset}} \) relevant potential limits for the adsorption/desorption mechanism investigated and \( I_{\text{off}} \) is the background contribution of the CV. By evaluating the \( Q_{\text{ECSA}} \) one may estimate the ECSA area \( A_{\text{ECSA}} \) by assuming a pure Pt overlayer forms on the catalyst, and compare it to the charge per area estimates evaluated from extended Pt polycrystalline samples:

\[
\frac{q_{\text{ref.}}^{\text{ECSA}}}{q_{\text{ref.}}^{\text{ECSA}}} = \frac{\sigma_{\text{Pt-poly}}}{\sigma_{\text{Pt-poly}}} \Rightarrow A_{\text{ECSA}}^{\text{ref.}} = \frac{q_{\text{ref.}}^{\text{ECSA}}}{\sigma_{\text{Pt-poly}}} 
\]  

(4)

Where the charge per area \( \sigma_{\text{Pt-poly}}^{\text{ref.}} \) is some relevant reference experimental value, in our case either the charge associated with H UPD or that of CO oxidation on polycrystalline Pt.

a) Hydrogen underpotential deposition (H UPD):

This method consists of studying the affinity of the Pt electrode surface to adsorbed hydrogen by integrating the region corresponding to reversible underpotential deposited hydrogen, i.e. hydrogen adsorbing/desorbing at potentials more positive than the equilibrium potential for the hydrogen evolution reaction\textsuperscript{10,72}. The H UPD charges were compared to that of flame-annealed polycrystalline Pt, where the H UPD charge area was \( \sigma_{\text{H UPD}}^{\text{Pt-poly}} = 191 \pm 8 \mu \text{C/cm}^2 \), based on 20 independent measurements. This value is consistent with other reports in the literature.\textsuperscript{10,74}

b) Stripping of carbon monoxide:

This CO-stripping involves the electrochemical adsorption and oxidation of CO on Pt electrode surfaces, and the measurement of its potentiodynamic oxidation charge.\textsuperscript{75,76} Similar to the H UPD, the CO-stripping charge is correlated to that of polycrystalline Pt. The experimental procedure can be summarized as follows: The sample was cycled 3 times in Ar-saturated electrolyte at 10 mV/s. Then, the electrode was maintained at 0.05 V vs. RHE while bubbling CO for 3 min saturating the electrode surface. The electrode potential was maintained at 0.05 V vs. RHE for 30 min while bubbling Ar gas purging the remaining CO from the electrolyte. The potential was then swept between 0.05 V and 1.00 V vs. RHE at 10 mV/s. The following anodic sweep exhibits the well-known CO oxidation peak of the CO adsorbed on the Pt surface, as:

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

(6)
Following the CO oxidation, the sample was cycled for a couple of scans ensuring no CO induced changes to the base CV and complete CO desaturation of the electrolyte occurred.

2.4. Stability measurements

We performed accelerated degradation tests on the thin films. These consisted of 10,000 potential cycles between 0.60 and 1.00 V vs. RHE in O₂-saturated electrolyte at 100 mV/s and room temperature (23 °C). The choice is based on the protocols of both the U.S. Department of Energy 77 and the Fuel Cell Commercialization Conference in Japan. 78 We note that further degradation may take place at elevated temperatures. 79 Following the stability test, we changed the electrolyte and measured the Ohmic resistance, RHE potential, and ORR activity. We must note that we changed the electrolyte under potential control and with great care towards the electrode integrity.

2.5. X-ray Photoemission Spectroscopy (XPS) and X-Ray Diffraction (XRD) measurements

X-Ray Diffraction (XRD) measurements have been performed with a PANalytical X'Pert Pro equipment with an X-ray wavelength of 1.54 Å for the CuKα line. The glancing incident X-ray diffraction spectroscopy (GI-XRD) was performed for angles from 20 ° to 90 °.

