

Characterization of Energy Materials for Water Splitting Using Electrochemical Scanning Tunneling Microscopy

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Abstract

In light of the large number of aspects that influence the reaction kinetics of electrocatalysts, such as their material composition, crystallographic orientation, or surface morphology, there are almost countless variations of conceivable catalyst designs. Therefore, gathering basic knowledge about electrochemical processes occurring on catalyst surfaces is crucial to optimize, e.g., fuel cells and electrolyzers. This work focuses on the two essential electrolysis reactions: the proton reduction/hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). The investigated systems are single crystalline Pd in 0.1M HClO₄ and MnO₂NS/HOPG, which consists of MnO₂-nanosheets (MnO₂NS) synthesized on highly ordered pyrolytic graphite (HOPG) in 0.1M KOH, respectively. As a key measuring method, tunneling current noise analysis in electrochemical scanning tunneling microscopy (n-EC-STM) was selected, allowing an *in situ* identification of the most active sites and, thus, formulating a framework for designing cost- and energy-efficient catalysts. In both investigations, an external group of density functional theory (DFT) scientists deepened the understanding of the observed electrochemical processes. In the first part of this study, the combined DFT, cyclic voltammetry (CV), and n-EC-STM investigations on selected Pd facets determine the following activity trend for the HER: Pd(211)>Pd(111)>Pd(110)>Pd(100). In addition, the n-EC-STM experiments assign the most active sites on Pd(111) and Pd(100) to step edges and a lower activity to terraces. Accordingly, these findings lead to a recommendation for the design of nanoparticles with a high coverage of Pd(211) and Pd(111) facets. Moreover, n-EC-STM measurements performed after CV experiments detect a transformation of the surface morphology and a shift of the most active sites. Subsequent DFT calculations suggest that this alteration originates in an increased surface strain caused by the formation of Pd hydrides after hydrogen absorption. The second part focuses on investigating the OER on the state-of-the-art catalyst MnO₂NS/HOPG, composed of the abundant elements Mn, O₂, and C. Here, the n-EC-STM and DFT studies independently identify the highest activity on top of the MnO₂NS step edges, followed by the MnO₂NS plateau, and the relatively inactive HOPG. Supported by the experiments, the DFT study reveals the reaction pathway, including its intermediate steps for each active site. Hence, this thesis enhances the general understanding of particular electrocatalytic processes, thus positively influencing the energy transition.

Zusammenfassung

In Anbetracht der zahlreichen Aspekte, die die Reaktionskinetik von Elektrokatalysatoren beeinflussen, wie beispielsweise die Materialzusammensetzung, die Kristallorientierung oder die Oberflächenstruktur, gibt es beinahe unzählige Variationen von konzipierbaren Katalysatoren. Daher ist es beispielsweise für die Optimierung von Brennstoffzellen und Elektrolyseuren von zentraler Bedeutung, Basiswissen über die elektrochemischen Prozesse auf Katalysatoroberflächen zu sammeln. Aus diesem Grund stehen die beiden wesentlichen Elektrolysereaktionen, die Proton Reduktion bzw. Wasserstoffentwicklungsreaktion (HER) und die Sauerstoffentwicklungsreaktion (OER) im Fokus dieser Dissertation. Die dabei untersuchten Systeme sind monokristallines Pd in 0,1M HClO_4 und $\text{MnO}_2\text{NS}/\text{HOPG}$, bestehend aus MnO_2 -Nanoblättern (MnO_2NS) synthetisiert auf hochgradig geordnetem pyrolytischem Graphit (HOPG), in 0,1M KOH. Als zentrale Messmethode wurde die Analyse des Tunnelstromrauschens aus Messungen der elektrochemischen Rastertunnelmikroskopie (n-EC-STM) eingesetzt, die eine *in situ*-Identifizierung der aktivsten Stellen ermöglicht, wodurch die Rahmenbedingungen für die Entwicklung kosten- und energieeffizienter Katalysatoren festlegen werden können. In beiden Projekten wurde das Verständnis der hierbei beobachteten elektrochemischen Prozesse durch externe Dichtefunktionaltheorie (DFT)-Experten vertieft. Im ersten vorgestellten Projekt wird bei der kombinierten DFT-, zyklische Voltammetrie- (CV) und n-EC-STM-Studie für die HER an ausgewählten Pd-Basalebenen der Aktivitätstrend $\text{Pd}(211) > \text{Pd}(111) > \text{Pd}(110) > \text{Pd}(100)$ festgestellt. Des Weiteren können in den n-EC-STM-Experimenten auf Pd(111) und Pd(100) die aktivsten Stellen den Stufenkanten und eine geringere Aktivität den Terrassen zugeordnet werden. Aus diesen Erkenntnissen ergibt sich eine Konstruktionsempfehlung für Nanopartikel mit einem großen Oberflächenanteil von Pd(211)- und Pd(111)-Basalebenen. Des Weiteren wird bei n-EC-STM-Messungen, welche nach CV-Experimenten durchgeführt wurden, eine Veränderung der Oberflächenmorphologie und eine Verlagerung der aktivsten Zentren festgestellt. Anschließende DFT-Berechnungen deuten darauf hin, dass diese Veränderung auf eine erhöhte Oberflächenspannung zurückzuführen ist, die durch die Bildung von Pd-Hydriden infolge einer Wasserstoffabsorption verursacht wird. Das zweite Forschungsprojekt befasst sich mit der Untersuchung der OER an dem wegweisenden Katalysator $\text{MnO}_2\text{NS}/\text{HOPG}$, der sich aus den häufig auftretenden Elementen Mn, O₂ und C zusammensetzt. Dabei zeigen die n-EC-STM- und DFT-Studien unabhängig voneinander, dass die höchste Aktivität oberhalb der MnO_2NS -Stufenkanten auftritt, gefolgt von dem MnO_2NS -Plateau und dem wenig aktiven HOPG. Gestützt durch die experimentellen Ergebnisse kann die DFT-Studie den Reaktionspfad mitsamt

seiner Zwischenschritte für jedes einzelne aktive Zentrum entschlüsseln. Diese Dissertation erweitert somit das allgemeine Verständnis über einzelne spezielle elektrokatalytische Prozesse und leistet dadurch einen konstruktiven Beitrag die Energiewende weiter voranzutreiben.

List of Publications and Conference Contributions

List of Publications: The following publications are sorted by their release date, starting with the earliest. Please note that a reprint of all first-author publications is provided in **Appendix G**. The additive ⁽⁺⁾ indicates the first authors, while * refers to the corresponding authors of the publication.

1. Haid R.W.,⁽⁺⁾ Kluge R.M.,⁽⁺⁾ Schmidt T.O., Bandarenka A.S.* *In-situ detection of active sites for carbon-based bifunctional oxygen reduction and evolution catalysis*. *Electrochimica Acta* **2021**, 382, 138285.
2. Kluge R.M.,⁽⁺⁾ * Haid R.W.,⁽⁺⁾ Riss A., Bao Y., Seufert K., Schmidt T.O., Watzele S.A., Barth J.V., Allegretti F., Auwärter W., Calle-Vallejo F.,* Bandarenka A.S.* *A trade-off between ligand and strain effects optimizes the oxygen reduction activity of Pt alloys*. *Energy & Environmental Science* **2022**, 15, 5181-5191.
3. Haid R.W.,⁽⁺⁾ Kluge R.M.,⁽⁺⁾ Schmidt T.O., Bandarenka A.S.* *Finding efficient catalyst designs: A high-precision method to reveal active sites*. *Chem Catalysis* **2022**, 2, 657-659.
4. Kluge R.M.,⁽⁺⁾ * Psaltis E.,⁽⁺⁾ Haid R.W., Hou S., Schmidt T.O., Schneider O., Garlyyev B., Calle-Vallejo F.,* Bandarenka A.S.* *Revealing the nature of active sites on Pt-Gd and Pt-Pr alloys during the oxygen reduction reaction*. *ACS Applied Materials and Interfaces* **2022**, 14, 19604-19613.
5. Schmidt T.O.,⁽⁺⁾ Ngoipala A.,⁽⁺⁾ Arevalo R.L., Watzele S.A., Lipin R., Kluge R.M., Hou S., Haid R.W., Senyshyn A., Gubanova E.L.,* Bandarenka A.S.,* Vandichel M.* *Elucidation of structure-activity relations in proton electroreduction at Pd surfaces. Theoretical and experimental study*. *Small* **2022**, 18, 2202410.
6. Gubanova E.,⁽⁺⁾ * Schmidt T.O.,⁽⁺⁾ Watzele S., Alexandrov V.,* Bandarenka A.S.* *Structure-dependent electrical double layer capacitances of the basal plane Pd(hkl) electrodes in HClO₄*. *J. Phys. Chem. C* **2022**, 126, 11414-11420.

7. Schmidt T.O.,⁽⁺⁾ Haid R.W., Gubanova E.L., Kluge R.M.,* Bandarenka A.S.* *Electrochemical scanning tunneling microscopy as a tool for the detection of active electrocatalytic sites*. Topics in Catalysis **2023**, 66, 1270-1279.
8. Schmidt T.O.,⁽⁺⁾ Wark A.,⁽⁺⁾ Haid R.W., Kluge R.M., Suzuki S., Kamiya K., Bandarenka A.S.*, Maruyama J.*, Skúlason E.* *Elucidating the active sites and synergies in water splitting on manganese oxide nanosheets on graphite support*. Advanced Energy Materials **2023**, 13, 2302039.
9. Yu H.,⁽⁺⁾ Schott C., Schmidt O.T., Schneider P.M., Song K.-T., Zhang Q., Capogrosso A., Deville L., Gubanova E.,* Bandarenka A.S.* *Investigation of active electrocatalytic centers under reaction conditions using operando microscopies*. Current Opinion in Electrochemistry **2023**, 42, 101386.
10. Schott C.M.,⁽⁺⁾ Schneider P.M., Song K.-T, Yu H, Götz R, Haimerl F, Gubanova E, Zhou J, Schmidt T.O., Zhang Q., Alexandrov V.,* Bandarenka A.S.,* *How to Assess and predict electrical double layer properties. Implications for electrocatalysis*. Chemical Reviews **2024**, 124, 12391-12462.
11. Ngoipala A.,⁽⁺⁾ Schott C.,⁽⁺⁾ Briega-Martos V.,⁽⁺⁾ Qamar M.,⁽⁺⁾ Mrovec M., Nikkhah S.J., Schmidt T.O., Deville L., Capogrosso A., Moumaneix L., Kallio T., Viola A., Maillard F., Drautz R., Bandarenka A.S., Cherevko S,* Vandichel M.,* Gubanova E.L.* *Hydride-induced reconstruction of Pd electrode surfaces: A combined computational and experimental study*. Advanced Materials **2024**, accepted. DOI: 10.1002/adma.202410951.
12. Wark A.,⁽⁺⁾ Schmidt T.O.,⁽⁺⁾ Haid R.W., Kluge R.M., Suzuki S., Siroma Z., Skúlason E.,* Bandarenka A.S.,* Maruyama J.,* *The role of manganese oxide nanosheets in pyrolyzed carbonaceous supports for water oxidation*, **submitted**.

Conference contributions: The visited conferences during this doctorate, including their presentation titles, are listed below.

73rd Annual Meeting of the International Society of Electrochemistry (ISE), Online Conference, September 2022, *In-Situ Identification of Electrocatalytically Active Areas on Palladium using Electrochemical Scanning Tunneling Microscopy*, **oral presentation**.

12th Energy Colloquium of the Munich Institute of Integrated Materials, Energy and Process Engineering (MEP), July 2022, *In-Situ Identification of Electrocatalytically Active Areas on Palladium using Electrochemical Scanning Tunneling Microscopy*, **oral presentation**.

Table of content

Abstract.....	I
Zusammenfassung.....	II
List of Publications and Conference Contributions.....	IV
Table of content.....	VII
1 Introduction.....	1
2 Theory and Fundamental Concepts.....	9
2.1 Electrochemistry.....	9
2.1.1 Electrochemical Cells.....	9
2.1.2 Electrical Double-Layer Region.....	10
2.1.3 Electrochemical Potentials and Kinetics.....	12
2.1.4 Heterogeneous catalysis.....	13
2.1.5 Concept of Active Sites.....	16
2.2 Electrochemical Applications and Processes.....	17
2.2.1 Hydrogen-Based Fuel Cells and Electrolysis.....	18
2.2.2 HER.....	20
2.2.3 OER.....	22
2.3 Measurement Methods and Techniques.....	22
2.3.1 Three-Electrode Setup and Potentiostat.....	23
2.3.2 Voltammetry.....	24
2.3.3 STM and EC-STM.....	28
2.3.4 DFT.....	38
2.4 Sample Materials.....	40
2.4.1 Single-Crystalline Pd.....	40
2.4.2 MnO ₂ NS/HOPG.....	42

3	Experimental Methodology	45
3.1	Experimental Setups	45
3.1.1	Standard EC-Cell Setup	45
3.1.2	Multimode Setup in Air Atmosphere	46
3.1.3	Multimode Setup in Ar Atmosphere	48
3.2	Preparative Procedures	50
3.2.1	Sample Preparations	50
3.2.2	Electrolyte Preparations	54
3.2.3	STM Head Preparation	54
3.3	Preparatory Considerations	57
3.3.1	The STM Device's Miniature EC Cell	57
3.3.2	The Utilization of a Standard RE at the EC-STM Setup	58
3.3.3	The Selection of Appropriate n-EC-STM Settings	59
3.4	Data Evaluation	60
3.4.1	Image Processing and Filtering	61
3.4.2	Quantitative Evaluation	63
4	Results and Discussions	68
4.1	Palladium Investigations	68
4.1.1	General Assessments on Pd(111), Pd(110), and Pd(100)	69
4.1.1.1	Morphologic Initial Investigations	69
4.1.1.2	Electrochemical Initial Investigations	71
4.1.2	Active Site Identification on Recently Annealed Pd	74
4.1.2.1	Annealed Pd (111)	75
4.1.2.2	Annealed Pd (100)	80
4.1.2.3	DFT-Based Activity Analysis	84
4.1.3	Active Site Identification on Annealed Subsequent Cycled Pd	86

4.1.3.1	Annealed and Cycled Pd(111).....	86
4.1.3.2	Annealed and Cycled Pd(100).....	90
4.1.3.3	DFT Discussion and the Impact of Compressive Strain.....	93
4.1.4	Summary and Prospects.....	96
4.2	MnO₂NS/HOPG Investigations.....	98
4.2.1	General Investigations.....	100
4.2.1.1	HOPG as Support Material.....	100
4.2.1.2	Morphologic Initial Investigations.....	102
4.2.1.3	Electrochemical Initial Investigations.....	104
4.2.2	Active Site Identification and n-EC-STM Measurements.....	106
4.2.2.1	Assignment of the Nanosheet Material.....	107
4.2.2.2	Extended Noise Analysis and Activity Allocation.....	111
4.2.3	DFT Results and Extended Elucidation of Electrochemical Processes.....	116
4.2.3.1	Basic Considerations and Conceptual Model Design.....	116
4.2.3.2	DFT Results and Reinterpretation of EC-STM Measurements.....	118
4.2.4	Summary and Prospects.....	121
5	Outlook: The Future of Active Sites.....	122
6	Conclusion.....	126
	Appendix A: Acknowledgments.....	129
	Appendix B: STM and CV Settings.....	131
	Appendix C: Additional Information About the Pd Investigations.....	135
	Appendix D: Additional Information About the MnO₂NS/HOPG Investigations.....	156
	Appendix E: List of Active Sites and Regions.....	167
	Appendix F: List of Abbreviations and Symbols.....	171
	Appendix G: Collection of First Autor Publications.....	175
	References.....	219

1 Introduction

The World Meteorological Organization (WMO) published in the beginning of 2024 a new report about the current global climate as of 2023 ^[1]. However, the elucidated update of the situation raises further concerns. In climate research, it is common to compare the current average temperatures with those of the mean temperature between 1850 and 1900 ^[2–4]. This so-called pre-industrial period represents the last epoch before artificial greenhouse gas emissions drastically increased, thus serving as an appropriate benchmark ^[5]. Based on six different global temperature data sets used for the calculations, this WMO report presented an average temperature increase during this period of about 1.45°C. In addition, it points out that the nine highest-ever recorded mean temperatures were measured in the past nine years, from 2015 to 2023. ^[1] This is a sobering outcome when comparing these numbers with the internationally set goal by the Paris Agreement in 2015 to limit the temperature increase to 1.5°C at the end of this century ^[6]. To recapitulate, in 1988, the Intergovernmental Panel on Climate Change (IPCC) was founded by the United Nations Environment Program (UNEP) and the WMO to bring the topic of climate change to the international stage ^[7]. Nine years later, in 1997, a milestone was set when a significant proportion of the international community discussed the further direction humanity is heading towards. In the so-called Kyoto Protocol, a clear climate-friendly course, including strategies and politics, was agreed upon to reduce greenhouse gas emissions. ^[1]

Despite this early awareness about the possible impact of climate change and the commendable intentions, the negative consequences of global warming are omnipresent nowadays. **Figure 1.1** shows a significant temperature increase in the entire world, except for particular areas. The current WMO report states that the apparent rising temperature in the Arctic Ocean considerably affects a drastic decrease in the annual growth of the Arctic sea ice. This decline led to a significant rise in the sea level, while its increasing rate doubled within the last ten years. Next to its height, the average ocean heat content in 2023 also showed the highest value ever measured since its recording in 1971. ^[1] However, areas on land, such as in Europe, show similarly significant temperature increases, as visible in **Figure 1.1**. In 2021, Weirhammer *et al.* discussed several studies about the impact of extreme weather phenomena in Europe and reported a correlating effect on human health and respective mortality. For this conclusion, next to the impacts of heat and cold waves, they considered droughts, wildfires, storms, and floods. ^[8] The latter made headlines in Germany in 2021 when a small stream in the Ahrtal in North Rhine-Westphalia became a raging river and claimed the lives of 134 individuals ^[9]. As a result of such occurrences,

Introduction

global warming has experienced rising attention in the last few decades. Reducing greenhouse gas emissions is now more important than ever, particularly concerning CO₂, CH₄, and N₂O, which are the three most critical ones recently specified by the WMO ^[1]. Especially regarding expected tipping points, such as a substantial CO₂ emission caused by the melting of the permafrost areas in Greenland, or unpredictable changes in the world weather system by a weakening or even collapse of the Atlantic Meridional Overturning Circulation (AMOC), a prompt change of the global course is essential ^[10].

