Operando Spectro-electrochemical investigations of Pt and Pt-alloys as fuel cell catalysts

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Chapter 1

Introduction

The notion that excessive CO_2 emissions from decades of burning fossil fuels has driven mankind to the verge of a dangerous environmental predicament, has already been thoroughly exhausted in just about every thesis, publication, conference paper and book report. It is assumed that the reader already has that context, so that this introduction can focus on the state of the art of the research concerning platinum and its alloys as fuel cell catalysts. Pulling on the thread that the devil is in the details, this thesis explores the intricacies of the electrode-electrolyte interface of Pt-based catalysts and their effects on electrocatalyst performance using X-ray spectroscopy techniques.

The overall theme of this thesis is to complement the electrochemical data acquired in fuel cell research with in situ X-ray photoelectron spectroscopy (XPS) and soft X-ray absorption spectroscopy (XAS). On the basis of recent theoretical and experimental studies in the literature, it has been revealed that electrocatalysts experience dynamic changes under experimental conditions, adapting their initial state to the changing environment[1–3]. Therefore, in situ identification of these changes in the electrocatalyst is key to understanding the atomic features that are associated with the performance of the electrocatalyst, separating them from spectator species. Precisely decoding the atomic scale configurations under realistic operation conditions has been a long-standing challenge in the electrocatalysis community due to experimental challenges, which we try to address in this thesis. The methodology described in this thesis forms a general approach that can be used for a wide variety of electrocatalytic systems. However, here we have focused on the oxygen reduction reaction (ORR) on platinum based catalysts.

1.1 Oxygen Reduction Reaction (ORR) and Polymer Electrolyte Fuel Cells

Fuel cells have the potential to play a pivotal role in the green energy transition[4]. Their main role is to supply carbon neutral energy when and where it is needed using a renewable fuel such as green hydrogen. Platinum and its alloys are at present the benchmark catalysts for the widely used proton exchange membrane fuel cell (PEMFC) because of their relatively high stability and low activation barrier for both half-cell reactions, i.e. the hydrogen oxidation reaction and the ORR[5] (see Figure 1.1). To understand the reaction environment that these Pt catalysts experience, I briefly describe the basic working principle of the PEMFC. The cell is divided into an anode and a cathode chamber, separated by a proton exchange membrane (e.g. Nafion). The anode and the cathode are connected electrically through an external circuit to which the cell delivers electrical power. Hydrogen gas is introduced into the anode chamber where it is oxidized into protons (Hydrogen Oxidation Reaction, HOR) which travel through the PEM membrane towards the cathode chamber. The electrons released during the hydrogen oxidation travel through the external circuit to the cathode where they combine with protons and oxygen (from the air) to produce water via the oxygen reduction reaction (ORR). The Gibbs free energy change for the overall reaction is 237.14 kJ/mol$_{H2}$, so that the fuel cell could theoretically deliver a potential of 1.23 V. However, energy losses within the fuel cell reduce the potential delivered when current is drawn. These energy losses arise to a large extend from the high activation barrier for the ORR[6], making this a key research focus in fuel cell research.

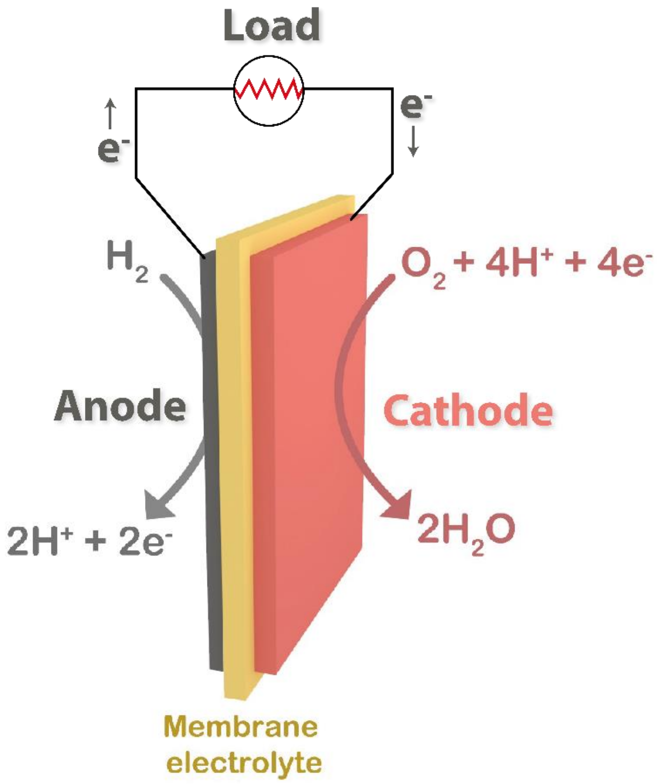

Figure 1.1: Schematic overview of a PEM Fuel Cell

Another key focus point for the research on Pt fuel cell catalysts is to lower the amount of Pt that is used in the catalyst film. The cost of the Pt in the fuel cell is one of the major hurdles towards its large-scale commercialization[7], since the Pt catalyst cost alone makes up for 40-60% of the price of the fuel cell stack. In this regard, extensive research has led to the reduction in Pt loading in commercial fuel cells, from 28 $mg_{Pt}cm^{-2}$ to 0.4 $mg_{Pt}cm^{-2}$ at the cathode and 0.05 $mg_{Pt}cm^{-2}$ at the anode[8], and there are continuous efforts to push towards even lower Pt loadings[9]. A key bottleneck for further reducing the catalyst loading is the degradation of the Pt catalyst on the cathode side during operation. Due to this degradation, an excess amount of catalyst has to be used to maintain long-term performance[10]. Therefore, understanding and mitigating Pt degradation is crucial to achieve affordable and long-term stable fuel cells.