X-ray Photoemission Spectroscopy (XPS) spectra for Pt alloys were recorded using an instrument from Theta Probe (Thermo Scientific). The base pressure in the chamber was 5x10⁻¹⁰ mbar, the analysis was done with monochromatized AlKα X-rays (1486.7 eV) and the electron energy analyzer had an acceptance angle of 60 °. No tilting of the sample was applied during measurement. Some samples were sputter cleaned to remove the first few layers of oxides and adsorbates from ambient sample transfer from deposition to XPS chamber. This was done using a 0.5 keV Ar⁺ 1.0 μA beam over a 6 x 6 mm² area for a few minutes. Several measurements on different locations of the samples were taken, using an X-ray beam spot size of 400 μm.

3. Results and discussion

3.1. Physical characterization
The XRD profile of a Pt thin film in comparison with the Pt powder reference is shown in Figure 3. It is possible to notice how the peaks match, meaning that a bulk structure of crystalline Pt is formed. The broadened peak around 43 ° is due to the interference from the carbon support. Figure 4 shows the XRD profile of a Pt_{2}Gd thin film, as compared with polycrystalline Pt_{2}Gd. The samples present a crystal structure similar to polycrystalline Pt_{2}Gd,\textsuperscript{46} and in accordance with the literature,\textsuperscript{80} with a hexagonal Cu_{2}Ca-type structure. This is an indication of the formation of an ordered intermetallic compound, even at the relatively low (300 °C) deposition temperature.

![XRD profile](image)

**Figure 3.** XRD on 40 nm Pt thin film deposited at 300 °C (black) as compared to Pt powder reference (blue).
Figure 4. XRD on a 50 nm Pt5Gd thin film deposited at 300 °C (blue) compared to Pt5Gd polycrystalline (red), with a schematic of the obtained crystal structure.

Figure 5 shows the Pt4f and the Gd4d peaks of a Pt5Gd thin film, as compared with bulk polycrystalline Pt5Gd samples. The peaks have been plotted with background subtraction (Shirley-type) and matched with the same peaks of a polycrystalline Pt5Gd reference sample. To ensure minimum signal from advantageous adsorbates after ambient transfer the samples were subjected to Ar sputter cleaning. Peak positions of the thin film seems to match those found for Pt5Gd bulk sample, indicating a Pt-Gd containing alloy was formed. However, from Figure 5b a slight shift on the order of 0.5 eV is observed for the Gd4d peak. This slight, but significant shift indicates at least some Gd-O coordination in the thin film surface and is caused by the fact that the thin films cannot be subjected to the same extended cleaning procedure as the polycrystalline sample due to their limited thickness.

To investigate the as-prepared thin film sample before and after electrochemical stability tests, XPS was conducted on samples which were not sputter cleaned. The ex situ XPS data obtained was moreover used as an indicator of unexpected species in the sputter deposited thin films. From the XPS survey (see Figure 6) and the zoom-ins of Pt4f, Gd4d, C1s and O1s peaks obtained before and after
stability test (see Figure 5) we can deduce that no unexpected metallic components have been incorporated into the thin films during fabrication. XPS zoom-ins of Pt4f, Gd4d, C1s and O1s peaks were also used to co-establish metallic ratios of the thin films. However, as XPS is a very surface sensitive technique and the as-prepared thin films are expected to energetically favor Pt surface termination, XPS could overestimate the metallic ratio of Pt vs. Gd.

**Figure 5.** XPS spectra of (a) Pt4f peaks and (b) Gd4d peaks measured on a 50 nm Pt5Gd thin film deposited at 300 °C (blue) and a bulk Pt5Gd polycrystalline sample (red), both Ar sputter cleaned.