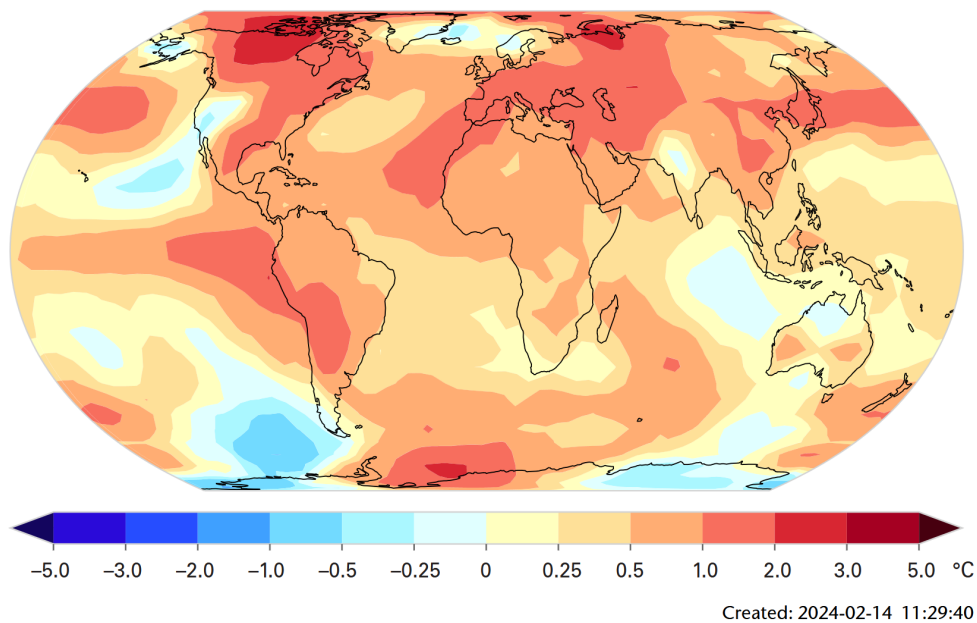


Figure 1.1. Regional deviation of the mean average in 2023 compared to the average temperature between 1991 and 2020. Here, the drastic heating at the poles and in the northern hemisphere becomes apparent, while only a few regions experience slight cooling. Reprinted from reference ^[1], licensed under CC BY-NC-ND 4.0 ^[11].

A solution to reduce the chance of reaching such a tipping point is the decrease of global warming by a comprehensive replacement of Carbon-based energy sources, such as oil, natural gas, or coal, with renewable ones produced by wind, water, solar, or thermal powered power plants. Energy collected by renewable sources is typically produced as electricity, which is an all-around energy form but has one significant drawback: it is difficult to store. The solution is often seen in converting electricity to easier, storable energy forms such as chemical, thermal, and mechanical energy. ^[12] Next to the pumped hydroelectric energy storage, the probably most famous applications in this context are batteries and electrolyzers. The latter devices are based on an

electrochemical cell (EC-cell) and convert electrical energy to chemical energy. When electricity is required, this transformation can be reversed. While an additional fuel cell is typically used to convert the chemical energy obtained during electrolysis back into electrical energy, a battery is a self-contained unit.^[13]

The typical currently used highly efficient batteries are primarily based on lithium, which is expected to become a scarce resource in the near future. In contrast, the current trend in the growing fuel cell technology is toward a hydrogen economy^[14,15]. Since hydrogen can be produced by water splitting using electrolysis and is available in all places on earth where humans live, it yields almost an inexhaustible fuel deposit. Moreover, gaseous H₂ has an outstanding 2.3 times higher specific energy density than gaseous methane, the most common natural gas utilized as an energy resource. On the other hand, its volumetric energy density is about 3.5 times smaller. In addition, when comparing liquid hydrogen with liquid methane and gasoline, it is about two and four times less dense in volume, respectively.^[16] Among general safety and leakage issues regarding hydrogen, this low volume density makes its storage challenging, especially for mobile applications with limited available space. Next to conventional approaches, such as solid-state and compressed or cryogenic hydrogen storage methods, a chemical binding of hydrogen, *e.g.*, by liquid organic hydrogen carrier (LOHC), is very promising.^[17] These reusable LOHCs allow the saving of large-scale transport and storage of hydrogen comparable with gasoline, hence the further usage of the liquid infrastructure^[18]. However, no hydrogen storage system has prevailed yet. The final decision will likely depend on future discoveries and politics. Since large energy consumers are stationary stakeholders, such as those in the steel industry, which would also require immense amounts of hydrogen, implementing mixed storage systems might be reasonable^[19].

Critical factors that strongly influence establishing a global hydrogen economy are the production costs and the availability of the required materials for fuel cells and electrolyzers. Consequently, using cheap, highly active, durable, and abundant energy materials in such devices would enable wide availability and thus significantly push the global energy transition.^[18] On the list of suitable catalyst materials for fuel cells and electrolysis are abundant materials like graphite or Ni and noble metals like Pt, Pd, Ir, Rh, and Ru^[20]. However, for typical electrochemical reactions relevant to the hydrogen economy, the latter group of more expensive materials or their metal oxides were determined to have excellent catalytic properties, especially in view of Pt-based alloys^[21–26]. Consequently, the costs could be significantly reduced by synthesizing nanostructured coatings of these materials on abundant support materials^[27]. However, for the design of novel, stable,

cheap, and efficient electrocatalytic coatings, it is mandatory to fundamentally understand the processes occurring on the catalyst's surface under reaction conditions.

Developing such processes on different catalytic materials for the primary electrochemical reaction of water splitting, the oxygen evolution reaction (OER), and the hydrogen evolution reaction (HER) was the subject of this doctorate. In this scope, the experimental techniques cyclic voltammetry (CV) and a technique based on the analysis of the tunneling current noise level under reaction conditions in electrochemical scanning tunneling microscopy (n-EC-STM) were combined with theoretical density functional theory (DFT) investigations. This joint study was possible due to the collaboration with partners from universities in Ireland and Iceland, who implemented the DFT calculations. The benefit of this collaborative approach is the independent research of specific electrochemical surface processes from different perspectives, which leads to a comprehensive overall picture. Next to DFT, especially the n-EC-STM technique played a central role in this research due to its ability to experimentally find the most electrochemical active areas, called active sites, under operando conditions in high-resolution up to the sub-nanometer scale ^[28,29]. The basic idea is that as soon as the active sites are identified, it is possible to create a blueprint for designing highly active but material-efficient nanostructured coatings, which could be synthesized on cheap support materials ^[30,31]. In this way, as a small cog in the machine, this work contributed further pieces of the puzzle in the search for cheap, stable, nationwide available, sustainable, and efficient catalysts for water splitting, and thus, to further drive towards energy transition. The research presented in this thesis is split into two main projects: the analysis of HER processes on different Pd single crystals and the investigation of the OER on MnO₂ nanosheets (MnO₂NS) synthesized on highly oriented pyrolytic graphite (HOPG), short MnO₂NS/HOPG.

Pd, the first material discussed in this thesis, has already been intensively studied for decades ^[32–35]. Its ability to absorb high amounts of hydrogen into its bulk, forming Pd hydrides (PdH), makes it a remarkable material ^[36–38]. Despite Graham's reporting of this phenomenon over 150 years ago in 1866, it is still an intensively studied topic in current research ^[39–42]. For instance, Moumaneix *et al.* recently investigated the hydrogen absorption mechanism on Pd nanoparticles. They found that the applied cell voltage predominantly determines the amount of absorbed hydrogen, while the loading duration plays a subordinate role. ^[41] Moreover, it is well known that hydrogen absorption induces a strain within the Pd lattice, which positively influences its HER activity. In 2006, Kibler intensively discussed this phenomenon but could not explain its origins completely. ^[43] Based on this finding, Janssonius *et al.* demonstrated in 2020 that a precise modification of the strain could increase the HER activity and, at the same time, reduce the hydrogen absorption ability ^[44].

Despite this outstanding absorption ability and knowledge about its regulation, Pd is not used as a hydrogen storage material because of its high price and the large amount required for large-scale applications. Instead, it is intended as a catalyst accelerating the hydrogen absorption into cheaper hydrogen storage material such as Mg. Furthermore, Pd yields an ideal candidate for hydrogen-related applications where only small amounts of the costly material are required. An example of this is the utilization of Pd in hydrogen sensors to detect even small amounts of hydrogen leakage and prevent accidents in laboratories and industry ^[45] . ^[46]

Next to these applications, there is an upcoming interest in using Pd-based nanostructured materials to catalyze the HER ^[47–49] . There is a rich discussion in the literature about various Pd nanostructures and monolayers synthesized on different materials to find an alternative to the currently prevalent but more expensive Pt-based HER catalysts ^[47–51] . For instance, a well-investigated hybrid material consists of thin Pd layers deposited on different Au substrates, significantly increasing the HER activity compared to their pristine counterparts ^[28,43] . Moreover, Smiljanić *et al.* presented in 2018 the power of the synergy between different materials when advancing this system by additional Rh. By depositing thin Rh and Pd layers on polycrystalline Au, they created a tri-metal catalyst with an even higher HER activity than the bi-metal Pd/Au. ^[52] Next to monolayered coatings, Pd nanoparticles are also intensively investigated for the catalyzation of the HER ^[53] . A remarkable finding was the innovative improvement of Pd nanoparticles presented by Cheng *et al.* in 2020. They introduced a molecule called bismuthiol I, which allows the amorphization of Pd nanomaterials at standard temperature and pressure. Here, the resulting nanoparticles exhibited high stability and a significantly increased HER activity compared to commercial Pd nanoparticles. ^[54] Moreover, Kumar *et al.* demonstrated that Pd synthesized on cost-efficient phosphorous-doped carbon nanoparticles (Pd/P-CNPs) could reach comparable stability and HER catalyzation ability to Pt supported on carbon black (Pt/CB) ^[55] .

Interestingly, a significant amount of Pd-related literature focuses on Pd nanoparticles or their application as a hybrid material. However, to completely reveal the hydrogen-Pd interactions, it is essential to understand the underlying processes and how hydrogen influences the properties of Pd ^[56] . For this purpose, an ideal test system is a single crystal, widely used as a simplified model for electrocatalysis research due to its well-defined unaltered surface and, thus, properties ^[57–59] . For this reason and in regard to the objective of this doctorate to contribute to the fundamental understanding of electrocatalytic materials, different Pd single crystals were analyzed in this thesis.

The second energy material investigated in this doctorate, $\text{MnO}_2\text{NS}/\text{HOPG}$, consists of the abundant elements C, O, and Mn and thus is an interesting candidate for sustainable catalysis. In this study, the catalytic ability of the OER in alkaline 0.1M KOH electrolyte was analyzed, which is the counterreaction to the HER in water splitting ^[60]. Current state-of-the-art electrocatalysts for the OER are IrO_2 and RuO_2 , which show outstanding activity ^[61]. However, both Ir and Ru are known to be expensive materials with limited availability. It was recently shown by Mince *et al.* that under socio-economic and geographic considerations, the mining capacities of Ir are far too low to meet the future requirements for a large-scale application of commercial proton exchange membrane (PEM) water electrolysis. Moreover, the authors state that the only possible scenario to avoid this bottleneck is to reduce the Ir load in catalysts and start intensive Ir recycling. ^[62] Unfortunately, the projections for Ru are similarly pessimistic, which further emphasizes the requirement for an alternative OER electrocatalyst, especially for less demanding applications ^[63].

When expanding the focus on already proven OER catalysts, one quickly encounters nature's O_2 production in leaves. Inside the plant cells are chloroplasts, which in turn contain thylakoid membranes, housing the enzyme Photosystem II (PS II) ^[64]. Here, water molecules get split by consuming atmospheric CO_2 and photons from the sun and bind the C atoms in biological matter while emitting O_2 as a byproduct. It is known that the decisive component in this process catalyzing the oxygen evolution is the so-called Mn_4CaO_5 cluster, which contains an Mn-O-Mn moiety ^[65]. ^[66] However, it is important to note that despite the natural selection of an Mn-Ca-O-based catalyst, it is not mandatorily the best possible OER catalyst. Instead, based on bionic considerations and following Darwin's evolution theory, it only indicates that these elements are suitable to catalyze the OER and abundant enough on Earth. And indeed, Mn is a widely distributed element with large deposits on the seafloors ^[67]. Nevertheless, regarding humans' exclusive ability to synthesize almost every known element and due to the absence of the need to build carbon chains like plants do, it is plausible that comparable but different material compositions will be humans' ideal OER catalyst. Inspired by these aspects, there is a significant interest in investigating Mn-based electrocatalysts for water splitting to find synergy effects with other elements ^[68–70]. In particular, different Mn-oxides (MnO_x) were widely investigated due to their remarkable OER activity ^[71–74].

These considerations also pave the way for investigating the electrochemical properties of $\text{MnO}_2\text{NS}/\text{HOPG}$ in this doctorate. The selected support material, HOPG, consists exclusively of carbon, one of the most abundant elements in the universe and on Earth ^[67]. Consequently, carbon-based materials, such as graphene, are cost-efficient and widely used in heterogeneous electrochemistry due to their electrical conductivity. In addition, graphene's highly ordered lattice

structure, created by pyrolysis, is very stable and yields a uniform and flat surface, ideal for different applications, such as electrochemical scanning tunneling microscopy (EC-STM) ^[75,76]. Interestingly, Mette *et al.* demonstrated in 2011 the reasonable OER activity of MnO_x synthesized on carbon nanotubes, underpinning the potential of the MnO_x-C synergy ^[77]. For this reason, the MnO₂NS/HOPG yields an ideal sample material to follow up on in the research of abundant energy materials for water splitting and identify its active sites to further enhance the fundamental electrocatalytic knowledge.

At the beginning of this thesis, the fundamental concepts of electrochemistry are discussed in **Chapter 2**, which provides a solid basic knowledge of the observed electrochemical processes. Moreover, the applied methods and measuring techniques are explained in detail to clarify the generation process of the presented results. In addition, the theoretical preliminary considerations are complemented by a short discussion of the most relevant physical and chemical characteristics of the individual sample materials. The subsequent methodology-related **Chapter 3** explains the experimental setups, preparatory procedures, and considerations before the measurements. Additionally, a comprehensive description of the applied evaluation techniques is shown. Subsequently, the findings of the individual sample materials are presented in **Chapter 4**, starting with the research of the HER on Pd single crystals. Here, the first part discusses the morphological and electrochemical properties of the investigated crystals Pd(111), Pd(110), and Pd(100). Furthermore, the second part is about the identification of the most active sites on freshly annealed Pd(111) and Pd(100) single crystals using n-EC-STM and their interplay with their relation with the formation of PdHs based on externally implemented DFT calculations. In addition, the impact of hydrogen absorption on their crystal structure and electrochemical properties is revealed and further explained by computational results in collaboration with the University of Limerick (Ireland). The second half of this chapter focuses on the OER catalyst MnO₂NS/HOPG, starting with the initial investigations. After showing the characteristics of the support material HOPG, the subchapter discusses the morphologic and electrochemical properties of MnO₂NS/HOPG. Subsequently, the sample's most active sites are presented using n-EC-STM and underpinned by a discussion of the distinction between the MnO₂NS and the support material. Analogous to the investigations on Pd, a DFT group from the University of Iceland provided valuable insights into the observed activity distribution. Moreover, after this discussion, a small outlook and future perspectives are presented regarding the research on MnO₂NS/HOPG and abundant catalyst materials in general. Since this thesis targets the enrichment of the universal knowledge of electrocatalysis by identifying active sites on different catalyst materials using n-EC-STM, the subsequent general outlook in **Chapter 5** deals with the

future detection of active sites using related measurement techniques. Taking everything into account, in the final conclusion, all key findings are recapitulated and concluded to an overall picture in **Chapter 6**.

2 Theory and Fundamental Concepts

This thesis investigates the near-surface processes of promising electrocatalytic materials and collects data about the most electrochemical active sites. Consequently, a fundamental knowledge of electrochemistry, the applied measuring methods, and sample materials is required to comprehend the presented findings. For this reason, the basic concepts and decisive information are presented below.

2.1 Electrochemistry

Electrochemistry is a broad field with countless application possibilities. In order to provide the information essential to understand the applied measuring methods and to follow the evaluation and interpretation of the results, this subchapter discusses selected electrochemical phenomena and concepts.

2.1.1 Electrochemical Cells

The simplest version of an EC-cell consists of two electrodes separated by an ion-conductive but electronically isolated electrolyte and an external electrical circuit. There are two different kinds of cells: electrolytic cells, such as electrolyzers, and galvanic cells, which are better known as fuel cells or batteries. In the case of electrolytic cells, an external voltage supply induces the electrochemical reactions occurring on the electrodes. The other way around, the electrical current flow in the external circuit appears in galvanic cells due to a potential difference originating from an unbalanced electrode charge. Here, the nonequilibrium is initiated by electrochemical reactions on the electrodes. In other words, galvanic cells convert chemically stored energy into electrical energy. It is important to note that different electrochemical reactions occur on the individual electrodes under operation conditions in both EC-cell types. In order to investigate these reactions separately, the EC-cells are typically divided into two half-cells. ^[13]

Irving Langmuir discovered the phenomenon of adsorption by investigating hydrogen gas in a light bulb and received the Nobel Prize in chemistry in 1932 ^[78]. With our current understanding of electrochemistry, this adsorption mechanism plays a key role in the occurrence of electrochemical reactions ^[79]. **Figure 2.1.1** explains the EC-cell's basic working principle using the example of an

electrolytic cell. Here, the initial species (reactant) diffuses to the right electrode and is adsorbed on its surface. During the electrochemical reaction, the reactant oxidizes by donating an electron (golden sphere). This process is called oxidation and occurs at the anode. In the next phase, the oxidized species (blue sphere) desorbs from the electrode and migrates through the electrolyte to the other electrode on the left side. Simultaneously, the donated electrons move to the left electrode through the external electrical circuit. Here, the desorbed species gets adsorbed again and subsequently accepts an electron during the so-called reduction. This process takes place on the cathode. Afterward, the reduced species desorbs and migrates into the electrolyte and ends as a product of the overall cell reaction. ^[80]

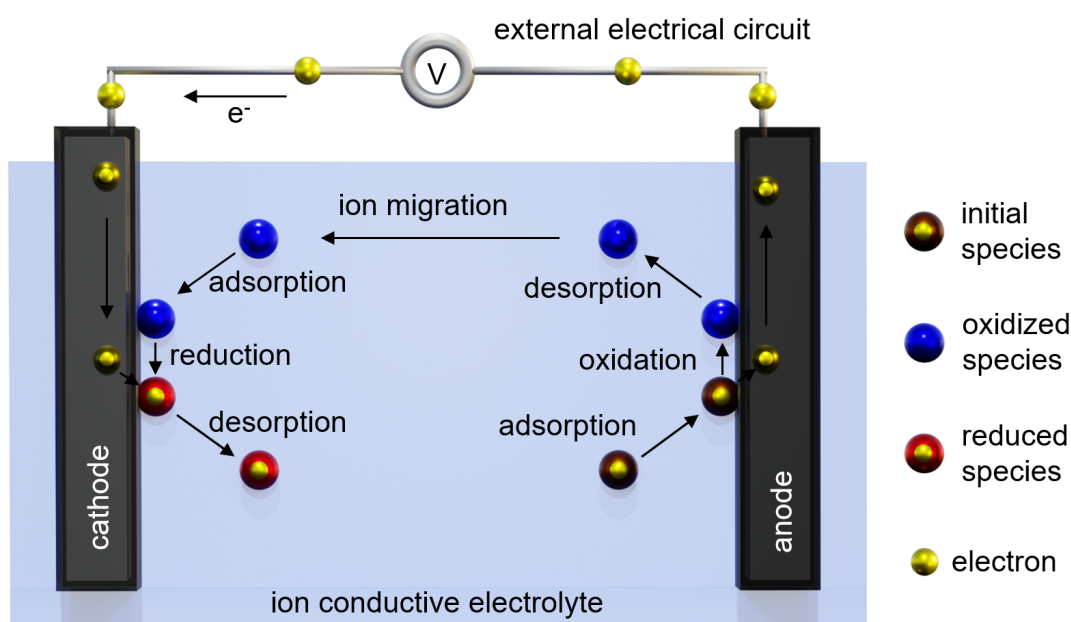


Figure 2.1.1. Schematic view of the working principle of an EC-cell using the example of an electrolytic cell connected to an external power source. Inspired by references ^[80] and ^[13].