1.2 Degradation Mechanisms in a Fuel Cell

There are a number of factors that are responsible for the decline in fuel cell performance over time such as platinum sintering, catalyst layer dissolution at the cathode and carbon support corrosion[11]. All of these primarily occur during changes in the potential of the fuel cell, for example when the fuel cell is started or when more or less current is drawn. Under these conditions, Pt atoms can detach from the catalyst nanoparticles and dissolve as ions into the polymer electrolyte. In part, these ions migrate towards the larger neighboring particles and attach to increase the particle size. This phenomenon is known as Ostwald ripening and becomes greater in magnitude with decreasing average particle size because of the greater thermodynamic driving force[12]. Ostwald ripening leads to an increasing average particle size over time and a decrease in the electrochemically active surface area (ECSA)[13,14], which lowers the catalytic activity during the ORR. In addition to Ostwald ripening, migration of the dissolved Pt into the polymer membrane also presents a major challenge, as it constitutes a loss off active material.

First hints about the chemistry involved in the Pt dissolution can be extracted from the thermodynamics of Pt. As depicted in the Pourbaix diagram[15] in Figure 1.2, metallic Pt is stable at potentials lower than ~1.05 V_{RHE} whereas higher oxidation states PtO (Pt^{2+}) and PtO_2 (Pt^{4+}) are stable at more positive potentials[8,16,17]. The onset oxidation on the surface of Pt nanoparticles starts a little earlier than predicted by the Pourbaix diagram (Figure 1.2), i.e. around 0.9 V_{RHE}. In relation to this, the rate of loss of active surface area of the catalyst has been shown to increase at potentials above 0.9 V_{RHE}. Furthermore, the dissolution rate is relatively much larger under dynamic potential conditions (load changes, startup/ shutdown) as compared to constant potential conditions(steady state operation)[18–20]. Therefore, Pt dissolution has been linked to the formation and reduction of Pt oxides[21,22]. Indeed, operando Pt dissolution measurements have shown that the Pt dissolution spikes during oxide formation and reduction, especially when the upper potential is >1.3 V_{RHE}[23–25]. In fuel cells, this is situation occurs during start-up/shut-down. Under these conditions, the fuel cell cathode potential temporarily reaches values of ~1.4 V_{RHE}, causing significant oxidation of the surface[26]. This potential spike lasts around a ~5 s before the potential returns to a steady state operation value (0.7 V_{RHE}-0.8 V_{RHE}) and causes a significant dissolution of the catalyst, as discussed earlier[26–30]. Despite that these start-up/shut-down potential spikes take up only a minute fraction of the operating time of a fuel cell, they cause around a 3rd of the overall deterioration[26,31], as shown in Figure 1.3. Due to this fast dissolution rate, (simulated) start-up/shut-down spikes are often used to study the mechanisms of Pt degradation.

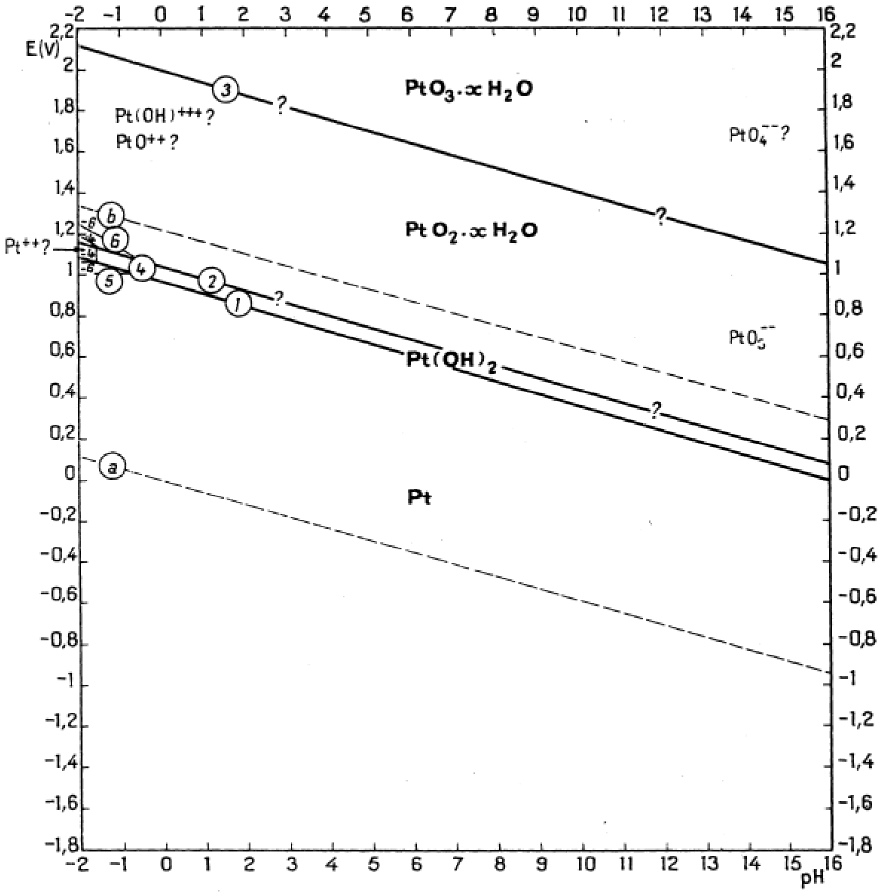

Figure 1.2: Potential-pH equilibrium diagram for the platinum-water system at 25°C[15]