**Figure 6.** XPS survey of Pt5Gd thin films as-prepared (red) and post 10,000 stability cycled (black), all samples subject to ambient conditions and not Ar sputter cleaned.
Figure 7 shows the non-sputter cleaned thin film sample as-prepared and after electrochemical tests (in both cases, the thin films had been ambient conditions before carrying out the XPS measurements). We were able to establish a rough elemental composition of the as-prepared films. The Pt:Gd:C:O composition percentages are respectively 40.0, 8.4, 28.6, and 23.0 %. The as-prepared Pt:Gd ratio from XPS is thus found to be 0.83:0.17, which corresponds to a 4.9 to 1.0 Pt:Gd ratio, close to the stoichiometric 5:1 ratio. Similarly, the Pt:Gd:C:O percentages of the Pt:Gd thin films after stability test are respectively 68.5, 2.6, 25.0, and 3.9 %. In this case, the Pt to Gd ratio increased to 26.3 to 1.0, likely due to the formation of the thick Pt overlayer, in agreement with our previous observations on polycrystalline Pt-lanthanide alloys.8,46,48

The peak associated with carbon in an oxidized state, denoted A in Figure 7a, disappear after electrochemistry, indicating that the carbon oxide has been removed from the surface of the thin film after the acid treatment. Moreover, Figure b indicates that at least some oxygen in a peak denoted B, likely in a metal-oxide state, is leached out the thin film in acid. One may speculate that the top-most layer of the as-prepared thin film consists of Pt, Gd, C, O and something resembling a native gadolinium oxide layer, which is removed during electrochemical cycling i.e. the surface of the thin film is somewhat oxidized however the bulk of the film is not.
Figure 7. XPS survey zoom-ins of Pt$_5$Gd as-prepared (red) and post 10,000 stability cycled (black) thin films (a) C1s (b) O1s (c) Pt4f and (d) Gd4d peaks with Shirley background (dashed), all samples subject to ambient conditions and not Ar sputter cleaned.

3.2. Electrochemical characterization

3.2.1. Electrochemically active surface area

Figure 8 shows a CV of a Pt$_5$Gd thin film in N$_2$-saturated 0.1 M HClO$_4$. The $Q_{\text{HUPD}}$ can be obtained as the average of both the H adsorption and H desorption regions, as follows:

$$Q_{\text{HUPD}}^{\text{ECSA}} = \frac{dI}{2dU} \left[ \int_{U_{\text{ad. onset}}}^{0.05 \text{ V vs. RHE}} I - I(U_{\text{H ad. onset}}) \, dU + \int_{U_{\text{H ad. offset}}}^{0.05 \text{ V vs. RHE}} I - I(U_{\text{H ad. offset}}) \, dU \right]$$ (5)
The above H\textsubscript{UPD} areas can be seen as the charge (blue) areas of Figure 8. For the Pt\textsubscript{5}Gd thin film sample, the measured charge was \( q_{\text{H}\textsubscript{UPD} Pt\textsubscript{5}Gd\textsubscript{thin\ film}} = 48.61 \mu C \). If we divide this value by the charge density (4) of a polycrystalline surface, we can get an estimate of the surface area of the thin film sample. The lower limit of 0.05 V vs. RHE in (5) has been established empirically as it is unclear when the Pt surface goes from H adsorption to H\textsubscript{2} evolution.\textsuperscript{10,72} We must note that the H\textsubscript{UPD} region might also contain a contribution from anion adsorption at steps.\textsuperscript{81} Moreover, hydrogen binding will vary from a flat polycrystalline sample compared to a rough one due to the increased presence of steps and kinks, locally changing the hydrogen saturation coverage.\textsuperscript{81}

Pt-based single-crystalline electrodes have been widely used as model surfaces to investigate the adsorption of H and OH.\textsuperscript{25,82} The H\textsubscript{UPD} area evaluation is also a commonly used technique for large surface Pt areas.\textsuperscript{72} However, discrepancies may arise from alloying, since altering the electronic properties of the Pt surface may modify the binding of H.\textsuperscript{83} As a consequence, the adsorption of H can be strongly suppressed by both strain and ligand effects, as recent works on both Pt-based single-crystalline\textsuperscript{25,82–84} and polycrystalline\textsuperscript{8} alloys demonstrate.