2.1.2 Electrical Double-Layer Region

The electrolyte-electrode interface is particularly interesting in an EC-cell, which is described by the model of an electrical double-layer (EDL) ^[13,81]. Already in 1879, Helmholtz elucidated that ions attracted by a charged electrode create a counterpart and, thus, a parallel plate capacitor at the EDL (*cf.* lower half of **Figure 2.1.2**). In addition, he found a linear reduction of the potential difference between the electrode (Φ_e) and solution (Φ_s) by increasing the distance to the electrode (*cf.* upper graph of **Figure 2.1.2**). ^[82] At the beginning of the 20th century, Gouy and Chapman

described a non-linear potential decrease for larger distances, denoted as the diffusion layer^[83]. This Gouy-Chapman model was combined with the Helmholtz model by Stern in 1924 by connecting the ideas of the capacitor and diffusion layer^[84]. In 1947, Grahame provided the preliminary final interpretation of the EDL by uniting the existing models in an overall picture^[85]. Grahame introduced the capacitive plane found by Helmholtz as the inner Helmholtz plane (IHP), while a second plane, including solvated ions, was denoted as the outer Helmholtz plane (OHP). In this area, the potential changes linearly. For greater distances than the OHP, the diffusion layer appears with a non-linear potential convergence towards Φ_s .^[83] In this model, ions directly adsorbed on the catalyst surface are termed specifically adsorbed, while ions within the OHP or diffusion layer are non-specifically adsorbed^[80].

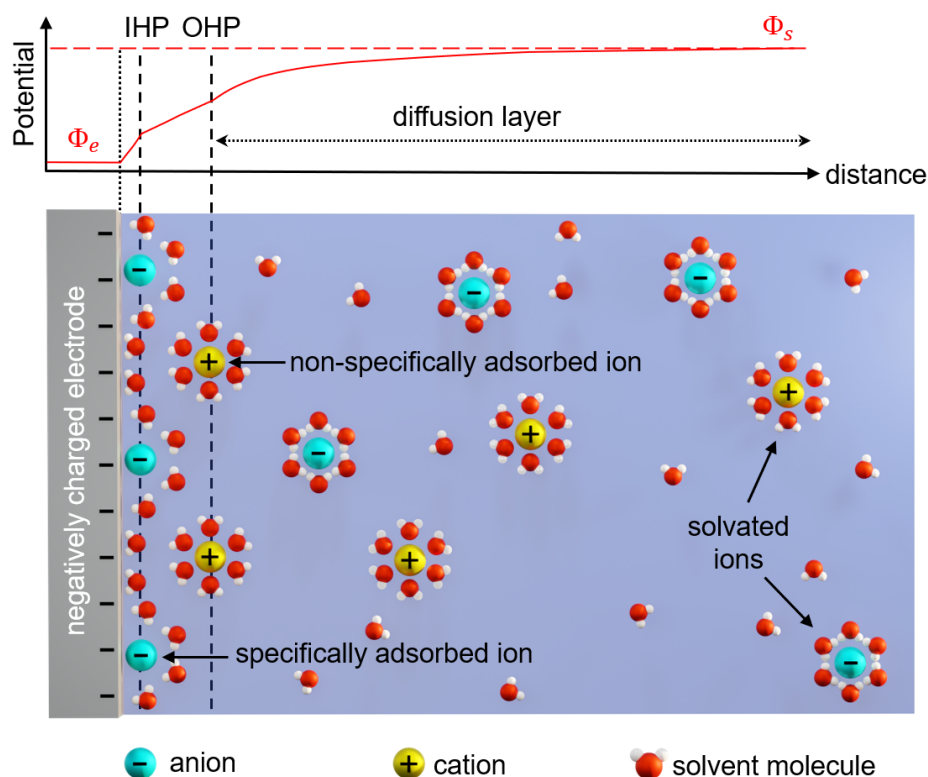


Figure 2.1.2. Overview of the EDL, exemplarily presented in aqueous electrolyte. Here, water molecules represent the solvent molecule. The top graph demonstrates the potential course for a negatively charged electrode with increasing distance. The lower figure schematically illustrates the theoretical arrangement of the electrolyte components at the respective distances to the electrode. The upper potential-distance graph was adapted from reference^[86] and licensed under CC BY 4.0^[87]. The lower EDL sketch was adapted from^[88], licensed under CC BY 4.0^[87], and further inspired by^[80].

It is important to note that the arrangements at the EDL charge the electrode and thus lead to a temporary induced current. This phenomenon is part of the so-called non-faradaic current, representing all currents in an EC-cell that do not originate from redox reactions. In contrast, the current induced by electrochemical reactions is denoted as faradaic current.^[89] Moreover, this limited current flow contributes to the non-zero current density within the double-layer region of CV measurements (*cf.* **Subchapter 2.3.2**)^[90].

2.1.3 Electrochemical Potentials and Kinetics

As soon as electrical current flows in an EC-cell, electrochemical reactions occur on the individual electrodes, donating or accepting electrons. Conversely, if there is no net current flow, the electron transfer originating from spontaneous electrochemical reactions becomes balanced by counterreactions on the same electrode. In this situation, the EC-cell is in equilibrium.^[91] The respective cell potential at which such an equilibrium occurs is denoted as the equilibrium potential or Nernst potential E_0 and is theoretically derived from the Nernst equation. The experimentally achieved equivalent is the so-called open-circuit potential E_{OC} . In ideal conditions, when no impurities interfere with the electrochemical processes and the reaction kinetics are fast enough, E_{OC} equals E_0 . For less optimal conditions, E_{OC} and E_0 are unequal. Moreover, the actual cell voltage and E_0 difference correspond to the electrode's overpotential η .^[92] Furthermore, it is important to note that the current's absolute value depends on the size of the investigated electrode area^[93]. As a result, to gain representative results, all currents in this thesis are divided by the measured area and presented as current densities.

In addition, different kinds of energy losses in EC-cells determine the cell current density. The individual losses are illustrated in **Figure 2.1.3** at a polarization curve of a half cell. As discussed before, when no current flows between the working electrode (WE) and counter electrode (CE) in a real-world setup, the cell potential equals E_{OC} ^[92]. At small overpotentials, non-linear activation losses dominate the half-cell kinetics. They could be minimized by applying a suitable electrocatalyst, as discussed in **Subchapter 2.1.4**. For further increasing overpotentials, the ohmic losses dominate. The linear relation between overpotentials and current density originates from the ohmic resistance of the external electric circuit and the ion transport within the electrolyte. Furthermore, the maximum cell current arises from non-linear mass transport losses for even larger overpotentials. Here, the reactant and product migration between the electrode and diffusion layer is not fast enough to further increase the reaction rate. In other words, the reactant

concentration significantly decreases in the EDL region. Consequently, at a specific overpotential, the current density reaches its maximum and does not further increase at even higher voltages. ^[94]

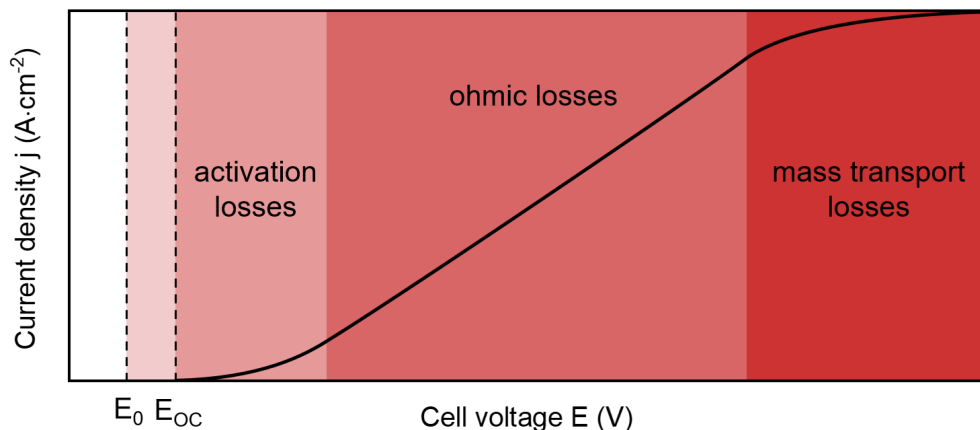


Figure 2.1.3. Polarization curve of an EC-cell on the example of positive currents for increasing overpotentials. Here, the solid black line schematically illustrates the relation between the cell voltage and the current density. The colored regimes represent the individual areas where the respective losses dominate. Inspired by reference ^[94].

2.1.4 Heterogeneous catalysis

Catalysts are materials that accelerate electrochemical reactions by changing the reaction pathway to one with a lower activation barrier, as schematically presented in **Figure 2.1.4a**. Here, the reaction pathways without (red) and with (blue) catalysts are shown with their respective activation barriers, E_1 and E_2 , as well as E_3 . The basic idea is that the sum of E_2 and E_3 is even smaller than E_1 . Thus, less activation energy is required, while the catalyst typically does not experience wear. Consequently, catalysts play a crucial role in chemical industrial processes and are indispensable in our modern society. Moreover, most chemical processes in living organisms are based on biological catalysts called enzymes, thus underpinning the importance of their existence. ^[95]

Heterogeneous catalysts are materials where the catalyzing surface has a different phase than those of the reactants ^[96]. They are typically solid and often consist of noble materials like Pt, Pd, or Rh, while their reactants are in the liquid or gas phase. Moreover, it is a common approach to minimize the electrochemical active noble material by using coatings or nanostructures synthesized on a more cost-efficient and abundant support material. ^[93] As discussed in

Subchapter 2.1.1, the reactant adsorbs on the electrode surface before an electrochemical reaction occurs and subsequently desorbs. **Figure 2.1.4b** schematically presents the reaction coordinates of this process with respect to the potential energy. In this example, the reactants (I) and (II) autonomously adsorb on the surface by a spontaneous reaction. For the actual reaction where (I) and (II) combine with the product (III), activation energy is required to overcome their energy barrier. In this example, the product desorbs in an endothermic step, thus also requiring energy. ^[93]

As typical for electrochemical reactions, the observed overall reaction consists of several intermediate reactions, each with an individual thermodynamic barrier ^[97,98]. Since every barrier must be overcome to run the reaction, one can assume that only the highest one limits the capability to accomplish the electrochemical reaction. Thus, if this decisive step can be passed, the remaining stages of the reaction pathway could also be overcome. Consequently, the intermediate step with the highest thermodynamic barrier found in a reaction is defined as the potential determining step (PDS). ^[99,100]

A common approach in electrochemistry is to use the change in free energy relative to the reactant at E_0 (ΔG_{react}) for the PDS as the descriptor for the observed reaction ^[99,101–105]. As demonstrated in **Figure 2.1.4c**, ΔG_{react} correlates with the binding strength of the reactant to the catalyst surface. Consequently, the energy level of the reaction intermediate is higher for the reactant at a weak binding ($\Delta G_{\text{react}} > 0$, red path) and lower for a strong binding ($\Delta G_{\text{react}} < 0$, orange path). The ideal case is the thermoneutral bonding with $\Delta G_{\text{react}} = 0$, shown as the blue path. Interestingly, if an overpotential is applied to the catalyst, the reaction intermediate's as well as the product's energy level shifts according to its algebraic sign as illustrated in **Figure 2.1.4d**. The benefit of this shift is that ΔG_{react} becomes zero or negative, which is thermodynamically favored. ^[105]

A model for the comparison of the suitability of a catalyst material for the observed reaction is based on the Sabatier principle, as demonstrated in **Figure 2.1.4e**. Typically, the y-axis of the volcano plot shows any representative of the electrochemical activity, such as the exchange current density (j_0), thermodynamic overpotential, or the reaction rate for the PDS ^[102,106,107]. In addition, its x-axis represents a descriptor, such as ΔG_{react} or the adsorption energy of the observed reactant. ^[102,108] All variants have in common that the optimum conditions for a catalyst material are at the top of the volcano plot. As presented in **Figure 2.1.4e**, the basic principle rests on a too-weak binding on the right side of the summit (red area), which decreases the reaction rate due to an insufficient amount of adsorbed reactants. In contrast, on the left side of the summit

(blue area), the binding is too strong, resulting in adhesive products and, thus, poisoning the catalyst surface. ^[93]

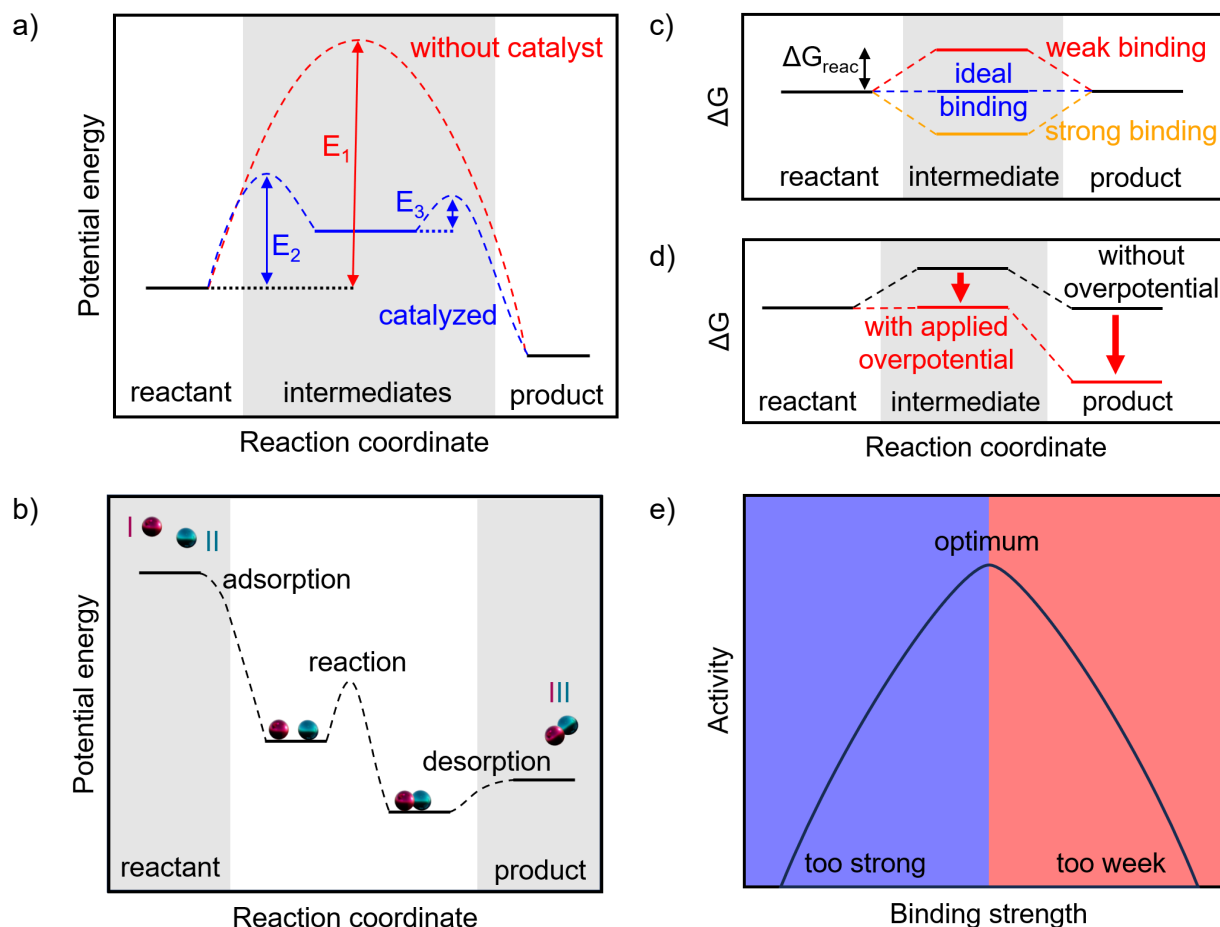


Figure 2.1.4. Working principle of a heterogeneous electrocatalyst. **a)** Impact of the usage of a catalyst (blue path) in comparison to the same reaction without a catalyst (red path). **b)** Schematic reaction pathway of a chemical reaction (cf. **Subchapter 2.1.1**). **c)** Free energy diagram for different binding strengths. **d)** Schematic sketch showing the impact of applying an overpotential. **e)** Illustration of the Sabatier principle. **a)** was inspired by references ^[109] and ^[105], **b)** by reference ^[93]. Figures **c)** and **d)** were adapted from reference ^[105] and licensed under CC BY 4.0 ^[87]. **e)** was inspired by reference ^[110].