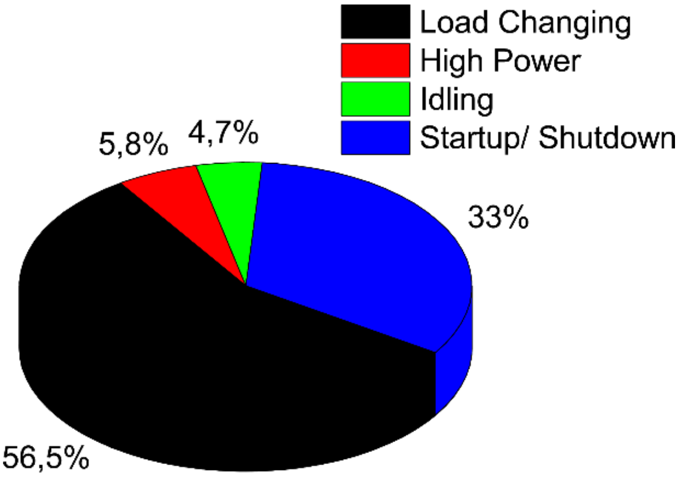

Figure 1.3: PEMFC degradation under different operating conditions[32]

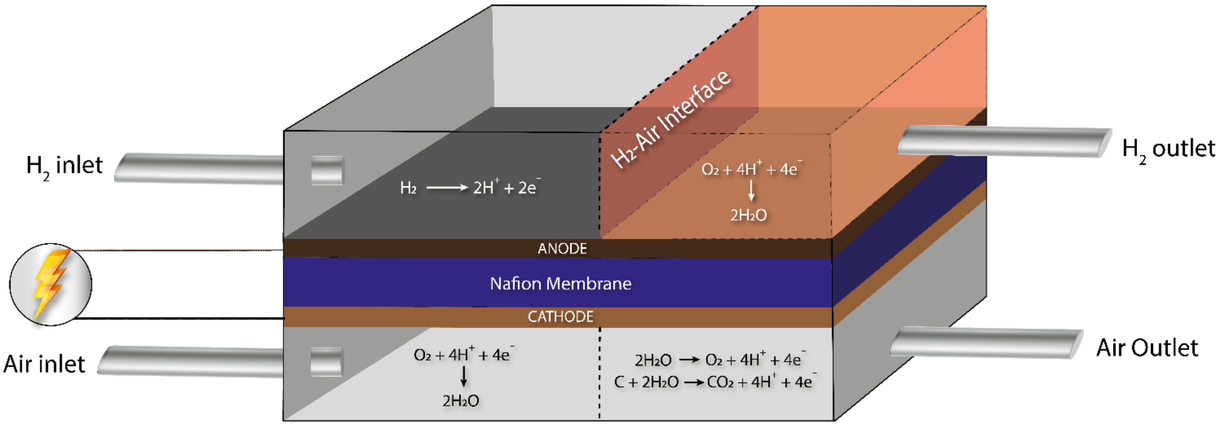

Figure 1.4: Establishment of H_2-Air interface in the Anodic chamber of the fuel cell, causing large potential spikes at the cathode during startup/ shutdown stages of the fuel cell

Zhang and coworkers[32] have investigated the reasons behind the transient voltage spikes and concluded that the formation of a H_2-Air interface (Figure 1.4) in the anodic chamber of the fuel cell produces momentary high potentials at the cathode surface, leading to oxidation of the catalyst as well as degradation of the catalyst support. Since the fuel cell startup and shut down fluctuations can be hard to simulate accurately, accelerated stress testing (AST) methods in regular liquid phase laboratory cells are frequently relied upon[33–35]. This is exemplified in Figure 1.5, where it can be seen that transient voltage fluctuations indeed have a rapid degradation effect on supported Pt nanoparticle catalyst, visible as a loss in active surface area. We will make use of this methodology in *Chapter 3.*

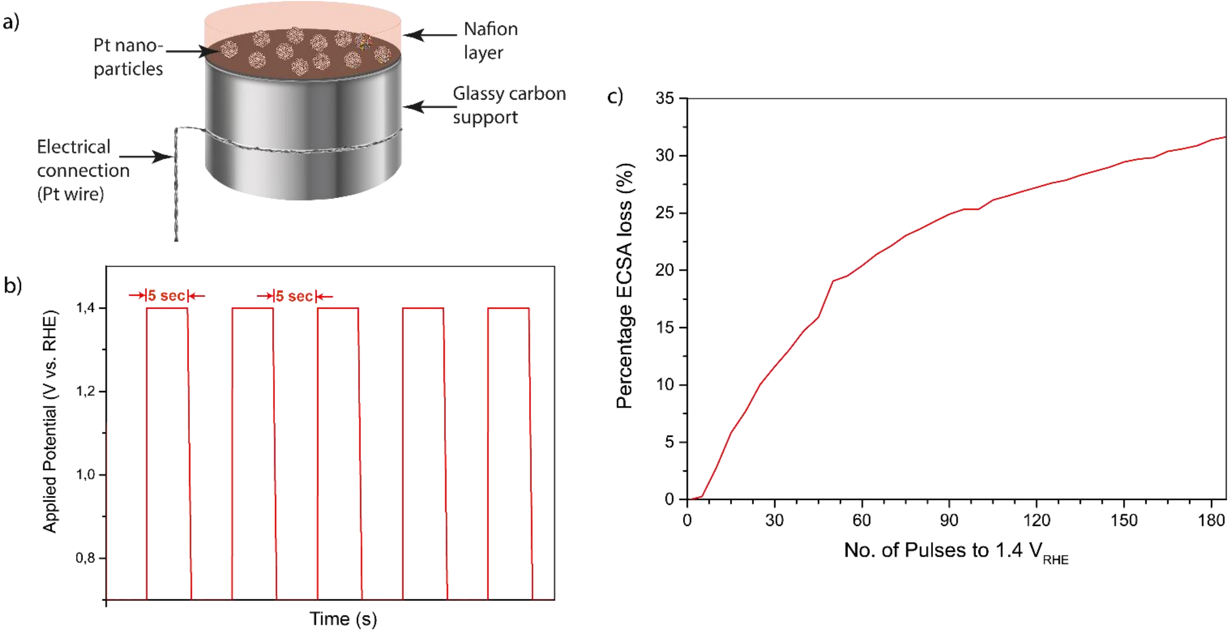

Figure 1.5: Pt transient degradation observed in 0.1 M H_2SO_4 electrolyte; a) shows 5 nm thick Pt nanoparticle catalyst sputter deposited onto a polished glassy carbon working electrode and coated with Nafion ionomer, b) shows the potential applied simulating transient voltage pulses, with 5 second duration for peak (1.4 V_{RHE}) and base (0.7 V_{RHE}) potentials and c) shows the progressive loss of active surface area as a consequence of transient degradation