**Figure 8.** Base CV of a Pt\textsubscript{5}Gd thin film with current densities evaluated using the geometric area of the electrode. The blue areas designate the charge area considered for ECSA evaluation using H\textsubscript{UPD}. The CV is measured at room temperature, 50 mV/s and 400 rpm in N\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4}. 
The ECSA was also evaluated by the CO-stripping method. Figure 9 shows the characteristic CO oxidation peak of a Pt\textsubscript{5}Gd thin film sample. If we subtract the anodic background from the CO-stripping cycle and integrate the CO oxidation peak between the two current intersects (from \(U_1\) to \(U_2\) in Figure 9), it is possible to estimate the CO charge:

\[
Q_{ECSA}^{CO} = \frac{dI}{dU} \int_{U_2}^{U_1} I - I_{background} dU \quad (7)
\]

From the integral under the stripping peak, corrected against the background, we can evaluate the ECSA following (3). The CO-stripping method is useful not only for the evaluation of the surface area, but also for gathering some insight into the surface morphology of the catalysts, as shifts in potential for CO desorption peak(s) gives information of the uniformity of the samples.\textsuperscript{76,85} Varying CO desorption potentials may indicate different desorption sites available on the surface e.g. terrace, step, kink or edge sites.\textsuperscript{83,86,87} As CO oxidation is likely a two electron transfer process (6), the CO-stripping charge area is approximately double that of H\textsubscript{UPD}, therefore a value of 420 \(\mu\text{C/cm}^2\) has previously been used in other studies.\textsuperscript{72,73} However, from the evaluations on polycrystalline Pt samples, an empirical factor of 349 ± 9 \(\mu\text{C/cm}^2\) was found from earlier studies.\textsuperscript{70,88} Hence, for consistency, we used this factor for our thin films’ ECSA evaluation. Although the CO-stripping method has been widely used for ECSA evaluation, we are aware that it can cause the rearrangement of the surface due to the strong CO binding to the Pt surface.\textsuperscript{73} For instance, CO smoothens Pt(111) single-crystalline surfaces\textsuperscript{67,87} but it can roughen Pt/C nanoparticles.\textsuperscript{89} One benefit of the CO-stripping method as compared to the H\textsubscript{UPD} area evaluation method is that the former is less sensitive to changes in adsorption/desorption potentials.\textsuperscript{83} However, it is noteworthy to mention that changes in CO desorption potential (e.g. from varying the distribution of available step, terrace or kink sites) should shift the saturation coverages.\textsuperscript{83,90}

In the evaluation of the area using both the H\textsubscript{UPD} and CO-stripping methods, we have assumed that, for the thin film samples, saturation coverages per area will match those of polycrystalline Pt. Moreover, we assume that ligand effects from Gd alloying do not play an important role in the H\textsubscript{UPD} and CO adsorption/desorption potentials, due to the formation of a thick Pt overlayer (4 to 6 atomic layers of Pt).\textsuperscript{8,46}
Figure 9. CO-stripping peak of a Pt_{5}Gd thin film sample. The blue area is the area considered for ECSA evaluation. Full line CV shows CO oxidation and dashed line the background cycle. In this case, a charge of \( Q_{\text{Pt}_{5}\text{Gd}_{\text{thin film}}}^{\text{CO}} = 81.15 \, \mu \text{C} \) was found. The CV is measured at room temperature in HClO\(_4\), at 10 mV/s with 200 rpm rotation during CO desorption and no rotation during the cycling.

In summary, we used CO-stripping evaluated ECSAs to normalize the specific activity of the Pt-based thin films. We chose the ECSA evaluated from the CO oxidation charge rather than the H\(_{\text{UPD}}\) region due to the fact that the H\(_{\text{UPD}}\) region is heavily affected by strain effects,\(^8\) as we observed both on polycrystalline Pt-lanthanide alloys\(^8\) and Gd/Pt(111) single crystals.\(^8^4\) Furthermore, the integration limits can be easily defined and it is possible to evaluate the Pt_{5}Gd thin film base CVs before and after CO-stripping, thus ensuring no significant changes in CV features arises from the CO-stripping procedure.