Interestingly, the adsorption energies of specific species are interrelated ^[93,111,112]. Consequently, when knowing the adsorption energies of a particular species for the observed reaction (such as for particular metal oxides at the OER) for a specific descriptor (e.g., $\Delta G_{\cdot O} - \Delta G_{\cdot OH}$), it is possible to conclude the adsorption energy of similar materials (e.g., metal oxides with different metals). Using these scaling relations leads to estimating promising electrocatalytic materials and simplifies the

design of novel electrocatalysts without calculating or experimentally investigating each possible material composition beforehand ^[113] . ^[93]

2.1.5 Concept of Active Sites

The concept of active sites was introduced in 1925 by Taylor and is relatively straightforward ^[114] . In brief, it means that most electrochemical reactions occur only at specific structures and not on the entire surface of a catalyst ^[76,115] . This concept is schematically presented in **Figure 2.1.5**. On a macroscopic scale, an electrode surface seems entirely active when the surface is relatively uniform (*cf.* **Figure 2.1.5a**). However, experience shows that on a microscopic scale, the surface appears rather rough with several atomic steps, as depicted by the model surface in **Figure 2.1.5b**. Here, it becomes apparent that only specific surface areas (golden-colored spheres) drive the majority of the electrochemical reactions. In other words, the bulk of the catalyst material and the non-active areas do not significantly contribute to the overall catalyst activity, while the active sites are decisive for the catalyst's electrochemical activity.

Another relevant factor to mention in this context is the generalized coordination number (GCN). In essence, it is a measure to describe the number of neighboring atoms while, in turn, taking their respective number of neighboring atoms into account. Depending on the observed material, each active site has a particular GCN. Due to this correlation, modern research fields investigate the GCN and use it as a tool to identify active sites computationally. ^[116] When the active sites of a specific material are determined, it is possible to use this knowledge to improve catalyst materials while saving resources. This enhancement could be realized by, *e.g.*, constructing nanostructures that include many active sites and synthesizing them on a cheap support material, as illustrated in **Figure 2.1.5c** ^[30,117] . Especially the utilization of rare or expensive highly efficient catalyst materials could be optimized by saving, *e.g.*, the inactive bulk material. In this way, as exemplified in **Figure 2.1.5d**, an optimized catalyst with a high ratio of active sites could be designed, mainly consisting of cheap support material but yielding the efficiency of rare and highly active catalyst material. ^[31] This consideration builds the foundation for selecting the n-EC-STM technique in this doctorate due to its ability to experimentally identify these active sites up to atomic resolution ^[28,29,118] .

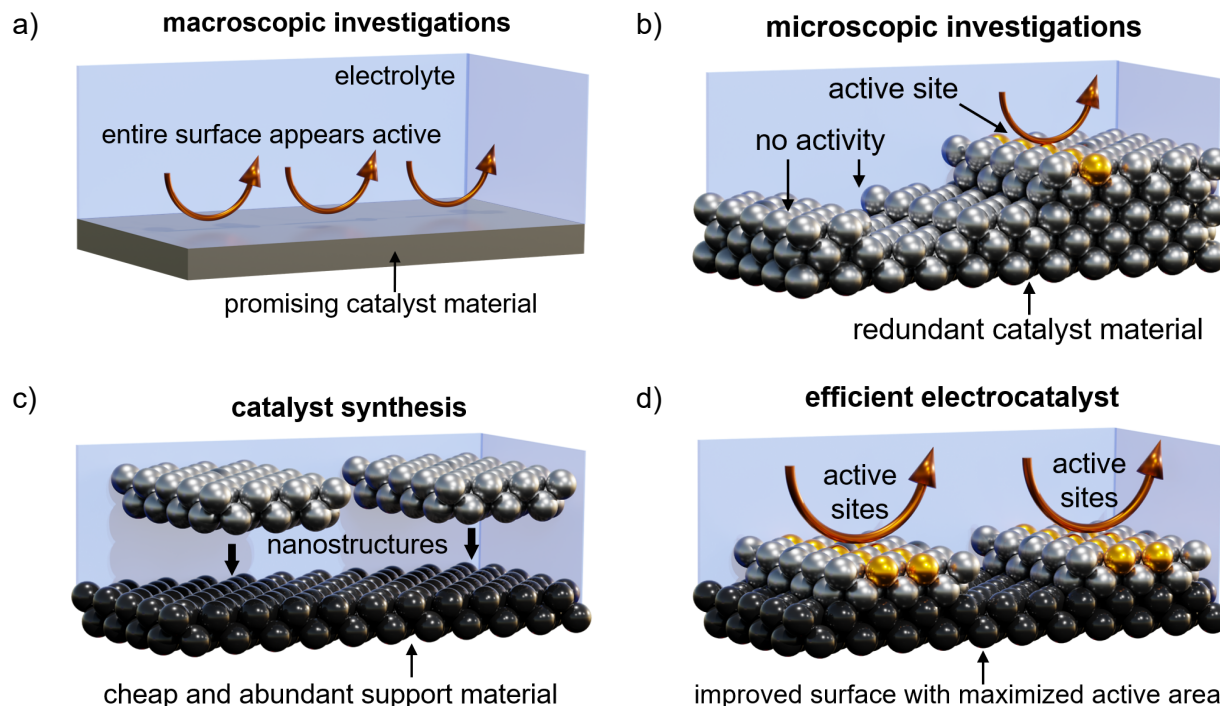


Figure 2.1.5. Schematic illustration of the application of the catalyst's active site knowledge. A promising but rare and expensive catalyst material appears very active over the entire surface, as shown in **a)**. When magnifying and investigating the surface activity, e.g., by *n*-EC-STM, it would turn out that only specific areas are active, as presented in **b)**. When replacing the redundant rare catalyst material below the active sites with a cheap and abundant support material (**c)**), it is possible to create an improved surface with maximized active area while saving redundant rare material, as depicted in **d)**. Images inspired by reference ^[30].

2.2 Electrochemical Applications and Processes

A widely discussed topic of the energy transition is the expansion of the hydrogen economy. As already elucidated in the introduction, hydrogen yields a unique gravimetric energy density ^[119]. Moreover, when using innovative storage systems, such as LOHC systems, it is even possible to further use the existing liquid energy infrastructure after modification, such as gas stations or oil tankers ^[120]. In order to provide a general picture of the basic systems typical for a hydrogen economy, this subchapter discusses the working principle of hydrogen-based fuel cells and electrolyzers. For simplification, the underlying idea of these devices is presented in acidic media, where protons are the exchanged ions. Moreover, it provides background information on the HER

and OER since these two decisive electrochemical reactions for water splitting are the primary reactions investigated in this doctorate.

2.2.1 Hydrogen-Based Fuel Cells and Electrolysis

The basic principle of a fuel cell is to convert chemically stored energy into electrical energy by two spatially separated electrochemical reactions. This conversion could begin from various fuels, having different chemical intermediates, before ending as a byproduct. The other way around, in electrolysis, electrical energy is converted into easier storable chemical energy. Prominent examples of fuel cells are, among others, the PEM fuel cell (PEMFC), the direct methanol fuel cell (DMFC), and the solid oxide fuel cell (SOFC). While the PEMFC uses pure hydrogen as a fuel, the DMFC is powered by methanol, which could also be produced from renewable sources. Both are low-temperature fuel cells, which means that their working temperature is between 30°C and 200°C. In contrast, the hydrogen-powered SOFC operates at elevated temperatures between 500°C and 1000°C, thus belonging to the high-temperature fuel cells. ^[121]

The performance of fuel cells and electrolyzers depends strongly on the efficiency of the electrochemical reactions that occur at the individual electrodes. **Figure 2.2.1a** introduces the polarization curves for hydrogen-based EC-cells in acidic media, using the example of PEMFC (red) and a PEM electrolyzer (blue) ^[122]. While the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) are the decisive overall fuel cell reactions, the respective ones in electrolysis are the HER and the OER ^[60].

An essential factor in hydrogen-based electrochemistry is the water decomposition voltage of 1.23V versus a reversible hydrogen electrode (RHE) (*cf.* **Figure 2.2.1a**). Water splitting occurs for sufficiently larger potentials than this voltage, while on the other hand, only voltages smaller than this 1.23V can be reached in hydrogen-based fuel cells. ^[123] The required changes in potentials are schematically shown as the sum of the respective half-cell overpotentials, which lead to the theoretical electrolyzer and fuel cell voltage ^[60]. It is important to note that mass transport effects limit the maximum cell current (diffusion-limited current), thus playing a crucial role in the design of fuel cells (*cf.* **Subchapter 2.1.3**) ^[124]. ^[60] Since the fuel cell and electrolyzer efficiency strongly correlate with the applied catalyst material, further investigation of the processes occurring on the electrode surface is essential ^[125,126].

A detailed illustration of acidic hydrogen-based fuel cells and electrolyzers is schematically shown in **Figure 2.2.1b** and **Figure 2.2.1c**, respectively. Here, the individual reactions are assigned, and the fundamental processes are schematically sketched.

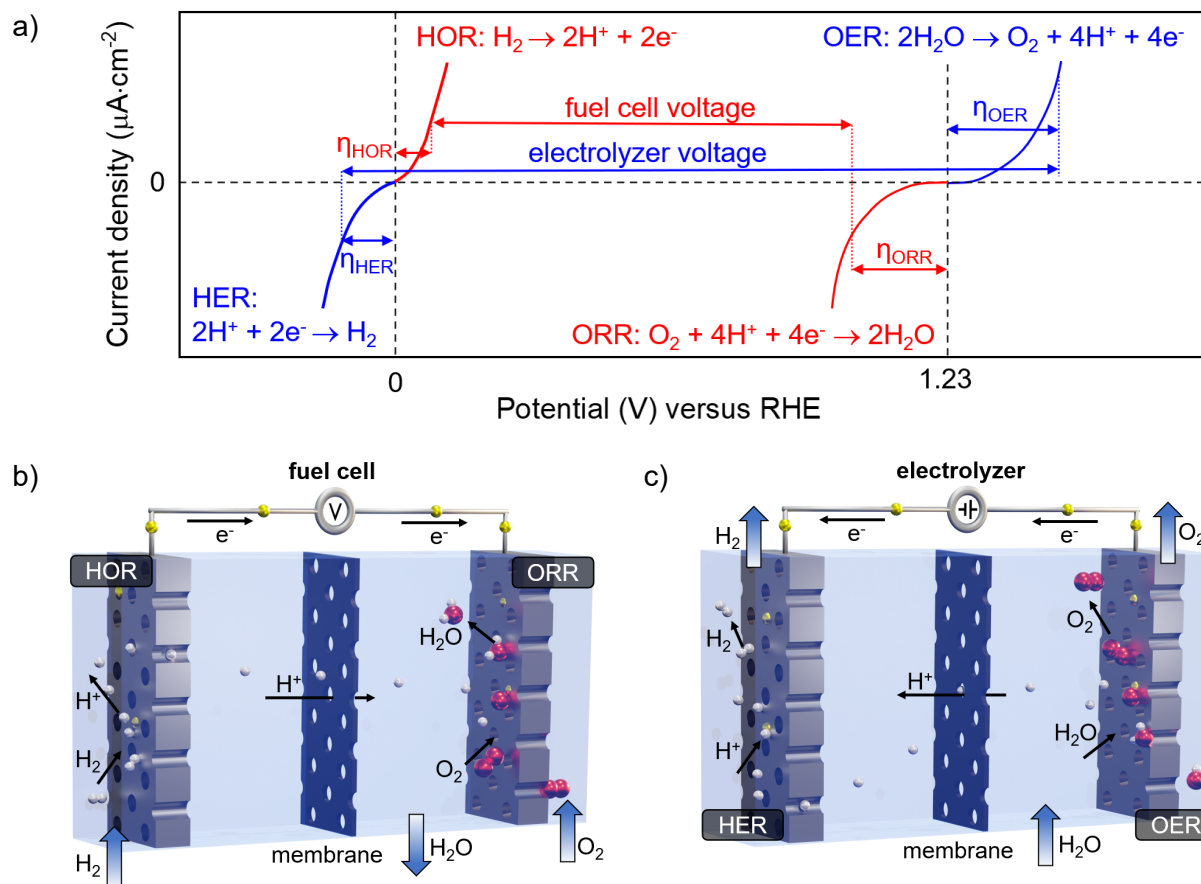


Figure 2.2.1. Overall reactions of hydrogen-based PEMFC and PEM electrolyzers in an acidic environment. In both cases, the proton yields the exchanged ion^[60]. **a)** Schematic overview of the current-potential relation for fuel cells (red) and electrolyzers (blue). The overpotentials η represent the difference between E_0 and the actually applied potential for a specific reaction. **b)** Simplified illustration of a fuel cell, and **c)** an electrolyzer setup. Here, the respective overall reactions are indicated schematically at each electrode. Figure a) is reproduced with minor adaptations from^[127] with permission from Springer Nature. Copyright 2016, Springer Science Business Media New York. Figures b) and c) are inspired by reference^[128].

In the fuel cell device, the hydrogen gas splits into protons during the HOR at the anode, which migrate through the membrane to the cathode side. Here, oxygen is reduced and reacts with the protons to water during the ORR. It is important to note that the electrons donated at the HOR

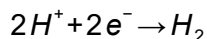
move in an external circuit to the cathode, where they are consumed during the ORR. In this way, electricity is provided while harmless water is produced as a byproduct.^[129] In contrast, electrolysis involves splitting water molecules during the OER into oxygen gas and protons. Analogous to the fuel cell, the protons from this reaction on the anode migrate through the membrane to the cathode. Here, they get fused to H₂ during the HER. This process requires external electrical energy and converts it into chemical energy in the form of hydrogen and oxygen gas. This chemical energy can be released when required, e.g., by using the fuel cell.^[130] It is important to note that the basic principle for alkaline-based fuel cells and electrolyzers is identical to that in acidic media. However, next to a difference in the overall reactions, in contrast to acidic cells, where H⁺ is the exchanged ion, in alkaline ones, OH⁻ migrates from one electrode to the other^[131].

An important region for the investigation of the HER, especially when using a scanning tunneling microscope (STM), is the potential range between E_0 and the exponential current increase^[28,29,132–134]. As shown in **Figure 2.2.1a**, the current is relatively small at this interval, and consequently, a small amount of evolved hydrogen is expected. This region is often termed the hydrogen underpotential deposition (H_{UPD}) region^[135–137]. In the literature, underpotential deposition (UPD) is defined as a phenomenon in which metal ions deposit as a monolayer onto a metal surface, even if the electrode potential is more positive than the predicted E_0 ^[138–140]. Regarding hydrogen as the depositing species, the H_{UPD} analogously describes a low amount of hydrogen adsorbed on a catalyst surface^[133,137]. In order to assign the potential interval with lower numbers of faradaic events, the reaction for these potentials will be termed as proton reduction in the following. In contrast, the reaction that induces H₂ gas bubble formation will be labeled HER. Nevertheless, to reach maximum transparency, the applied potentials of each discussed measurement are presented in the respective subchapters.

2.2.2 HER

The HER has been investigated intensely due to its importance in the hydrogen economy. In the past, it was studied for acidic and alkaline electrolytes and various electrode materials, such as Pt, Ru, Ir, Ni, Fe, Co, and Pd^[141–151]. Moreover, as indicated before, the HER has different overall reactions and intermediate steps depending on the pH value of the electrolyte. Since the investigations on Pd presented in this thesis are performed in perchloric acid (HClO₄), the following introduction of the HER is limited to the acidic pathway and relevant fundamental concepts.

The overall reaction in acidic media is defined by the following relation: ^[60]



This reaction can be further divided into three different intermediate steps ^[60] :



Here, H^{+} symbolizes a proton and e^{-} an electron. As visualized in **Figure 2.2.2**, the HER always begins with the Volmer step (grey background), where a proton becomes adsorbed on active sites, denoted as *. After its adsorption, it could react to H_2 by the Tafel or the Heyrovsky reaction. In the Tafel mechanism (red background), two adsorbed protons combine and get desorbed as H_2 . In contrast, in the Heyrovsky mechanism (blue background), the second proton comes directly from the electrolyte and, together with an additional electron, creates the H_2 molecule. Nevertheless, in both cases, the overall reaction remains the same ^[152].

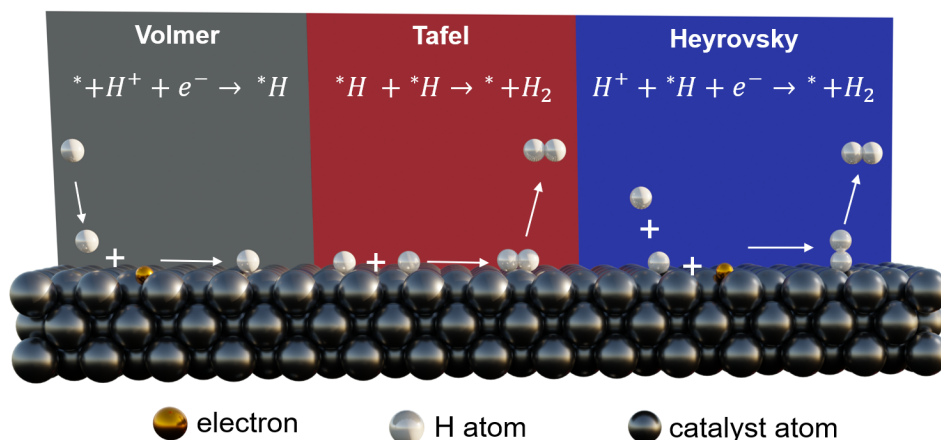
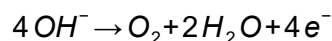


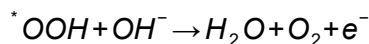
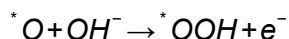
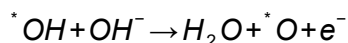
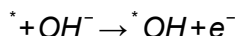
Figure 2.2.2. Sketch of the intermediate steps of the HER in acidic media. The grey spheres represent the catalyst surface atoms. In addition, the white H atoms in direct contact with the catalyst represent adsorbed protons. The consumed electrons, presented in golden color, are provided by the charged catalyst. Equations are taken from ^[60]. The image design is inspired by ^[153].

2.2.3 OER

Analogous to the HER, the OER differs for acidic and alkaline media with varied exchange ions. This work investigated the OER exclusively in potassium hydroxide (KOH), which is an alkaline electrolyte. For this reason, this subchapter focuses on the alkaline reaction pathway of the OER ^[154] :



This overall reaction is typically separated into four intermediate steps, as shown below ^[154] :



Here, the exchange ion is OH⁻, while the * symbol indicates the adsorption on the catalyst surface. Interestingly, the reaction rate of the OER was found to be about two orders of magnitude slower than the one of the HER, making it the bottleneck of water splitting ^[112] .

2.3 Measurement Methods and Techniques

Different methods and techniques were applied to identify active sites in this thesis. For all investigated sample materials, the same methodological scheme was exercised. Initial STM investigations without any previous electrochemical experiments helped to unveil the surface morphology and provided backup data in case subsequent electrochemical studies changed the surface topography. Following this, the CV experiments explored the general electrochemical behavior without providing information on the origin of its activity. However, these investigations created the electrochemical scope for the following EC-STM study, allowing an *in situ* analysis of local surface activity, thus determining the most active sites. This subchapter introduces the working principles of the applied measuring devices and presents the fundamental considerations for the theoretical investigations.