While the discussion above shows that the conditions leading to fuel cell degradation are fairly well understood, the molecular-scale mechanisms for Pt degradation remain a debated topic in the electrochemical community. The integration of in situ X-ray spectroscopy alongside conventional electrochemical measurements has a strong potential for unraveling these mechanisms, as it offers the possibility to directly couple electrochemical signals to atomic-scale surface structures. In this thesis, I will explore this direction using in situ X-ray photoelectron spectroscopy and soft X-ray absorption spectroscopy.

In our Spectro-electrochemical studies, we have focused not only on pure Pt catalysts, but also on a Pt_3Ni alloy. In recent years, alloying Pt with transition metal catalysts such as Ni and Co has emerged as a highly effective strategy to improve the activity and stability of the fuel cell catalyst. Through modulation of the (electronic) structure of the surface Pt layers[36,37], Pt-Ni alloy catalysts to have exceptionally high ORR activity when compared to benchmark commercial Pt catalysts[38,39]. Also, catalyst degradation studies on Pt-alloy catalysts have revealed the suppression of mechanisms such as coalescence and Ostwald ripening[40].

1.3 Near-ambient Pressure X-ray Photoelectron Spectroscopy

To facilitate the Spectro-electrochemical analysis of my samples and to be able to do that independent of the time and logistical limitations of the synchrotron, I undertook the task of commissioning the in situ X-ray Photoelectron Spectroscopy set-up at our own lab in the Leiden Institute of Chemistry. From buying the smallest of the screws to facilitating the purchase of the analyzer module, today it stands in all its glory measuring both ex situ and in situ electrochemical samples. The purpose of this section is to refresh the reader's knowledge about the working principle of in situ XPS.

Starting off with the customary tribute to the inventors, the concept of XPS is based on the photoelectric effect discovered by Heinrich Hertz in 1887. Photoemission as a result of irradiation by X-rays was first discovered in 1914 by Robinson and Rawlinson, and its first demonstration as a method of material analysis can be accredited to Steinhardt and Serfass in 1951[41]. The bulk of the work done to formally develop XPS as it is used today is attributed to Kai Siegbahn from the University of Upsala in the 1970s, for which he was awarded the Nobel prize in 1981[42].

XPS is a surface-sensitive technique where soft X-rays (<2 keV) are bombarded onto the sample, which excites electrons inside the material[43,44], as shown schematically in Figure 1.6. The electrons absorb the photon energy and are expelled from the material, after which their kinetic energy is measured by the electron energy analyzer. The emission of the electron is a result of complete transfer of the photon energy to the electron, which can be expressed mathematically through Equation 1[45] .

$$h\upsilon = B.E + K.E + \boldsymbol{\phi}_{spectrometer} \qquad (1)$$

where $h\upsilon$ is the energy of the incoming X-rays, B.E and K.E are the binding energy and the kinetic energy of the core electron and $\boldsymbol{\phi}_{spectrometer}$ is the spectrometer work function, which is a constant. Using Equation 1, the measured kinetic energy can be converted into a binding energy. This binding energy is typical to the element and core level from which the electron was ejected. Consequently, an XPS spectrum displays separate peaks for every element and core level, as exemplified in Figure 1.7.

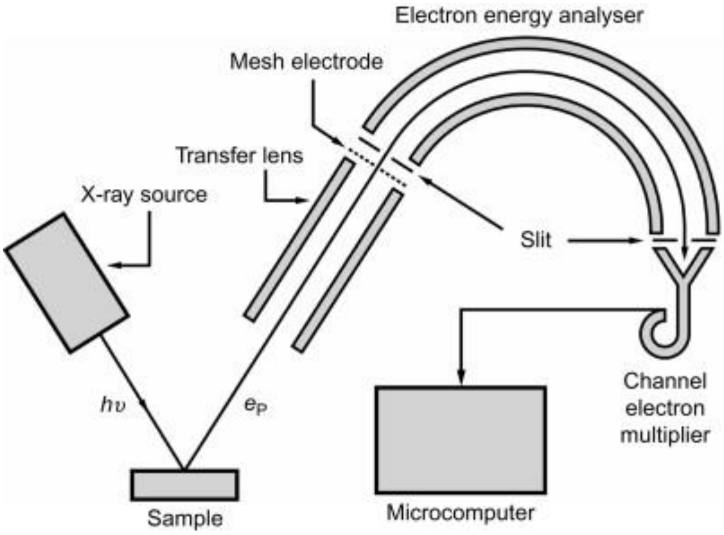

Figure 1.6: Working principal of the XPS [46]

Figure 1.7 shows the XPS survey spectrum of a gold single crystal electrode, where the peaks from different Au core levels can be seen. The spectrum also shows O 1*s* and C 1s peaks, originating from adsorbates on the surface. This sensitivity to surface species is a key property of XPS, which originates from the measurement principle: only the photo-electrons emitted a few nanometers from the surface will be able to make it out of the sample to reach the detector. As a result, the detected XPS signal only reflects the properties of the top 1-8 nm of the sample.