### 3.2.2. Cyclic voltamograms in the absence of oxygen

Figure 10 shows the evolution of the Pt_{5}Gd thin film surface when cycled in the N\(_2\)-saturated HClO\(_4\) electrolyte. We observe that the shape or the CVs changes with cycling, especially during the first 50 cycles. This is partially due to the removal of surface impurities that had been deposited during transport between the sputter chamber and the electrochemical setup, but mostly due to the formation
of the Pt overlayer, and to the rearrangement of the surface to a minimum energy (stable) condition. Observing the rearrangement of the CVs is important since it is an indication of both the formation of the right catalysts surface and the cleanliness of the RDE setup apparatus. The initial activation cycles are performed at 50 mV/s in order to monitor and observe the evolution of the CVs. However, once a set behaviour of the evolution of the Pt5Gd thin film samples have been established, one may prefer to perform accelerated activation cycling (e.g. at 200 mV/s), as this lowers overall experiment time, minimizing contamination issues from prolonged electrochemical exposure.

Figure 10. Activation CVs in N2-saturated 0.1 M HClO4 at room temperature, 50 mV/s and 400 rpm for a Pt5Gd thin film.

Figure 11 shows the CVs in N2-saturated electrolyte of a Pt thin film compared with a flame-annealed bulk polycrystalline Pt (PtPoly). The observed differences in the CVs indicate different surface structure for the two Pt samples. This results in distinct adsorption/desorption energies for H, OH and O.81 Nevertheless, the roughness estimated with HUPD method difference less than 10% for the Pt and Pt5Gd thin film samples (see Table 1). We note the difference in the distinctiveness of the features associated with hydrogen adsorption/desorption at Pt(110) step sites at ~0.12 V vs. RHE and at Pt(100) step sites at ~0.28 V vs. RHE.91 It is observed that thin films have lower amount of (100) sites than polycrystalline Pt, which would be in agreement with an increase of (111) domains.92 Moreover, it is
worth mentioning that the presence of the (110) and (100) features in the polycrystalline Pt CVs indicates good cleanliness of the system, and shows that the flame-annealing procedure have been appropriately conducted.93

![Image of CVs](image.png)

**Figure 11.** Base CVs in N₂-saturated 0.1 M HClO₄ electrolyte of a Pt thin film (30 nm) deposited at 300 °C (green) compared with polycrystalline Pt (black), measured at room temperature, 400 rpm and 50 mV/s scan rate.

**Table 1.** Roughness and ECSA for the different samples.

*For extended surfaces, ECSA has been defined as the geometric electrode area.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Roughness Factor (HUPD)</th>
<th>Roughness Factor (CO-stripping)</th>
<th>( A_{ECSA}^{HUPD} ) [cm²]</th>
<th>( A_{ECSA}^{CO} ) [cm²]</th>
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<td>1.0</td>
<td>0.196</td>
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<tr>
<td>Pt5Gd polycrystalline*</td>
<td>1.0</td>
<td>1.0</td>
<td>0.196</td>
<td>0.196</td>
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<tr>
<td>Pt thin films</td>
<td>0.9 ± 0.1</td>
<td>1.0 ± 0.1</td>
<td>0.18 ± 0.04</td>
<td>0.19 ± 0.04</td>
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<tr>
<td>Pt5Gd thin films</td>
<td>1.6 ± 0.4</td>
<td>1.4 ± 0.2</td>
<td>0.25 ± 0.12</td>
<td>0.26 ± 0.08</td>
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</table>
Figure 12. CVs of a Pt$_5$Gd thin film (50 nm thick) compared with polycrystalline Pt$_5$Gd, Pt thin film (15 nm thick) and polycrystalline Pt. All CVs are measured in N$_2$-saturated 0.1 M HClO$_4$ at room temperature, with a rotation speed of 400 rpm, at 50 mV/s.