2.3.1 Three-Electrode Setup and Potentiostat

As a basis for all electrochemical investigations, a three-electrode setup was used, as schematically presented in **Figure 2.3.1**. The underlying consideration is that when using an EC-cell, which only consists of a WE and CE (*cf.* two electrodes in **Subchapter 2.1.1**), it is likely that the current flow measured between these electrodes will change between individual measurement sessions. Consequently, the experiments could not be correctly reproduced. These discrepancies originate from the measured current's strong dependence on the applied voltage. This potentially exponential relation causes considerable changes in the measured current, even at relatively small changes in the applied voltage. Next to solution and electrode properties, the physical distance between the WE and the CE significantly influences the actual WE potential. ^[75,155]

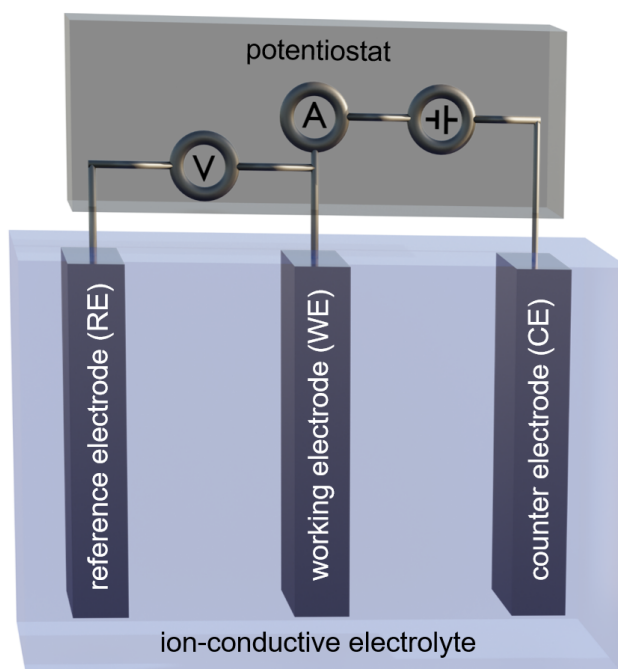


Figure 2.3.1. Schematic illustration of a three-electrode setup connected to a potentiostat. Inspired by reference ^[156].

Moreover, this distance may vary between measuring sessions and could change when groups in different laboratories perform the same experiments. Consequently, a two-electrodes setup (*cf.* **Subchapter 2.1.1**) has significant reproducibility drawbacks. In order to ensure that the potential remains the same under similar conditions, a third electrode is placed between the WE and CE, ideally close to the WE. This so-called reference electrode (RE) serves as an additional

sensor that allows the potentiostat, which is the potential controlling device, to adjust the WE potential relative to the potential measured at the RE. Despite the short distance between WE and RE, a reduced potential is also measured at the RE due to potential losses resulting from the distance between these two electrodes. Consequently, the input potential set by the operator and the one measured at the RE will not be the same. However, since both potentials are referenced to the ground, it is possible to calculate their difference. Knowing this difference makes it possible to amplify the applied cell voltage by the operational amplifier within the potentiostat to compensate for these losses. By this mechanism, a potentiostat can reliably reproduce a specific WE potential with respect to the applied RE independent of the measuring person or experimental setup. Even though an RE has minor variations in E_0 , it is designed to recover quickly and thus provide a mostly stable potential ^[157] . ^[158] In summary, a three-electrode setup connected to a potentiostat is crucial to control the WE potential and, hence, is the basis of all electrochemical experiments performed in this thesis.

However, since a potential only shows a voltage difference relative to a reference, it cannot be treated as an absolute value. Nonetheless, it is possible to recalculate the measured potential relative to another RE by using the Nernst equation and comparing different data from different experimental setups ^[80] .

The potential versus standard hydrogen electrode (SHE), termed E_{SHE} , is known for several commonly used reference electrodes ^[159] . At room temperature, it could be converted to a potential versus RHE (E_{RHE}) by using the following equation, which also demonstrates the strong dependency of the reference electrode potential on the pH value of the electrolyte ^[126] :

$$E_{RHE} = E_{SHE} + 59 \text{ mV} \cdot \text{pH} \quad (1)$$

2.3.2 Voltammetry

One potential controlling electrochemical experiment technique is voltammetry, which captures the currents induced by faradaic and non-faradaic processes at different potentials. Voltammetry can be classified into two types: stationary approaches, such as linear sweep voltammetry (LSV) or CV, and hydrodynamic approaches, such as flow cell or rotating disc electrode experiments. Moreover, anodic stripping voltammetry could be categorized as a subclass mixed out of stationary and hydrodynamic categories. ^[75]

In this subchapter, the two stationary methods, LSV and CV, which played a significant role in the data acquisition in the research of this thesis, are discussed in detail. As introduced in the previous subchapter, both techniques investigate the current-potential dependence on a WE using a classical three-electrode setup in the electrolyte. In brief, during the measurements, the potential is continuously changed by a specific scan rate while recording the current at the WE. Since the scan rate stays constant during the entire measurement, a particular time passes when changing the potential for a specific voltage interval. This velocity is called scan rate and has the units $\text{mV}\cdot\text{s}^{-1}$. As a result, the absolute current density captured during a particular period relates to the number of elapsed electrochemical reactions and provides information about the respective reaction rate. The measured current consists of a faradaic current induced by chemical reactions on the electrode and a non-faradaic current resulting partly from the charging of the EDL (*cf. Subchapter 2.1.2*)^[89,90] .^[160]

Linear sweep voltammetry: Typically, for LSV, an electrochemically neutral potential is selected as a starting point and positively or negatively varied until the mass transport losses dominate (*cf. Subchapter 2.1.3*).^[75] A simple schematic example of such an LSV measurement is illustrated in **Figure 2.3.2a**. Here, the potential continuously decreases from the starting point E_1 to the end value E_2 . As visible, the current decreases exponentially with decreasing potential. A linear area appears when plotting the current density in logarithmic scales, which decreases exponentially for potentials close to zero (red solid line), as shown in **Figure 2.3.2b**.

The value of the one-dimensional extension of the linear region (red dashed line) at a potential of 0V, where no overpotential is applied, corresponds to the logarithm of the exchange current density $\log(j_0)$. As a variable of the Butler-Volmer equation and strongly dependent on the temperature, j_0 plays a significant role in the activation losses of an EC-cell. The slope of the red dashed line provides further information about the reaction kinetics. When measuring the so-called Tafel slope s_{Tafel} , it is possible to derive the charge transfer coefficient α , which significantly influences the shape of the current-overpotential curve of the half cell.^[124] In addition, the value of s_{Tafel} indicates the rate-determining step (RDS) of the observed electrochemical reaction, which represents the bottleneck of an electrochemical reaction^[161–164] .

It is important to note that an experimentally determined j_0 correlates with the number of active sites in the observed area. Despite each sample surface being unique and thus surfaces of the same material might vary, j_0 does not consider differences in surface morphology. Moreover, critics point out that j_0 is insufficiently suited to determine the catalyst's total current for particular overpotentials due to the lack of information on the respective s_{Tafel} . Consequently, a higher j_0 value

does not guarantee a higher current density for all possible overpotentials when two different catalysts have a strongly differing s_{Tafel} . Based on these considerations, its suitability as an accurate descriptor for the overall electrochemical activity of an electrocatalyst is the subject of debate in the literature.^[165–169] Nevertheless, applying it to indicate the catalyst's activity is a common approach, while the mentioned points should be considered^[102,170–172].

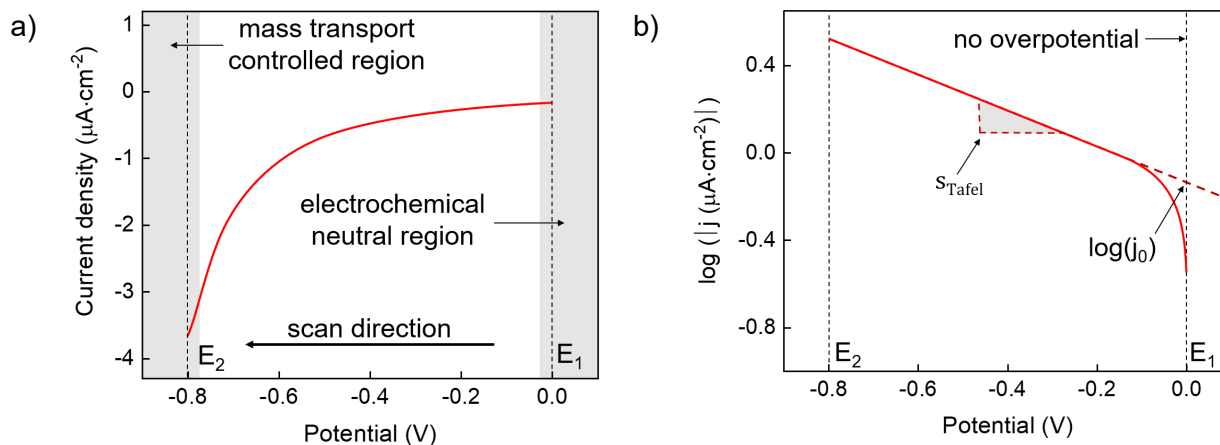


Figure 2.3.2. Schematic illustration of LSV measurements and their interpretation. **a)** The Polarization curve for a hypothetical measured potential interval between E_1 and E_2 is colored in red. The mass transport-controlled regions and the electrochemically neutral region yield the natural range for this type of measurement. **b)** In this Tafel plot, the fitted dashed red line enables the calculation of s_{Tafel} and the identification of j_0 . Here, R is the gas constant, T is the temperature, α the charge transfer coefficient, n is the number of transferred electrons, and F is the Faraday's constant.^[75] Figure a) is inspired by^[124]. Figure b) is adapted from reference^[173] and licensed under CC BY 4.0^[87].

Cyclic Voltammetry: CV is the predominantly applied voltammetry method in this thesis. Depending on the specific material and electrolyte composition, the resulting current-overpotential graph has an individual shape. As a result, it provides information about the observed material and, in the case of crystalline samples, even its crystalline orientation^[43,174]. In contrast to LSV, the potential sweeps continuously back and forth between two set potentials, as demonstrated in **Figure 2.3.3a**. Here, E_1 represents the starting point, E_2 illustrates the turning point and maximum potential, and E_3 shows the minimum applied potential. Typically, the scan starts at an electrochemically neutral potential, where the faradaic activity is minimized, such as at the double-layer region, as shown in the example cycle of a Pd(111) CV in **Figure 2.3.3b**. This double-layer current is a background current consisting, among others, of film formations, impurities, and capacitive processes at the EDL^[90].

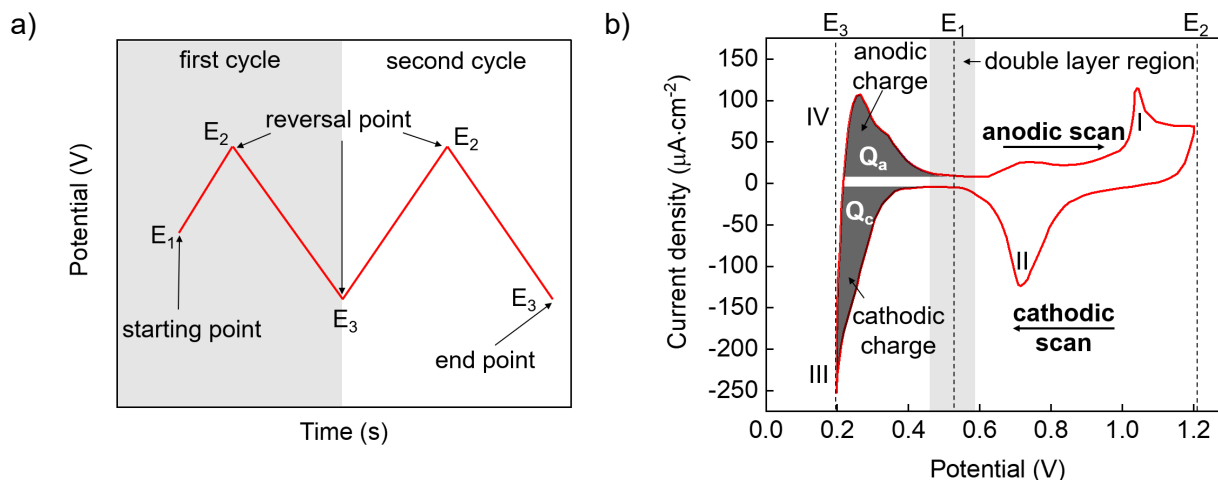


Figure 2.3.3. Basic principle of CV measurements. **a)** Potential time dependency during CV measurements. The red line presents the course of the applied voltage and underpins its continuous scan rate. **b)** First cycle of a CV measurement on Pd(111) in 0.1M HClO_4 , explaining the most relevant characteristics. Figure a) is inspired by [75]. Data of b) published in reference [175].

In the simplified case, when only considering the potentials higher than the one at the double-layer (between E_1 and E_2), two notable current peaks (peaks I and II) appear. This example interval represents the typical surface oxide formation, dissolution, and surface oxide reduction region for Pd [176]. The underlying reason for the occurrence of these peaks is the increase of faradaic reactions at higher potentials. Thus, when leaving E_1 in the double-layer region in a positive potential direction, the reactants close to the electrode get oxidized (oxide formation) at an increasing rate until the maximum current is reached at about 1.1V versus RHE (peak I). At this point, the effect of mass transport limits further growth, and diffusion processes play a significant role. In addition, the double-layer's thickness increases for even higher potentials, further inhibiting faradaic activity. Consequently, the current decreases again. This potential sweep in the positive direction is denoted as the anodic scan. When decreasing the potential again after reaching the potential sweep point E_2 , the electrode starts to provide electrons, and the reduction of the reactants starts. Since the concentration of oxidized species close to the electrode is very high, the current decreases drastically until a minimum of 0.7V versus RHE (peak II) is reached (oxide reduction). For even lower potentials, the reaction rate and, thus, the measured current decrease until the double-layer region is reached. This potential sweep in the negative direction is defined as the cathodic scan. [75,89,160]

Analogous, the HUPD region on Pd comprises the H ad- and absorption peak (III) and H desorption peak (IV) ^[176]. In the hypothetical case, without absorption, all adsorbed reactants would have to be desorbed as products in order not to poison the surface. Consequently, the areas of the anodic charge Q_a and cathodic charge Q_c should be the same. By integrating these sections, the estimated absorption relative to the adsorbed is roughly given by the following equation: ^[175]

$$absorption = 100 - \left(\frac{Q_a}{Q_c} \cdot 100 \right) \text{ with } Q_c < Q_a \quad (2)$$

2.3.3 STM and EC-STM

In 1982, Binnig and Rohr presented the first research article about the invention of STM ^[177]. Four years later, in 1986, they were honored with the Nobel Prize and earned the science community's attention ^[178]. In the same year, Sonnenfeld and Hansma introduced STM measurements in water, thus laying the fundament for EC-STM ^[179]. Moreover, together with Drake and Schneir in 1987, they demonstrated that detecting surfaces before and after electrochemical processes is possible without removing the sample from the solution. These experiments investigated a graphite surface before and after gold plating in a 2mM saline solution. ^[180] The final breakthrough in the invention of EC-STM was made in 1988. Mostly simultaneously, Itaya *et al.* and Lustenberger *et al.* combined the STM technique with a three-electrode setup and a separate control of the WE and tip potential, thus creating the basic principle of modern EC-STMs ^[181,182].

In order to shed light on the brilliance of this innovation, this subchapter introduces the most relevant aspects of STM and EC-STM. Moreover, it explains the working principle of n-EC-STM, which is a specific application of EC-STM and was the central tool for identifying active sites in this doctorate.

STM: An STM device basically consists of a very sharp tip, which ideally has a single exposed apex-atom, a feedback loop, which controls the tip movement, and a computer, serving as the operating interface. **Figure 2.3.4a** illustrates that the STM tip, typically made out of tungsten or Pt/Ir, scans the electrically conductive sample surface up to a distance lower than 1nm. Due to a bias voltage of about 10mV to 1V applied between sample and tip, the tunneling of electrons is achieved. Here, typical tunneling currents are in the range of 0.2nA to 10nA.

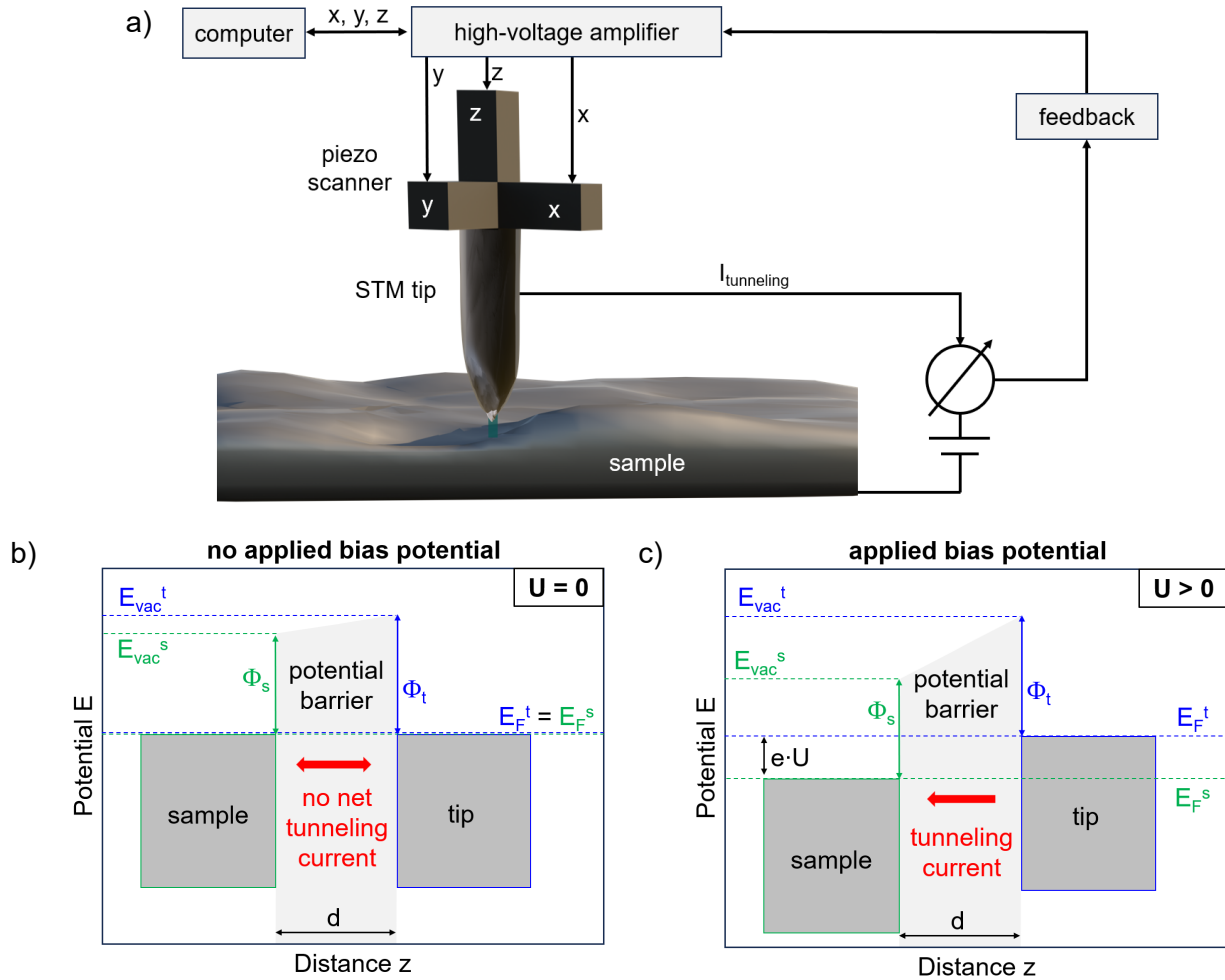


Figure 2.3.4. Working principle of an STM device. **a)** Schematic illustration of the relation between the STM tip, sample, feedback unit, and high-voltage amplifier. **b)** Energy diagram of the sample-tip interface when no bias potential is applied. Due to the equal height of the Fermi levels, there is no net tunneling current. **c)** Analog diagram, as in b) with an applied potential U and thus different Fermi levels. Consequently, an oriented tunneling current occurs. Figure a) is inspired by ^[183], while Leon Haase designs the STM tip. Figures b) and c) are adapted from ^[184] with permission from SNCSC. Copyright 2016, Springer Science Business Media Dordrecht.