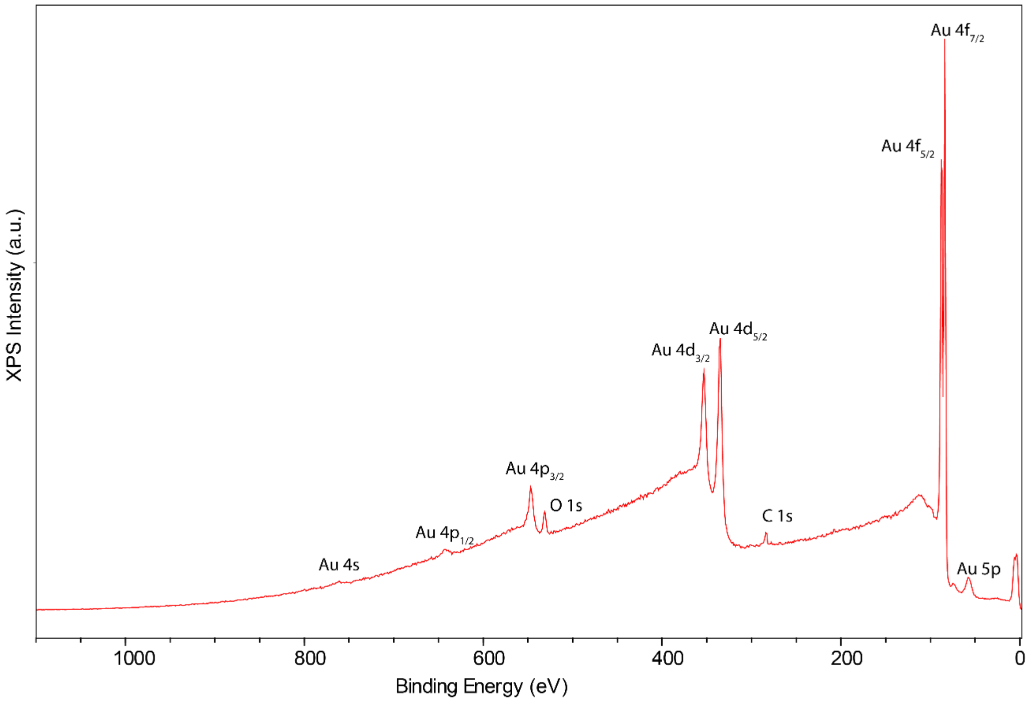

Figure 1.7: XPS Survey spectrum of an Au electrode

XPS experiments are normally done in an ultra-high vacuum environment to reduce the scattering of the emitted photoelectrons by gas phase molecules as they fly from the sample to the detector, and to avoid surface contamination. Also, the X-ray source operates at a very high voltage (~15 kV) and will cause arcing even at low vacuum pressures.

In near-ambient pressure XPS (NAP-XPS), the latter problem is solved by introducing a silicon nitride (SiN_x) window, which separates the measurement chamber from the X-ray source enabling the measurement chamber to operate at a higher (near-ambient, ~1 mbar) pressures while the X-ray source is at a high vacuum. In addition, several differential pumping stages are placed between the main chamber and the electron energy analyzer, producing ~9 orders of magnitude reduction in pressure. This greatly reduces scattering of the photoelectrons with gas molecules, making it possible to detect photoelectrons while there is a mbar pressure in the main chamber. In this way, the catalyst-adsorbate interaction can be probed under reaction conditions, which is critical for correlating the activity and stability of a catalyst with the change in its structural properties under reaction conditions.

The instrument present in our lab is an electrochemical NAP-XPS, which is capable of doing precisely that; resolving the oxidation states at the surface as well as the chemical state of the adsorbates under electrochemical conditions. To maintain a stable electrolyte film on the electrode surface under vacuum conditions, the electrocatalyst is sandwiched between a membrane and bilayer graphene, as further detailed in *Chapter 2*. Previously, access to membrane-based electrochemical XPS was limited to a few synchrotron beamlines in the world and even those were highly limited in the choice of electrolytes. Our setup removes both of these limitations and allows us to employ XPS to investigate changes in both sides of the electrode-electrolyte interface as a function of applied potential. This enables us to study a wide array of reactions under operando electrochemical conditions. The details of this instrument will be discussed in *Chapter 2* of this thesis.

1.4 Soft X-ray Absorption Spectroscopy

Another spectroscopy technique that was employed using the same experimental geometry, was soft X-ray Absorption Spectroscopy (XAS). XAS is a powerful tool which yields element-specific information about the unoccupied states in the electronic structure of the catalyst. Unlike XPS, the X-ray energy is swept during a measurement, and the X-ray absorption as a function of X-ray energy is measured. Due to the requirement of a tunable X-ray energy, one needs to go to a synchrotron facility for the measurements.

In the studies presented in this thesis XAS is used to complement XPS. The excitations of core electrons to unoccupied valence states are highly sensitive to the bonding environment of an atom, often more so than in XPS. In the following chapters, we will exploit this sensitivity to track subtle changes in the bonding configuration and electronic structure of the catalyst.

The photon energy of the X-rays defines the type of XAS being used; they are broadly categorized into soft (<2 keV), tender (2-5 keV) and hard X-rays (>5 keV)[47]. Due to the nature of absorption edges required in the research work presented in this thesis, we rely on soft X-rays for our XAS measurements.

1.5 Outline of the thesis

This thesis aims to combine electrochemical measurements with in situ electrochemical X-ray spectroscopy to explore the (near) surface chemistry of fuel cell catalysts, addressing the mechanisms responsible for their activity and stability.

Chapter 2 presents the details of the in situ electrochemical NAP-XPS commissioned at Leiden Institute of Chemistry. We provide the details of the design and the components used to construct the instrument, and highlight its application to study all components of the electrode-electrolyte interface in electrochemical systems using the case study of the Pt-0.1 M H_2SO_4 interface.