The CVs in N$_2$-saturated electrolyte of a Pt$_5$Gd thin film compared with Pt$_5$Gd polycrystalline sample and pure Pt are shown in Figure 12. As can be observed, the shape of the CVs on both Pt$_5$Gd thin film and polycrystalline Pt$_5$Gd presents similar characteristic features. The similar H adsorption region of the Pt$_5$Gd thin film and bulk crystalline sample suggests comparable surface areas. We estimated the roughness of the thin films using the CO-stripping method. Table 1 shows the roughness factors (calculated as the ratio $A_{ECSA}/A_{geo}$), and the average electrochemical surface area for the thin films as well as the polycrystalline samples. Figure shows the comparison between typical CO-stripping peaks for Pt and Pt$_5$Gd thin films. The roughness of the thin films is comparable with that of the polycrystalline samples, suggesting similar surface morphology, i.e. polycrystallinity. We also show a typical CO-stripping CV on a bulk polycrystalline Pt electrode. The pre-peak on polycrystalline Pt can be explained by the stripping of CO adsorbed at step sites, as proposed by Cuesta et al.
Figure 13. CO-stripping peaks for Pt and Pt₅Gd thin films compared with the CO-stripping on polycrystalline Pt. All the CVs were recorded in Ar-saturated 0.1 M HClO₄ at 10 mV/s and 200 rpm at room temperature. In this case, charges of $Q^{\text{CO}}_{\text{Pt₅Gd thin film}} = 81.14 \mu\text{C}$ (blue) and $Q^{\text{CO}}_{\text{Pt thin film}} = 67.32 \mu\text{C}$ (green) was found, corresponding to roughness factors of 1.2 and 1.0, respectively.

3.2.3. Oxygen reduction reaction activity and stability

The ORR catalytic activity was obtained in O₂-saturated electrolyte, cycling in a potential range between 0.00 and 1.00 V vs. RHE. Figure 14a shows the CVs on Pt and Pt₅Gd thin films, as well as polycrystalline Pt and Pt₅Gd, for comparison, in O₂-saturated 0.1 M HClO₄. Evidently, there is a considerable positive shift in the electrocatalytic activity of both Pt₅Gd thin films, as compared to pure Pt thin films and polycrystalline Pt, in the potential region of mixed kinetic transport. This means that the overpotential for the Pt₅Gd thin films has been substantially decreased, similar to our previous results on sputter-cleaned polycrystalline Pt₅Gd. Mass-transport corrected kinetic current $j_k$ can be extrapolated from the Koutecky-Levich relation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_l}$$ (8)
Where \( j \) is the measured total current density (corrected with \( \text{AESCA} \)) and \( j_l \) is the measured diffusion limited current density.

To have a graphic comparison of the catalytic activities, the logarithm of the kinetic current is plotted against the RHE potential to obtain a Tafel plot. Figure 14b shows the Tafel plots for Pt\(_5\)Gd thin film, polycrystalline Pt\(_5\)Gd, Pt thin film and polycrystalline Pt. The specific activities, i.e. the kinetic current density values, are calculated at 0.9 V vs. RHE. Pt\(_5\)Gd thin films show a 4.5-fold improvement in specific ORR activity compared to polycrystalline Pt, with an activity of \( 9.0 \pm 0.6 \text{ mA/cm}^2 \), and the result is comparable with the one obtained for polycrystalline Pt\(_5\)Gd exhibiting specific activities of \( 10.6 \pm 0.5 \text{ mA/cm}^2 \). Figure 14 also shows that the ORR activity of Pt thin films is considerably larger than that of bulk polycrystalline Pt. This is consistent with the (110)-like voltammetric features in the in the base CVs (Figures 11 and 12), as (110) steps\(^{13,95,12} \) seem to enhance the ORR activity.

**Figure 14.** ORR activity plots of Pt\(_5\)Gd and Pt thin films and polycrystalline samples, all obtained in O\(_2\)-saturated 0.1 M HClO\(_4\) at room temperature, 50 mV/s scan rate and 1600 rpm. (a) Anodic sweep of the geometric current density. (b) Tafel plot showing the kinetic current density evaluated using the CO evaluated ECSA.