By measuring this current using an appropriate detector and feeding this information into a feedback unit and a high-voltage amplifier controlled by a computer, it is possible to regulate the tip-sample distance. In order to achieve a fast and controlled movement, piezo elements were used, which enabled the adjustment of the tip position in three dimensions. During the measurement, the tip moves back and forth in the x-direction close to the sample surface and

captures the change in tunneling current or distance depending on the utilized STM mode. The resulting two-dimensional line scan shows the sample morphology along the x-direction, which is defined as the fast scan axis. After reaching the initial tip position, the piezoelectrics move the tip slightly in the y-direction, where the next line scan is captured. This direction is further denoted as the slow scan axis. In this way, STM reveals the surface morphology of a specific area, which is defined by the selected scan size. Typical values for the maximal vertical and horizontal resolution are 0.1Å and 0.02Å, respectively. In order to maximize its resolution, the STM technique is usually applied in a vacuum at ultra-low temperatures. However, it can also be operated in an air atmosphere in ambient conditions. ^[185,186]

The STM device operates when the tip converges the electrical conductive sample with an approximate distance between 0.3nm and 1nm ^[186]. As illustrated in **Figure 2.3.4b**, dependent on the used sample and tip materials, the individual work functions Φ_s and Φ_t vary, respectively. Analogous, their vacuum levels E_{vac}^s and E_{vac}^t differentiate, which determines the height of the potential barrier ^[187]. Even if the energy of the electrons is too low to overcome the potential barrier, they can swap between the tip and sample by quantum mechanical tunneling. If no potential U is applied, for a fixed tip-sample distance d , the Fermi levels of the tip E_F^t and the sample E_F^s are equal. In this situation, at a hypothetical temperature of 0K, one might find electrons with a probability of 50% at these energy levels ^[188]. As a result, the system is in equilibrium, and no measurable net tunneling current occurs. This situation changes as soon as potential U is applied, as presented in **Figure 2.3.4c**. Due to the reduced number of electrons on the sample surface, when applying a positive potential, E_F^s decreases by $e \cdot U$ while e is the elementary charge. Since the work function remains the same, the potential barrier also decreases, but it can still not be overcome if the applied voltage is not high enough. However, due to the decreased E_F^s , and hence relatively higher E_F^t , there are unoccupied states in the sample material that are lower than those of the tip. Consequently, the electron tunneling has a preferred direction, resulting in a net tunneling current unequal to zero ^[189]. As indicated in **Figure 2.3.4a**, since the STM device is connected to the electrical grid, it is possible to maintain this difference in Fermi levels and thus create a permanent tunneling current that appropriate detectors could measure. Due to the circumstance that the tunneling current exponentially varies with the tip-sample distance d , and thus, even minor variations in height result in significant tunneling current changes, it is possible to observe the sample surface with high precision. Moreover, it is important to note that the captured surface morphology mirrors the shape of the local density of states at the Fermi level instead of showing the actual position of the nucleus. ^[189–191]

The two modes typically employed at STM measurements are the constant height and constant current modes. At the constant height mode presented in **Figure 2.3.5a**, the piezoelectrics hold the tip-sample distance d at a fixed value while scanning the surface. At the same time, the varying tunneling current is captured. In the case of a surface elevation, the tunneling current increases drastically due to its exponential relation to the distance d . In contrast, as soon as the surface-tip distance d rises, the tunneling current decreases. The raw images captured during this doctorate consist of 512 measuring points in the fast scan direction, creating a single line scan, while 512 line scans produce an STM image. The advantage of measuring in constant height mode is that the turned-off feedback loop allows a high scan velocity, which is beneficial when targeting high-resolution images. On the other hand, thermal shifts might be less compensated, and the chance of a tip crash increases. ^[190]

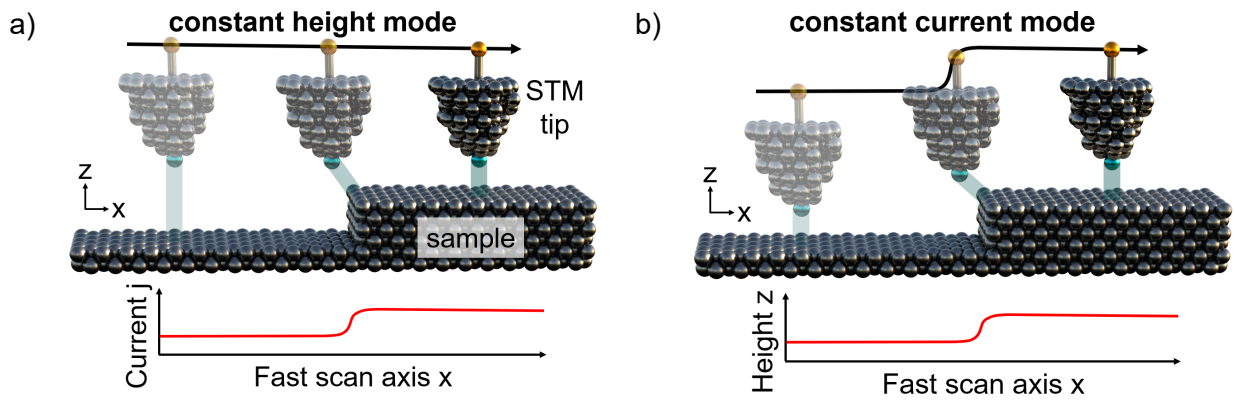


Figure 2.3.5. Overview of typical STM modes. The image's upper half represents the STM tip's motion relative to the sample surface for **a)** the constant height mode and **b)** the constant current mode. The turquoise sphere at the apex of the STM tip illustrates the tunneling atom, while the turquoise beam indicates the tunneling direction. The corresponding variations in the current and height signals are presented in the lower half of the image. Both figures are inspired by ^[192].

Next to the damage on the sample surface, such a tip crash typically results in a deformation of the tip apex and thus requires the replacement of the entire tip. Due to the small size of the observed area, it is usually impossible to find the investigated position again after the tip change. Consequently, the investigation of observed structures is also interrupted. For this reason, the preferred STM method used for the data acquisition in this doctorate was the constant current mode, as depicted in **Figure 2.3.5b**. Here, the feedback unit permanently adjusts the tip-sample distance d to hold a certain tunneling current. The threshold for this current determines the current

setpoint (CS), which yields the maximum value of the detected tunneling current before the tip retracts from the surface ^[185]. Compared to the constant height mode, the constant current mode enables the measurement of rougher surfaces with a minimized chance of crashing the tip. On the other hand, the adequate scan velocity is smaller in this mode, which is disadvantageous for high-resolution imaging. However, since the captured overall current consists of the actual tunneling current and additional leakage current for both modes, reconstructing the actual height d from the detected current signal is challenging ^[193]. ^[190] Two closely situated tip spikes could form a double-tip, manipulating the captured surface morphology ^[194]. An example of the impact of a double-tip is shown in **Figure 2.3.6** for the constant current mode. Here, an STM tip apex with two spikes schematically moves over a sample with a step of multiple atomic layers.

As presented in **Figure 2.3.6a**, the tunneling occurs at the left spike (turquoise) on flat surfaces since it is closer to the sample than the right spike (red). When the tip moves further in the x -direction, the distance between the red spike and the upper side of the step becomes lower than between the sample and the turquoise spike. Due to the resulting increase in tunneling current, the piezoelectrics retract the tip from the surface until the initial tunneling current is reached. Consequently, the STM device records a step edge, as depicted by the black line above the tip. Moreover, as illustrated in **Figure 2.3.6b**, tunneling occurs at the red spike for a short period. However, when moving further in the x -direction, the turquoise spike starts to tunnel again, and the tip retracts further (*cf.* **Figure 2.3.6c**). As a result, the STM unit captures the same tip for a second time. Despite the artificially double-captured step edge, the rest of the tunneling signal appears unsuspecting, as **Figure 2.3.6d** indicates. Consequently, it is challenging to distinguish between two closely neighbored steps captured by a single-spiked tip and an artificially captured double-step originating from a double-tip.

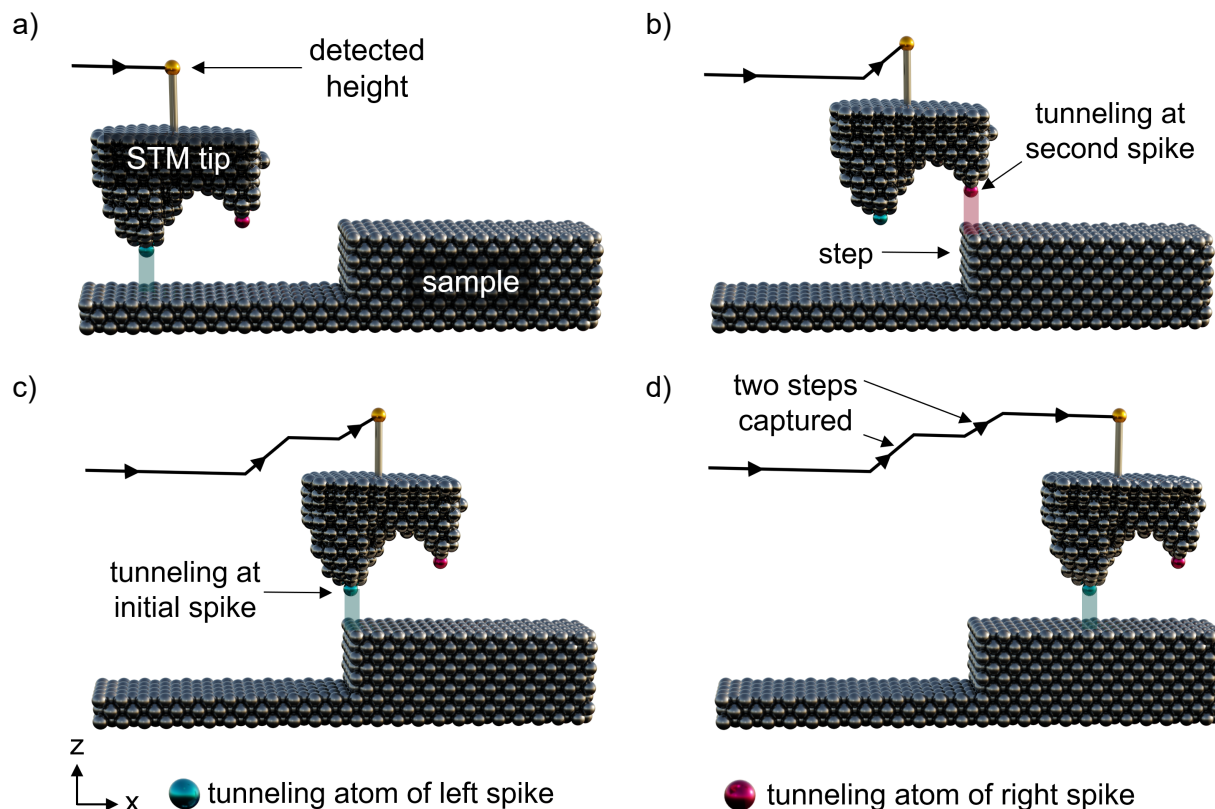


Figure 2.3.6. Schematic illustration of a twice-measured step edge. The condition for such a phenomenon is a lower height difference between at least two spikes at the apex of the STM tip than the height of the observed step. **a) - d)** Intermediate positions when scanning a multi-atomic layered step with a double-tip with two spikes. The black line above the tip represents the height profile, which the STM device records.

EC-STM: An EC-STM device merges the basic concepts of a three-electrode setup and an STM unit, thus allowing the investigation of electrochemically induced influences on the sample surface. As discussed before, it is challenging for STM to find the exact position twice due to the small areas of several hundreds of nm. Consequently, it would be a great advantage if the electrochemical experiments could be implemented without removing the sample from the electrolyte and to compare the surface morphology before and afterward. In addition to the feedback loop, which controls the tip-sample distance as indicated in **Figure 2.3.7a**, the EC-STM device includes an entire three-electrode setup connected to a potentiostat (*cf.* **Figure 2.3.7b**). Furthermore, the potentiostat controls the STM tip potential with respect to the RE to reduce the influence induced by faradaic currents from reactions on the tip surface to the tunneling signal. Consequently, an EC-STM device represents a four-electrode setup. To further reduce faradaic tip current, the entire tip

surface except for its apex is covered by an insulating coating to minimize the exposed area to the electrolyte.^[190]

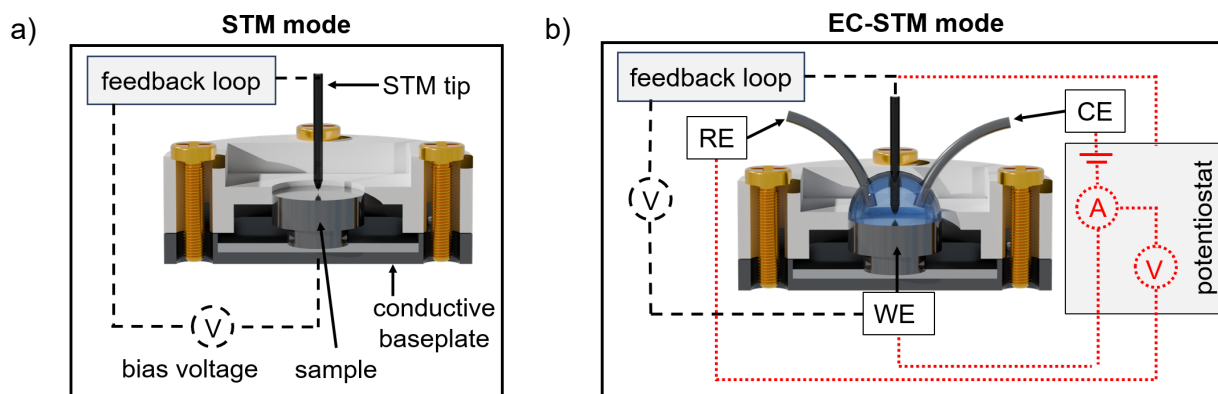


Figure 2.3.7. Schematic view of the individual parts of the STM sample holders. A drop of electrolyte covers the exposed surface of the sample, which serves as WE. **a)** and **b)** illustrate cross-sections of the sample holder and describe the essential parts when used for STM or EC-STM, respectively. Here, simplified electrical circuits are shown. The electrical circuit for the STM mode in **a)** is inspired by ^[190]. Electrical circuits for the EC-STM mode in **b)** are inspired by ^[156] and ^[190].

This powerful setup allows the *in situ* application of Voltammetry and STM experiments within the same measurement session. Consequently, EC-STM plays a crucial role in surface science, such as in corrosion, electrodeposition, or catalysis studies^[195–198]. Moreover, a special application of the EC-STM setup is n-EC-STM, which enables the identification of the electrocatalyst's active sites^[28].

Historically, a fundamental article that indicated the potential of EC-STM to investigate faradaic processes locally was presented by Meier *et al.* in 2002. They elucidated that the STM tip could be applied as a probe to investigate the HER activity on Pd nanoparticles on a gold substrate.^[199] One year later, Hugelmann *et al.* described that even the presence of a monolayer of water molecules between the STM tip and the surface can increase the width of the tunneling barrier and thus influence the tunneling current. Additionally, they postulated that the tunneling current at a solid-liquid interface is non-exponential, which impedes estimating the actual tip-sample distance at EC-STM.^[200] In 2017, Pfisterer *et al.* demonstrated the power of the n-EC-STM technique. They presented the active sites on the boundary of Pd islands on an Au(111) substrate for the HER in 0.1M H₂SO₄ and on Pt(111) step edges for the ORR in 0.1M HClO₄. Here, the fundamental

principle rests on the influence of changes in the medium within the tunneling barrier on the tunneling current. ^[28]

In n-EC-STM and other electrochemical processes, the reactants continuously adsorb and desorb under reaction conditions on the electrode surface ^[75]. In addition, the electrolyte concentration in the electrode's close proximity also changes but is limited by mass transport effects ^[160]. As a result, for a constant tip-sample distance, the tunneling current varies due to its vulnerability to the tunneling medium's composition ^[201]. Consequently, when the STM tip scans an area where faradaic processes appear in constant current mode, the STM device has to frequently adjust the tip-sample distance to keep the preset CS. ^[28] To illustrate the working principle, imagine the CS is set to 10nA, and the STM image is measured in the constant current mode without any leakage current. Moreover, suppose an electrochemical reaction within the tunneling barrier temporarily increases the tunneling current to 12nA. In that case, the STM's piezo unit will retract the STM tip from the sample surface to decrease it to the initial value of 10nA. For a simplified assumed linear current-distance relation, the STM device would measure a tunneling current of 8nA when the reaction is over and the initial state is restored. As a result, the tip has to approach the surface again. By this mechanism, the STM unit records a peak, which results in faradaic processes instead of representing any actual surface structures. Due to the exponential relation between tunneling current and distance, in reality, this effect is more pronounced and strongly dependent on the selected gain settings, as explained in detail in **Subchapter 3.3.3** ^[190]. This fluctuation in the STM signal is called noise and represents the additive n in n-EC-STM.