Chapter 3 explores the evolution of oxidation states of Pt within the potential range relevant for fuel cell start-up degradation. We present a data model comparing the electrochemical signals measured during AST cycles to the oxidation state evolution detected by in situ spectroscopy, which directly links electrochemistry to the surface oxide structure on the Pt nanoparticles.

Chapter 4 describes the potential-dependent restructuring of a Pt_3Ni alloy catalyst. We show that, even though the catalyst surface of the Pt-alloy catalyst is composed of pure Pt, the subsurface Ni takes part in the surface chemistry via electron density donation and subsurface migration. We show that this migration has a profound effect on the catalytic activity of the material, making the catalytic properties of the Pt-Ni alloy potential-dependent.

I believe that in order design the optimal fuel cell catalyst, we have to improve our understanding right down to the Pt atom, understand its environment, see what it sees at reaction conditions, so in short: try to observe the world from its point of view. Through the course of these chapters, we try to achieve that by recreating those conditions and then probing them spectroscopically in real time to improve the atomistic understanding of the electrode-electrolyte interface. I hope the readers find that journey as insightful as I did.

References

(1) Chang, C. J.; Lin, S. C.; Chen, H. C.; Wang, J.; Zheng, K. J.; Zhu, Y.; Chen, H. M. Dynamic Reoxidation/Reduction-Driven Atomic Interdiffusion for Highly Selective CO2Reduction toward Methane. *J Am Chem Soc* **2020**, *142* (28), 12119–12132. https://doi.org/10.1021/jacs.0c01859.

(2) Wang, J.; Tan, H. Y.; Zhu, Y.; Chu, H.; Chen, H. M. Linking the Dynamic Chemical State of Catalysts with the Product Profile of Electrocatalytic CO2 Reduction. *Angewandte Chemie - International Edition* **2021**, *60* (32), 17254–17267. https://doi.org/10.1002/anie.202017181.

(3) Zhu, Y.; Wang, J.; Chu, H.; Chu, Y. C.; Chen, H. M. In Situ/ Operando Studies for Designing Next-Generation Electrocatalysts. *ACS Energy Letters* **2020**, *5* (4), 1281–1291. https://doi.org/10.1021/acsenergylett.0c00305.

(4) Zawodzinski, C.; Gottesfeld, S.; Materials, E.; Group, D.; Lahoralory, L. A. N.; Alamos, L. PEM Fuel Cells for Transportationand Stationary Generation Applications. *International Association of Hydrogen Energy* **1997**, *22*, 1137–1144.

(5) Rasmussen, K. D.; Wenzel, H.; Bangs, C.; Petavratzi, E.; Liu, G. Platinum Demand and Potential Bottlenecks in the Global Green Transition: A Dynamic Material Flow Analysis. *Environ Sci Technol* **2019**, 11541–11551. https://doi.org/10.1021/acs.est.9b01912.

(6) Borup, R.; Meyers, J.; Pivovar, B.; Kim, Y. S.; Mukundan, R.; Garland, N.; Myers, D.; Wilson, M.; Garzon, F.; Wood, D.; Zelenay, P.; More, K.; Stroh, K.; Zawodzinski, T.; Boncella, X. J.; Mcgrath, J. E.; Inaba, O. M.; Miyatake, K.; Hori, M.; Ota, K.; Ogumi, Z.; Miyata, S.; Nishikata, A.; Siroma, Z.; Uchimoto, Y.; Yasuda, K.; Kimijima, K.; Iwashita, N. Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation. *Chem Rev* **2007**, *107* (10), 3904–3951. https://doi.org/10.1021/cr050182l.

(7) US Department of Energy. Heavy-Duty Fuel Cell System Cost - 2022. *DOE Hydrogen and Fuel Cells Program Record* **2023**, 1–11.

(8) Yousfi-steiner, N.; Moc, P. A Review on Polymer Electrolyte Membrane Fuel Cell Catalyst Degradation and Starvation Issues : Causes , Consequences and Diagnostic for Mitigation. **2009**, *194*, 130–145. https://doi.org/10.1016/j.jpowsour.2009.03.060.

(9) Tang, H.; Geng, K.; Aili, D.; Ju, Q.; Pan, J.; Chao, G.; Yin, X.; Guo, X.; Li, Q.; Li, N. Low Pt Loading for High-Performance Fuel Cell Electrodes Enabled by Hydrogen-Bonding Microporous Polymer Binders. *Nat Commun* **2022**, *13* (1). https://doi.org/10.1038/s41467-022-34489-x.

(10) Wu, J.; Zi, X.; Martin, J. J.; Wang, H.; Zhang, J.; Shen, J.; Wu, S.; Merida, W. A Review of PEM Fuel Cell Durability : Degradation Mechanisms and Mitigation Strategies. **2008**, *184*, 104–119. https://doi.org/10.1016/j.jpowsour.2008.06.006.

(11) Yu, Y.; Li, H.; Wang, H.; Yuan, X.; Wang, G.; Pan, M. A Review on Performance Degradation of Proton Exchange Membrane Fuel Cells during Startup and Shutdown Processes : Causes , Consequences , and Mitigation Strategies. *J Power Sources* **2012**, *205* (1), 10–23. https://doi.org/10.1016/j.jpowsour.2012.01.059.

(12) Yu, Y.; Tu, Z.; Zhang, H.; Zhan, Z.; Pan, M. Comparison of Degradation Behaviors for Open-Ended and Closed Proton Exchange Membrane Fuel Cells during Startup and Shutdown Cycles. *J Power Sources* **2011**, *196* (1), 5077–5083. https://doi.org/10.1016/j.jpowsour.2011.01.075.