ORR stability is also of profound relevance for ORR catalysts.\(^{6,8} \) We carried out stability tests consisting of 10,000 cycles between 0.60 and 1.00 V vs. RHE in O\(_2\)-saturated HClO\(_4\). Figure 15 shows the activity and stability of Pt\(_5\)Gd 50 nm thin films as compared with polycrystalline Pt\(_5\)Gd. The activities for both Pt thin films and polycrystalline Pt have also been plotted for comparison. Overall,
the thin films maintained around 80% of their initial activities, which is a value comparable to the one obtained for polycrystalline samples (around 85%). This means that the overall Pt\textsubscript{5}Gd thin films activity is almost 5 times higher than the one of polycrystalline Pt and more than doubles the one for pure Pt thin films, while still showing a >3-fold improvement over polycrystalline Pt after stability test.

![Figure 15. Specific activity at 0.9 V vs. RHE of Pt\textsubscript{5}Gd thin films and polycrystalline samples before and after stability tests, compared with pure Pt thin film and polycrystalline samples.](image)

**4. Conclusions**

In this study, we present the fabrication of Pt\textsubscript{5}Gd thin films via sputter deposition under UHV conditions, underlying the importance of an oxygen-free environment when dealing with lanthanides. We show benchmarking protocols to test the electrochemical performance of Pt-lanthanide thin films by means of cyclic voltammetry. XPS and XRD show the successful formation of an oxygen-free Pt\textsubscript{5}Gd thin film alloy, with a hexagonal Cu\textsubscript{5}Ca-type structure, in agreement with previous reports on polycrystalline Pt\textsubscript{5}Gd.\textsuperscript{8,46} We have used the rotating ring disk electrode technique to measure the ORR activities in acidic environment. Pt\textsubscript{5}Gd thin films show a 4.5-fold improvement compared to pure polycrystalline Pt, and a 2.5-fold improvement compared to Pt thin films. Pt\textsubscript{5}Gd presented similar
stability than polycrystalline $\text{Pt}_5\text{Gd}$,\textsuperscript{46} retaining ca. 80% of their initial ORR activity. The presented methods will facilitate the future fabrication and characterization of thin films and investigation of Pt-lanthanides alloys, enabling an easy comparison between different ORR catalysts. It also paves the way for thin films catalysts of Pt-rare earth alloys to be implemented and tested as ORR catalysts in PEMFCs.

**Acknowledgments**

We gratefully acknowledge the Danish Council for Strategic Research’s project NACORR (12-133817) for funding this work. *This work was supported by a research grant (9455) from VILLUM FONDEN.* M.E.-E. acknowledges the Danish Council for Independent Research for her Individual Postdoctoral grant and Sapere Aude: Research Talent grant. K. D. J. acknowledges funding from the KDFuelCell project of Denmark’s Innovation Fund, project 20735.

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Active site formation and stability of Gd/Pt(111) single crystals: an *in-situ* surface X-ray diffraction study


Active site formation and stability of Gd/Pt(111) single crystals: an in-situ surface X-ray diffraction study

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Keywords: Oxygen reduction, electrocatalysis, in-situ, Pt(111), Pt-alloy, X-ray diffraction

Abstract

Pt-Gd alloys present significant activity enhancement over pure Pt for the oxygen reduction reaction, both in the form of extended electrode surfaces and nanoparticulate alloys. A compressed Pt overlayer is formed on Gd/Pt(111) single-crystalline surfaces upon exposure to the electrolyte by acid leaching. Herein we present the strain and correlation lengths of the Pt overlayer using in-situ synchrotron surface-sensitive X-ray diffraction on Gd/Pt(111). The overlayer forms upon exposure to electrolyte under open circuit conditions and the compressive strain relaxes slightly upon repeated electrochemical cycling in the potential range 0.6 V to 1.0 V vs. the reversible hydrogen electrode (RHE). In addition, the strain relaxes strongly when exposing the electrode to 1.20 V vs. RHE and the crystalline thickness of the overlayer increases with potential above 1.3 V vs. RHE.
## List of Abbreviations

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- Symmetry factor of ORR reaction ...................................................... 98
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Z:
- Impedance in units of [Ω] ................................................................. 32
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- Impedance zero point in units of [Ω] .................................................. 32
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