Since electrochemical reactions are expected to occur randomly and STM devices are known to be able to emulate white noise, *e.g.*, seen in scanning noise microscopy (SNM), the detected STM noise might also correspond to a white noise signal ^[190,202]. This hypothesis would also explain why a Gaussian distribution yields an appropriate approximation to characterize the noise signal, as discussed in **Subchapter 3.4.2** and shown in previous works ^[175,203–207].

If suitable gain values are set and when no electrochemical reactions occur, the STM device can scan the surface very smoothly and map the surface morphology. This state is usually reached when the applied potential is set within the double-layer region (*cf.* **Figure 2.3.3**) and will be denoted as a reaction 'Off' in the following. **Figure 2.3.8a** illustrates three representative positions of an STM tip movement across a single atomic stepped surface in the fast scan direction for reaction 'Off'. As presented in the graph, the entire surface is noise-free, while the contours of the step are apparent. On the other hand, when selecting the applied potential within a faradaic active region, as presented in **Figure 2.3.8b**, it is termed as reaction 'On'. As discussed before, under

these conditions, the captured STM signal becomes noisy if the tip crosses an active site (golden-colored step atoms).

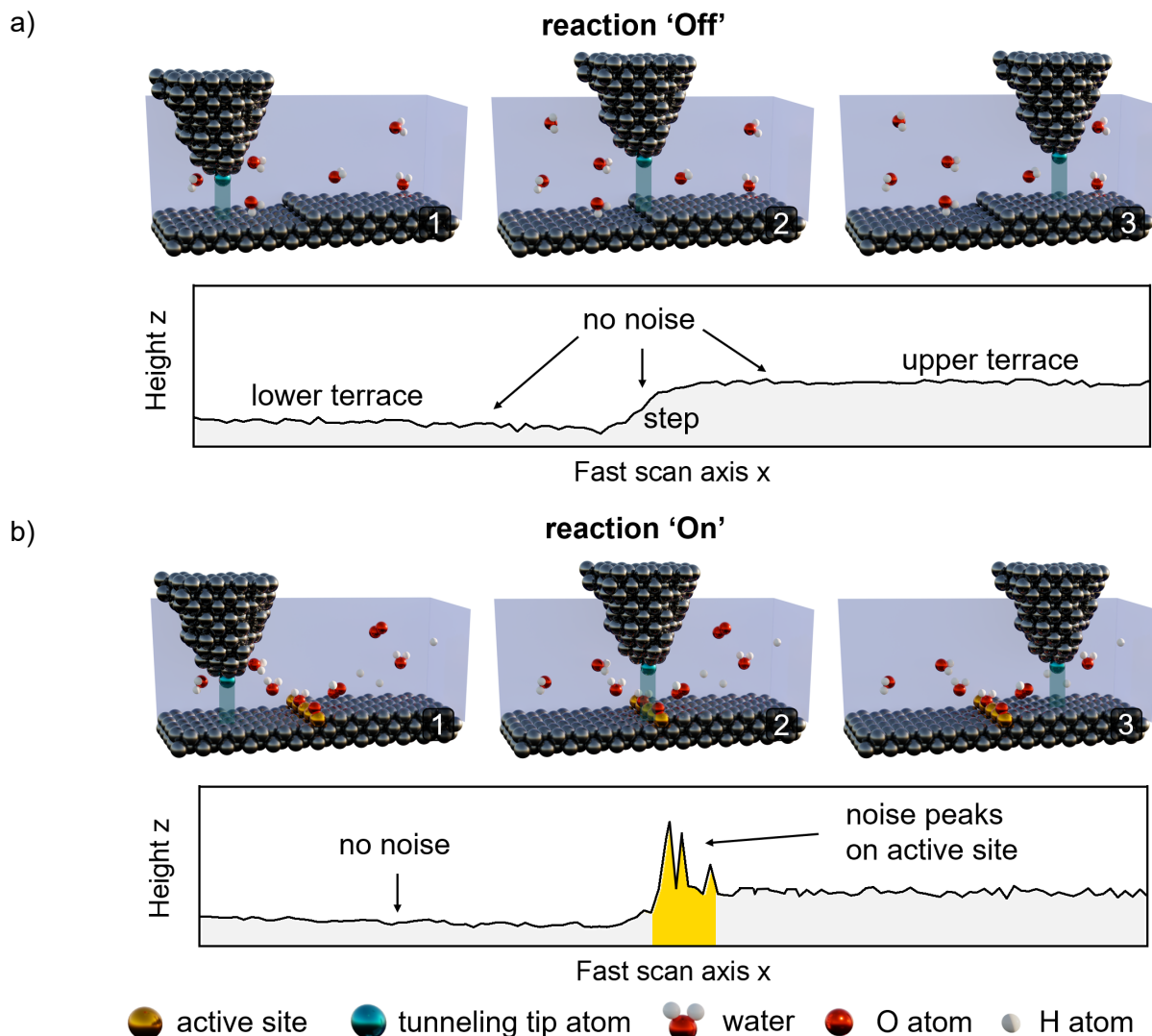


Figure 2.3.8. Schematically illustrated procedure of an *n*-EC-STM measurement. **a)** Different moments (1-3) showing an STM tip moving over a surface. The turquoise sphere at the bottom of the tip represents the tunneling atom. In addition, the graph below the three-dimensional images demonstrates the hypothetical captured corresponding line scan. Here, the morphology of the lower and upper terraces separated by the step becomes apparent. **b)** Analogous graphic under reaction conditions. Here, the water molecules schematically split into O_2 and H_2 atoms on the step edge, representing the active site in this example. Both Figures are inspired by ^[208].

In contrast, the less active areas (grey) do not show any such conspicuous spikes. In this way, it is possible to identify the active sites of various electrocatalytic active materials.^[28] It is important to note that applied potentials that are too high or too low induce many faradaic events and thus create a visible gas bubble on the tip-sample interface^[118,204]. As a result, due to the surface tensions of the gas bubble, the measurement cannot be continued, and the entire tip needs to be temporarily removed from the electrolyte. Nevertheless, the functionality of the n-EC-STM's working principle and its ability to identify active sites have already been verified in several previous research projects^[175,204–206,208–213]. Remarkably, this technique also enables the investigation of the active sites in an outstanding resolution, up to atomic scale^[29,118].

Moreover, it is essential to note that STM and n-EC-STM are approaches where the captured line scans represent a particular moment. As a result, due to the randomness of the noise combined with likely thermal shift, which might slightly influence the scan angle, each line scan presents a unique snapshot. With this in mind and regarding the fast scan velocity of the tip, it also becomes apparent that the noise's width and height are not representative and, thus, will not be further evaluated in this thesis. Nevertheless, Haid *et al.* demonstrated that increasing the data pool to a sufficient size is possible by holding the tip above an active site. Using this representative data set, they determined the turnover frequency (TOF) and found a linear relation between noise and reaction rate. However, a precondition for such a measurement is a large active site or a low thermal shift to fix the tip position for an adequate duration. Consequently, depending on the target of the research project, it is possible to gain valuable information about the reaction kinetics of a sample by using the n-EC-STM technique. Another exciting fact highlighted in their work is that the fast scan axis also represents a time scale due to the constant scan velocity during STM measurements.^[203]

Building on this capability in investigating electrocatalysts and regarding the objective of this thesis to further explore promising energy materials, the n-EC-STM technique yields the primary method used for the research in this doctorate.

2.3.4 DFT

Combining theoretical and experimental approaches is a powerful strategy to investigate complex matters. When performing EC-STM measurements, DFT can significantly supplement the insights and provide an extended interpretation of the findings due to its ability to predict the electronic structure of materials. In addition, it is capable of determining the Gibbs free energies of electrochemical reactions and their intermediates and, thus, the detailed reaction pathway.^[108] In this study, this advancement was made possible through collaboration with universities in Ireland and Iceland. This subchapter will present the essential considerations and initial insights required to understand the computational approaches of the DFT investigations on Pd and MnO₂NS/HOPG.

Fundamental insights into the Pd investigation: According to the Sabatier principle introduced in **Subchapter 2.1.4**, an efficient catalyst should bind a reaction intermediate neither too strongly nor too weakly. For this reason, a common DFT approach to investigate the activity of catalyst material is to determine the binding energy between the reactant and the catalyst, *i.e.*, the thermodynamic landscape of the studied reaction mechanism^[214–217]. The group of Dr. Matthias Vandichel from the University of Limerick (Ireland) investigated the H intercalation in Pd single crystals for different surface facets and calculated the corresponding changes in Gibbs free energies ΔG_{H^+} . In order to comprehend the implemented approaches and selected concepts presented in **Subchapter 4.1**, the following paragraph presents the most important considerations published in Schmidt *et al.*^[175]:

The fundamental idea of the theoretical investigation on the Pd single crystals is that when hydrogen gets absorbed into the Pd crystal, it randomly fills the voids within the Pd lattice's top layers^[175,218,219]. With this in mind, the group of Dr. Matthias Vandichel found that depending on the number of intercalated H atoms, the volume of the observed PdH supercell varies due to steric repulsion between Pd and H (*cf.* **Figure 2.3.9 A1a**). Furthermore, an optimal amount of H within the bulk can be found when considering the formation energy E_{form} of PdH crystals with different H contents (for more information on the computational procedure, see^[175]). Thus, these results provide information about the likelihood that the H atom stably binds in the crystal, forming PdH. From a thermodynamic point of view, as a consequence, hydrogen tends to be located at octahedral and tetrahedral sites up to a proportion of three H atoms and two Pd atoms (negative values for E_{form} in **Figure 2.3.9 A1b**). The lowest formation energy and, thus, the most preferred configuration was found for a one-to-one H-Pd ratio (the lowest point in **Figure 2.3.9 A1b**). However, a much lower ratio was used for the calculations made in **Subchapter 4.1** to simulate

the conditions of the EC-STM measurements as well as possible. This decision is based on the fact that the applied potential used for the n-EC-STM experiments was selected within the H_{UPD} region, where only a small H-absorption is expected (cf. **Subchapter 2.2.1** and references ^[135] and ^[175]). Furthermore, as demonstrated by the STM investigation in **Subchapter 4.1**, there is no indication of a change in morphology during the STM measurements; thus, a low amount of absorbed H during these experiments is plausible.

In addition, as illustrated in **Figure 2.3.9 A2**, the preliminary considerations suggested the highest absorption energy at the octahedral site with -0.26eV, thus revealing it as the most preferred site for the PdH formation in crystalline Pd(111). The second favored site is the lower tetrahedral with -0.20eV, followed by the upper tetrahedral site (-0.18eV). Based on these findings, the DFT calculations in this subchapter focused on the octahedral sites with a one-to-one H-Pd ratio. Moreover, the computational investigation assumed a layer-by-layer H-occupation of the Pd single crystal starting from the top in order to unveil the processes during H-absorption. Consequently, for each investigated crystallographic plane, all calculations were performed for the pristine Pd single crystal (0 PdH sublayers) as well as up to four PdH sublayers. An illustration of the individual crystal facets for four PdH sublayers and an overview of the investigated supercells is provided in **Figure 2.3.9 A3** in **Appendix C**.

Conceptional overview of the $MnO_2NS/HOPG$ investigation: As discussed in **Subchapter 2.1.4**, the intermediate step with the highest thermodynamic barrier of an electrochemical reaction is defined as the PDS and limits the reaction rate. In order to ascertain the most likely reaction process, the DFT approach presented in **Subchapter 4.2** aimed to identify the overpotential of the PDS (η_{PDS}) of several promising atomic configurations on the model system ^[213]. In DFT, one can select different models and functionals depending on the observed system and specific properties. In the case of the DFT calculations presented in **Subchapter 4.2.3**, the DFT expert selected the function of Perdew, Becke, and Ernzerhof combined with the Hubbard correction as the most suitable approach for the $MnO_2NS/HOPG$ system ^[213]. In order to learn more about these functionals, references ^[220–223] are recommended.

2.4 Sample Materials

The investigated sample materials in this thesis were different Pd single crystals and the hybrid material MnO₂NS/HOPG, which consists of HOPG support with MnO₂ nanosheets on top. The following subchapters provide an overview of their material properties, dimensions, and particular characteristics.

2.4.1 Single-Crystalline Pd

Pd is a transition metal that appears as a silver-white colored face-centered cubic (fcc) crystal in its pure form. Its melting temperature of approximately 1552°C must not be exceeded during annealing, and it plays a crucial role in the sample preparation (cf. **Subchapter 3.2.1**).^[224] Despite its general oxidation resistance, it is known that the surface discolors at temperatures above 350°C in an oxygen-rich environment^[224–228]. Consequently, the single crystalline Pd preparation requires special treatment in an oxygen-free atmosphere.

The ability of Pd to absorb hydrogen in a significant amount makes it a popular material in hydrogen catalysis research, especially as thin Pd sublayers or nanoparticles on support materials^[46,102,229–231]. As discussed in the results part of this thesis, PdHs formed after hydrogen absorption influence the crystal properties^[175,232]. Literature shows that this modification could even alter the crystal's lattice constant, which is around 0.389nm for pristine Pd^[102,233]. Moreover, for the HER, layered but also polycrystalline Pd occupies the top positions of the volcano plot besides Pt, Ir, and Rh, as shown in **Figure 2.4.1a**. Due to its relatively high current exchange density in correlation to slightly negative values for ΔG_{H^+} , Pd is a promising catalyst material for hydrogen evolution.^[46,102,161]

Interestingly, the electrocatalytic activity for crystals depends on the material composition and the crystallographic orientation^[43]. For this reason, the sample materials in this doctorate included different crystalline facets. The main focus was set on Pd(111), Pd(110), and Pd(100) for the experimental investigations and also on Pd(211) for the computational study. **Figure 2.4.1b** visualizes these different facets and highlights the surface plane and atoms in blue and turquoise, respectively. Especially in the three-dimensional models, the step-like characteristics of the Pd(211) surface become apparent. Moreover, for the subsequent discussion of the findings on the Pd crystals, it is helpful to have an approximate idea of the dimensions of a single atomic step.

Based on different TEM, ellipsometry, and STEM experiments, the literature describes the height of a monolayer on Pd(111) as about 0.223nm^[234–238].

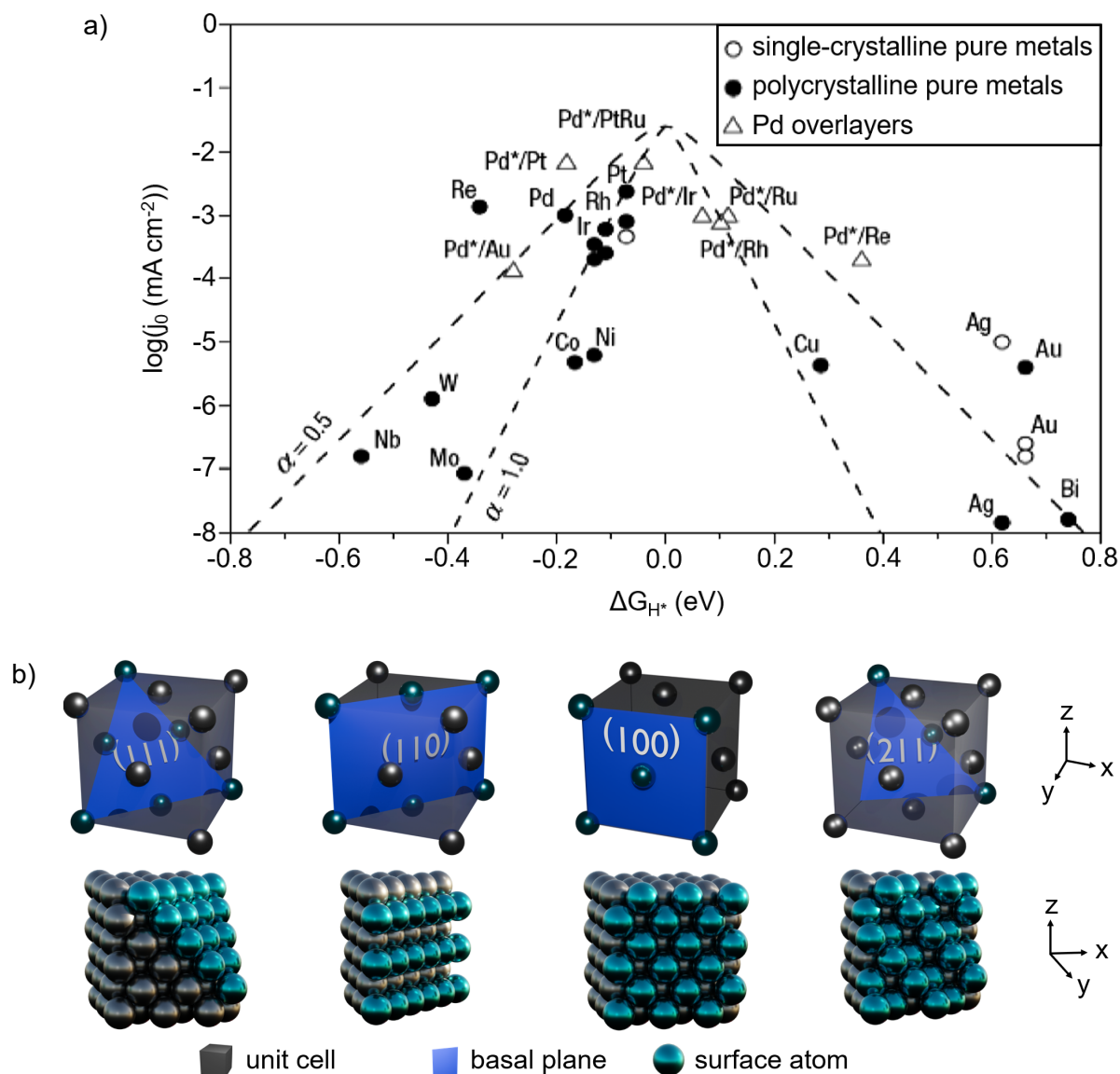


Figure 2.4.1. Overview of relevant Pd characteristics. **a)** The volcano plot presents the HER exchange current densities of several crystalline metals and Pd overlayers against the Gibbs free energies for hydrogen adsorption. **b)** Modeled crystallographic planes and designed surfaces for the investigated crystal facets Pd(111), Pd(110), Pd(100), and Pd(211). Figure a) is reprinted with minor reformatting with permission from ^[102]. Copyright 2010, John Wiley and Sons. The upper images in b) showing the basal planes are created according to ^[239], while the lower three-dimensional atomic model crystals are inspired by ^[175].