(13) Lopes, P. P.; Tripkovic, D.; Martins, P. F. B. D. B. D.; Strmcnik, D.; Ticianelli, E. A.; Stamenkovic, V. R.; Markovic, N. M. Dynamics of Electrochemical Pt Dissolution at Atomic and Molecular Levels. *Journal of Electroanalytical Chemistry* **2017**, *819* (September), 0–1. https://doi.org/10.1016/j.jelechem.2017.09.047.

(14) Cherevko, S.; Zeradjanin, A. R.; Keeley, G. P.; Mayrhofer, K. J. J. A Comparative Study on Gold and Platinum Dissolution in Acidic and Alkaline Media. *J Electrochem Soc* **2014**, *161* (12), H822–H830. https://doi.org/10.1149/2.0881412jes.

(15) Goeke, R. S.; Datye, A. K.; Atanassov, P.; St-Pierre, J. Model Electrode Structures for Studies of Electrocatalyst Degradation. *ECS Trans* **2010**, *33* (1), 361–368. https://doi.org/10.1149/1.3484534.

(16) MOSELEY, P. T. International Workshop on Degradation Issues in Fuel Cells. *J Power Sources* **2008**, *182* (2), 389–475.

(17) Merte, L. R.; Behafarid, F.; Miller, D. J.; Friebel, D.; Cho, S.; Mbuga, F.; Sokaras, D.; Alonso-mori, R.; Weng, T. C.; Nordlund, D.; Nilsson, A.; Cuenya, B. R.; Roldan Cuenya, B. Electrochemical Oxidation of Size-Selected Pt Nanoparticles Studied Using in Situ High-Energy-Resolution X - Ray Absorption Spectroscopy. *ACS Catal* **2012**, *2* (11), 2371–2376. https://doi.org/10.1021/cs300494f.

(18) Ettingshausen, F.; Kleemann, J.; Marcu, A.; Toth, G.; Fuess, H.; Roth, C. Dissolution and Migration of Platinum in PEMFCs Investigated for Start/Stop Cycling and High Potential Degradation. *Fuel Cells* **2011**, *11* (2), 238–245. https://doi.org/10.1002/fuce.201000051.

(19) Borup, R. L.; Davey, J. R.; Garzon, F. H.; Wood, D. L.; Inbody, M. A. PEM Fuel Cell Electrocatalyst Durability Measurements. *J Power Sources* **2006**, *163* (1 SPEC. ISS.), 76–81. https://doi.org/10.1016/j.jpowsour.2006.03.009.

(20) Guilminot, E.; Corcella, A.; Charlot, F.; Maillard, F.; Chatenet, M. Detection of Pt[Sup Z+] Ions and Pt Nanoparticles Inside the Membrane of a Used PEMFC. *J Electrochem Soc* **2007**, *154* (1), B96. https://doi.org/10.1149/1.2388863.

(21) Ahluwalia, R. K.; Arisetty, S.; Peng, J.-K.; Subbaraman, R.; Wang, X.; Kariuki, N.; Myers, D. J.; Mukundan, R.; Borup, R.; Polevaya, O. Dynamics of Particle Growth and Electrochemical Surface Area Loss Due to Platinum Dissolution. *J Electrochem Soc* **2014**, *161* (3), F291–F304. https://doi.org/10.1149/2.051403jes.

(22) Mitsushima, S.; Kawahara, S.; Ota, K.; Kamiya, N. Consumption Rate of Pt under Potential Cycling. *J Electrochem Soc* **2007**, *154* (2), B153. https://doi.org/10.1149/1.2400596.

(23) Topalov, A. A.; Cherevko, S.; Zeradjanin, A. R.; Meier, J. C.; Katsounaros, I.; Mayrhofer, K. J. J. Towards a Comprehensive Understanding of Platinum Dissolution in Acidic Media. *Chem Sci* **2014**, *5* (2), 631–638. https://doi.org/10.1039/c3sc52411f.

(24) Topalov, A. A.; Katsounaros, I.; Auinger, M.; Cherevko, S.; Meier, J. C.; Klemm, S. O.; Mayrhofer, K. J. J. Dissolution of Platinum: Limits for the Deployment of Electrochemical Energy Conversion? *Angewandte Chemie - International Edition* **2012**, *51* (50), 12613–12615. https://doi.org/10.1002/anie.201207256.

(25) Cherevko, S.; Keeley, G. P.; Geiger, S.; Zeradjanin, A. R.; Hodnik, N.; Kulyk, N.; Mayrhofer, K. J. J. Dissolution of Platinum in the Operational Range of Fuel Cells. *ChemElectroChem* **2015**, *2* (10), 1471–1478. https://doi.org/10.1002/celc.201500098.

(26) Ferreira-aparicio, P.; Chaparro, A. M.; Folgado, M. A.; Conde, J. J.; Brightman, E.; Hinds, G.; Antonia, M.; Conde, J. J.; Brightman, E.; Hinds, G. Degradation Study by Start-Up/Shut-Down Cycling of Superhydrophobic Electrosprayed Catalyst Layers Using a Localized Reference Electrode Technique. *ACS Appl Mater Interfaces* **2017**, *9* (1), 10626–10636. https://doi.org/10.1021/acsami.6b15581.

(27) Jo, Yooyeon; Cho, Eunae; Kim, J. A Study on Performance Degradation of PEMFC by Repetitive Startup_Shutdown Cycling. *Transacitons of the Korean Hydrogen and New Energy Society* **2009**, *20* (8), 318–322.

(28) Babu, S. K.; Spernjak, D.; Dillet, J.; Lamibrac, A.; Maranzana, G.; Didierjean, S.; Lottin, O.; Borup, R. L.; Mukundan, R. Spatially Resolved Degradation during Startup and Shutdown in Polymer Electrolyte Membrane Fuel Cell Operation. *Appl Energy* **2019**, *254* (August), 113659. https://doi.org/10.1016/j.apenergy.2019.113659.

(29) Joo, S.; Kim, S.; In, J.; Woong, C.; Lee, J.; Song, I.; Lee, N.; Kim, K.; Park, J. Lifetime Prediction of a Polymer Electrolyte Membrane Fuel Cell via an Accelerated Startup e Shutdown Cycle Test. *Int J Hydrogen Energy* **2012**, *37* (12), 9775–9781. https://doi.org/10.1016/j.ijhydene.2012.03.104.

(30) Ã, P. P.; Chang, Q.; Tang, T. A Quick Evaluating Method for Automotive Fuel Cell Lifetime. *Int J Hydrogen Energy* **2008**, *33* (1), 3829–3836. https://doi.org/10.1016/j.ijhydene.2008.04.048.

(31) Bruijn, F. A. De; Dam, V. A. T.; Janssen, G. J. M. Review : Durability and Degradation Issues of PEM Fuel Cell Components. *Fuel Cells* **2008**, *8* (1), 3–22. https://doi.org/10.1002/fuce.200700053.

(32) Zhang, T.; Wang, P.; Chen, H.; Pei, P. A Review of Automotive Proton Exchange Membrane Fuel Cell Degradation under Start-Stop Operating Condition. *Appl Energy* **2018**, *223* (January), 249–262. https://doi.org/10.1016/j.apenergy.2018.04.049.

(33) Myers, D. J.; Wang, X.; Smith, M. C.; More, K. L. Potentiostatic and Potential Cycling Dissolution of Polycrystalline Platinum and Platinum Nano-Particle Fuel Cell Catalysts. *J Electrochem Soc* **2018**, *165* (6), F3178–F3190. https://doi.org/10.1149/2.0211806jes.

(34) Mitsushima, S.; Koizumi, Y.; Uzuka, S.; Ota, K. I. Dissolution of Platinum in Acidic Media. *Electrochim Acta* **2008**, *54* (2), 455–460. https://doi.org/10.1016/j.electacta.2008.07.052.

(35) Shao-Horn, Y.; Sheng, W. C.; Chen, S.; Ferreira, P. J.; Holby, E. F.; Morgan, D. Instability of Supported Platinum Nanoparticles in Low-Temperature Fuel Cells. *Top Catal* **2007**, *46* (3–4), 285–305. https://doi.org/10.1007/s11244-007-9000-0.

(36) Markovié, N. M.; Gasteiger, H. A.; Ross, P. N.; Division, M. S. Oxygen Reduction on Platinum Low Index Single Crystal Surfaces in Sulfuric Acid Solution. **1995**, *99* (11), 3411–3415.

(37) Brazovski, S. A.; Rice, M. J.; Mele, E. J.; Jackiw, R.; Semenoff, G.; Goldstone, J.; Wilczek, F.; Kivelson, S.; Ortega, J.; Flores, F.; Yeom, H. W.; Thouless, D. J.; Niu, Q.; Thouless, D. J.; Hughes, T. L.; Peierls, R. F.; Marzari, N.; Mostofi, A. A.; Yates, J. R.; Souza, I.; Vanderbilt, D.; Xiao, D.; Niu, Q. Identification of Active Sites in CO Oxidation and Water-Gas Shift over Supported Pt Catalysts. **2015**, *350* (6257), 185–189.

(38) Bunch, J. S.; Van Der Zande, A. M.; Verbridge, S. S.; Frank, I. W.; Tanenbaum, D. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L. Improved Oxygen Reduction Activity on Pt3Ni(111) via Increased Surface Site Availability. *Science (1979)* **2007**, *315* (5811), 490–493. https://doi.org/10.1126/science.1136836.

(39) Cui, C.; Gan, L.; Heggen, M.; Rudi, S.; Strasser, P. Compositional Segregation in Shaped Pt Alloy Nanoparticles and Their Structural Behaviour during Electrocatalysis. *Nat Mater* **2013**, *12* (8), 765–771. https://doi.org/10.1038/nmat3668.

(40) Colón-Mercado, H. R.; Popov, B. N. Stability of Platinum Based Alloy Cathode Catalysts in PEM Fuel Cells. *J Power Sources* **2006**, *155* (2), 253–263. https://doi.org/10.1016/j.jpowsour.2005.05.011.

(41) Steinhardt, R. G.; Serfass, E. J. X-Ray Photoelectron Spectrometer for Chemical Analysis. *Anal Chem* **1951**, *23* (11), 1585–1590. https://doi.org/10.1021/ac60059a019.

(42) Siegbahn, K. Electron Spectroscopy for Atoms, Molecules and Condensed Matter - an Overview. *J Electron Spectros Relat Phenomena* **1985**, *36* (2), 113–129. https://doi.org/10.1016/0368-2048(85)80013-X.

(43) J., C. *Handbook of X-Ray Photoelectron Spectroscopy*; 1992.

(44) Susi, T.; Pichler, T.; Ayala, P. X-Ray Photoelectron Spectroscopy of Graphitic Carbon Nanomaterials Doped with Heteroatoms. *Beilstein Journal of Nanotechnology* **2015**, *6* (1), 177–192. https://doi.org/10.3762/bjnano.6.17.

(45) Stevie, F. A.; Donley, C. L. Introduction to X-Ray Photoelectron Spectroscopy. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2020**, *38* (6). https://doi.org/10.1116/6.0000412.

(46) Seyama, H.; Soma, M.; Theng, B. K. G. *X-Ray Photoelectron Spectroscopy*, 1st ed.; Elsevier Inc., 2013; Vol. 5. https://doi.org/10.1016/B978-0-08-098259-5.00007-X.

(47) Smith, J. W.; Saykally, R. J. Soft X-Ray Absorption Spectroscopy of Liquids and Solutions. *Chem Rev* **2017**, *117* (23), 13909–13934. https://doi.org/10.1021/acs.chemrev.7b00213.