The Pd(111), Pd(110), and Pd(100) single crystals investigated in this doctorate were produced by MaTeCK, Jülich, Germany, with a purity of 99.999%. Furthermore, the orientation accuracy of the 5mm in diameter crystals is better than 0.1° , and their surface roughness is smaller than $0.01\mu\text{m}$.

2.4.2 MnO₂NS/HOPG

Since MnO₂NS/HOPG is a barely explored state-of-the-art hybrid material, it is reasonable to discuss the properties of the individual components HOPG and MnO₂ in order to understand its characteristics. HOPG, which consists of ordered C atoms, is known for its good electrical conductivity and thus is a popular support material in catalysis research. **Figure 2.4.2** illustrates that the hexagonally arranged C atoms form graphene layers stacked to graphite. A significant advantage of this material is the easy creation of very flat surfaces by removing their surface layers using commercial adhesive tape. ^[240] Its characteristic honeycomb structure has a diameter of approximately $2.46\text{\AA}$ and the closest distance to the neighbored C atom of about $1.42\text{\AA}$ ^[241]. The distance between the graphene layers attracted by Van der Waals forces is approximately $3.35\text{\AA}$ ^[75].

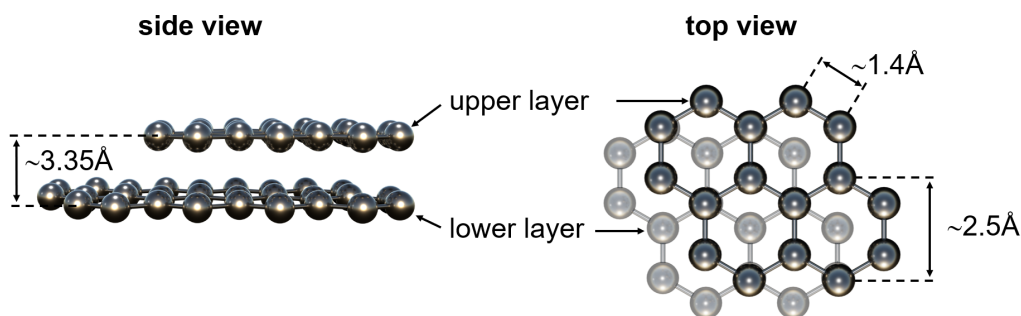


Figure 2.4.2. The schematic shows two HOPG layers from the side (left side) and top (right side), including their distances to the relevant neighbored atoms. Inspired by ^[242].

The nanosheet material MnO₂ is typically arranged in different configurations: the hollandite (α -MnO₂), pyrolusite (β -MnO₂), Ramsdellite (R-MnO₂), nsutite (γ -MnO₂), birnessite (δ -MnO₂) and spinel (λ -MnO₂) polymorphs ^[243]. Before receiving the samples from our collaboration partners in Japan, they performed several preliminary experiments to identify their configuration. Here, particular peaks in their X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) experiments indicated the δ -MnO₂ polymorph as the most likely

configuration. Based on this data, the pseudo-radial structure function (RSF) results predict the Mn-O and Mn-Mn atom distances as 1.47Å and 2.49Å, respectively. These values are close to those found by another group for birnessite of 1.91Å and 2.85Å^[244]. According to these findings, the subsequent DFT calculations focused on the δ -MnO₂ configuration. The schematic illustration in **Figure 2.4.3a** presents the layered structure of this polymorph, while a single layer was used as the theoretical model for the nanosheet material.^[213]

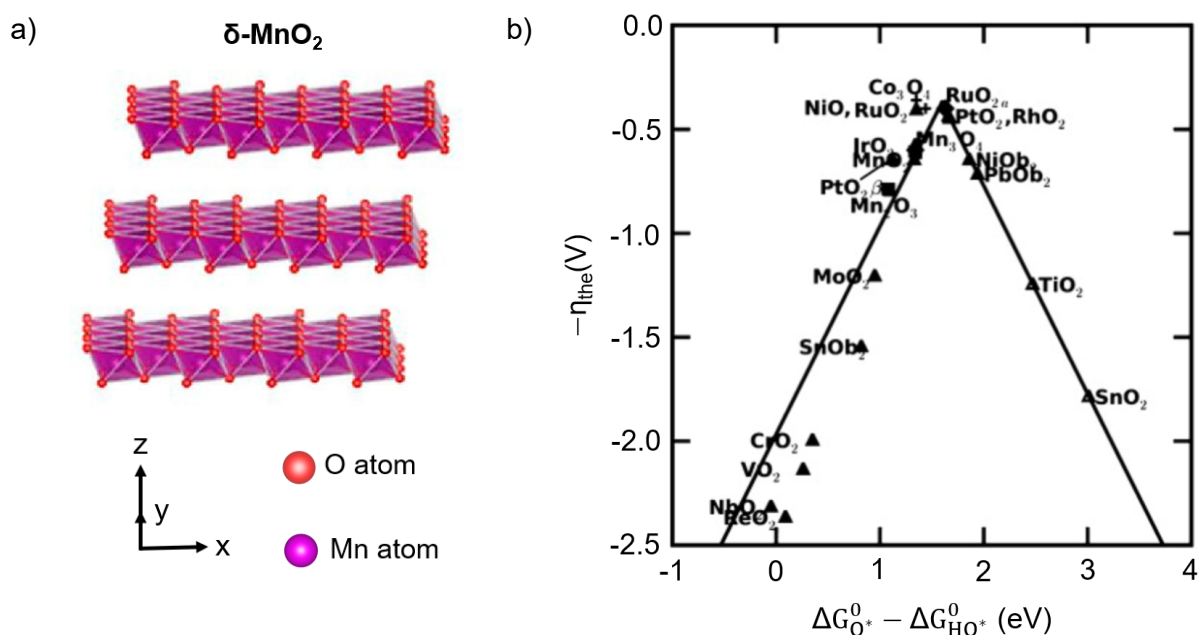


Figure 2.4.3. Overview of relevant Mn characteristics. **a)** Schematic illustration of the birnessite configuration of MnO₂, which builds the basis for the computational investigations of the nanosheets on MnO₂NS/HOPG. **b)** Volcano plot of different oxides, including MnO₂. It provides an overview of their OER activity with respect to the universal OER descriptor $\Delta G_{O^*}^0 - \Delta G_{HO^*}^0$ ^[72]. Figure a) is adapted with permission from^[243]. Copyright 2020 SAGE Publications. Figure b) is reprinted with minor reformatting with permission from^[72]. Copyright 2011, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Moreover, as depicted in **Figure 2.4.3b**, Man *et al.* summarized in 2011 the potential of Mn_xO_x as an OER catalyst. Here, they found the OER step from HO* to O* (cf. **Subchapter 2.2.3**) as the potential determining step and, thus, introduced it as the universal descriptor for the OER.^[72] In the presented volcano plot, MnO₂ is located at the top position next to other promising oxides, such as IrO₂ or RuO₂, which are known to be excellent OER catalysts^[245,246].

Furthermore, using a Langmuir-Blodgett trough device, the final $\text{MnO}_2\text{NS}/\text{HOPG}$ material was created by synthesizing a KMnO_4 powder on a HOPG support ^[213]. The detailed preparation procedure for this sample is explained in **Subchapter 3.2.1**.

3 Experimental Methodology

For the successful implementation of CV and STM measurements, several different preparatory procedures and considerations must be taken into account. This chapter presents utilized experimental setups, explains the preparations before each measurement, and summarizes the most essential measurement-related considerations and data evaluation techniques.

3.1 Experimental Setups

Different experimental setups are required depending on the research's application and objective. Two multimode and one EC-cell setups applied in this doctorate will be presented below.

3.1.1 Standard EC-Cell Setup

A commercial EC-cell was applied for the voltammetry measurements and electrochemical cleaning, as illustrated in **Figure 3.1.1a**. At the beginning of each session, the electrolyte was filled into a preconditioning cell with an immersed tube connected to a gas bottle and a gas outlet protected by a water lock to prevent the influx of air. In this way, each electrolyte can be saturated with a specific gas. Furthermore, as visible in **Figure 3.1.1b**, the primary cell consists of a case with an EC-cell inside, highlighted by a white and black dashed line, respectively. In order to prevent the electrolyte from being exposed to air, the case was flushed by a selected gas before the electrolyte was decanted from the preconditioning cell. The electrolyte can be poured into the EC-cell by opening a valve on the bottom side of the preconditioning cell. As **Subchapter 2.3.1** describes, the WE, RE, and CE were immersed in the electrolyte within the EC-cell. Moreover, an additional wire was dipped in the electrolyte, operating as a dummy electrode. Before the actual measurement of the WE starts, the EC-cell circuit was tested using the dummy electrode instead of the WE to prevent damage to the sample by, e.g., too high currents caused by, for example, bad connections or corrupted cables. In an ideal case, the dummy electrode and CE materials equal the WE material to reduce impurities by dissolution during the electrochemical experiments. All electrodes were connected to a VSP-300 potentiostat from Bio-Logic (France) and monitored by a computer. Here, the applied software was EC-Lab® V11.30, provided by Bio-Logic.

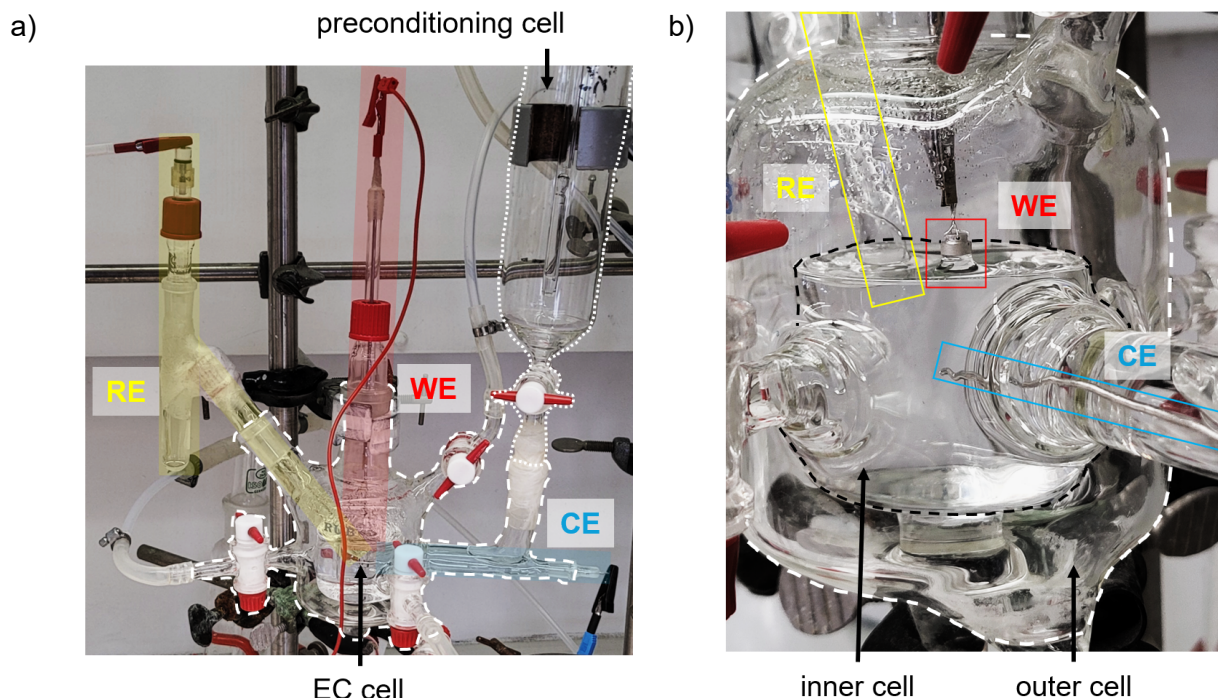


Figure 3.1.1. Pictures of a standard EC-cell which was used for the CV experiments and the electrochemical cleaning of the Pd single crystals. **a)** Here, a white dashed line frames the main cell, while a white dotted line pictures the preconditioning cell. The yellow, red, and blue highlighted areas present the RE, WE, and CE positions, respectively. **b)** A magnified view of the main cell (white), including its inner cell (black). Here, the capillary of the RE holder (yellow), a Pd single crystal (red), and a Pd wire serving as CE (blue) are immersed into the electrolyte. In order to ensure that only the intended crystal orientation of the single crystal has contact with the electrolyte, it was lifted again after immersion to create a bridge between the lower side of the crystal and the electrolyte by means of surface tension.

3.1.2 Multimode Setup in Air Atmosphere

The multimode device produced by Veeco, now Bruker, can operate as an STM or AFM device, depending on the mounted microscope head. This older device, illustrated in **Figure 3.1.2a**, which was utilized for all STM measurements on MnO_2/HOPG , is a Nanoscope III SPM Multimode manufactured by Veeco in 2007. Despite the performance of preliminary AFM measurements at the beginning of the investigation of new samples, the results shown in this thesis are limited to STM images since these results provide the highest information value. During the STM experiments, the STM tip is steadily fixed on the STM head while the sample itself moves during the measurement. The sample holder is magnetically attached to the scanner's baseplate and can be moved precisely in all three dimensions powered by piezoelectric elements. The electrical

signal detected at the microscope head is further evaluated inside the Nanoscope IIID controller, where the scanner's overall operation is managed. Critical measurement influencing parameters, like the precise movement of the scanner base plate, are autonomously adjusted by the feedback control system based on the measured tunneling current. Furthermore, for EC-STM, the interaction between RE, CE, WE, and STM tip potential is controlled by a Veeco Nanoscope Universal bipotentiostat, thus building the basis for the n-EC-STM measurements. Finally, a computer connected to the Nanoscope IIID controller is the user interface. The supplied software is NanoScope version 5.30r3.sr3, which allows real-time measurement monitoring.

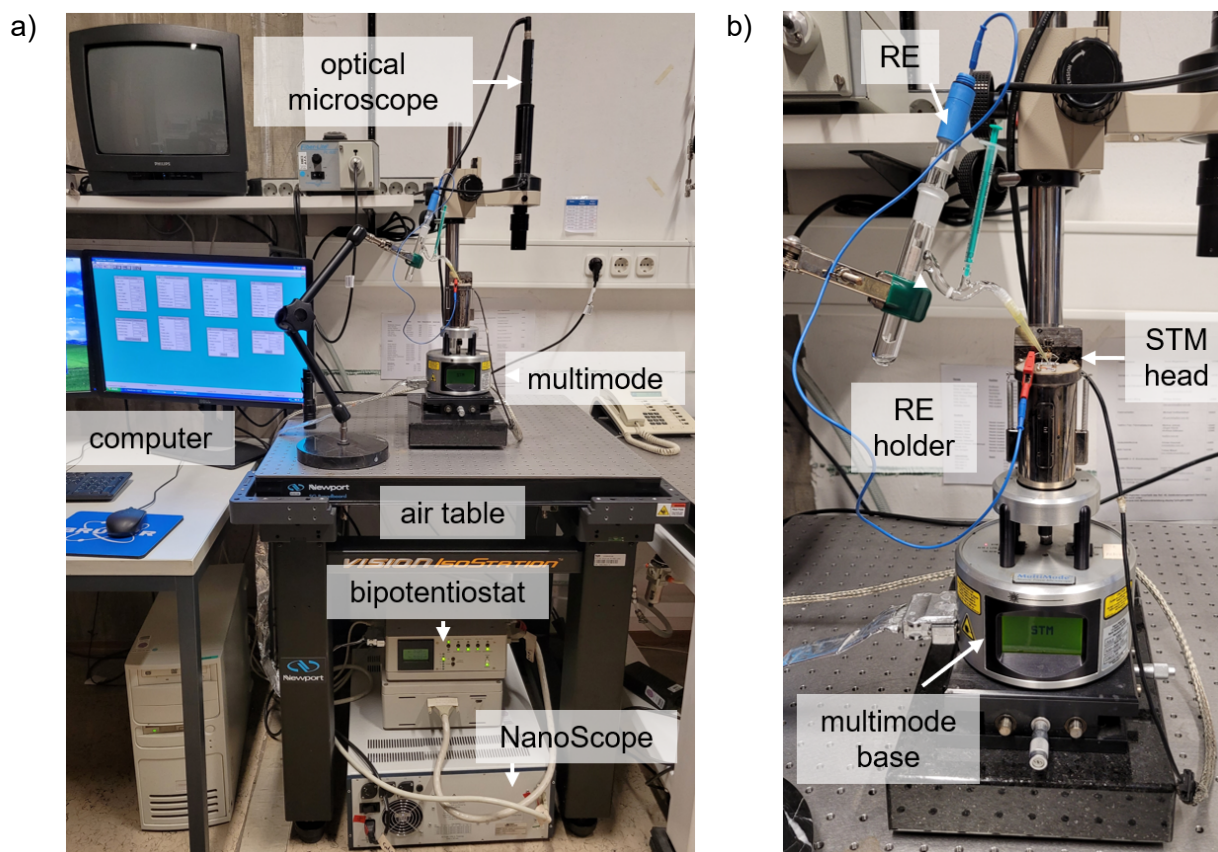


Figure 3.1.2. Overview of the multimode setup in air atmosphere. **a)** Picture of the entire multimode setup on top of the air-isolated table, including all relevant components. **b)** Multimode device during operation, including the latest version of the RE holder.

Since SPM measurements are generally highly vulnerable to mechanical interruptions like environmental vibrations, the multimode operates on a passive anti-vibration isolation table VH3660W-OPT from Newport powered by air pressure and utilized for the data acquisition by this

setup.^[190,193] An external RE holder is visible in **Figure 3.1.2b**, which allows using a standard RE for EC-STM measurements. In addition, an optical microscope enables preliminary visual investigations and an accurate sample alignment. More detailed information on the functionality is provided in **Subchapter 2.3.3** and the multimode's user manuals^[185].

Due to recent restructuring in the laboratory, as pictured in **Figure 3.1.2a**, the isolation table was replaced by a more compact version, M-VIS3030-SG2-325A, from Newport. Analogous to the predecessor model, it is powered by air pressure and has comparable isolation properties^[247].

3.1.3 Multimode Setup in Ar Atmosphere

In order to investigate the nature of active sites on oxygen-sensitive materials like single crystalline Pd and to double the measuring capacity at this chair, an additional STM setup was purchased. For this purpose, as part of this doctorate, a newer multimode device from Bruker Corporation was installed inside an Ar (Argon 5.0, Westfalen, Germany) flooded glovebox (GS GLOVEBOX Systemtechnik GmbH, GS ALPHA X-Line) as pictured in **Figure 3.1.3a**. Here, analogous to the older version from Veeco, a Bruker MultiMode 8 SPM for AFM and STM applications, a NanoScope V SPM Control Station, and a Universal Bipotentiostat for Electrochemistry on MultiMode SPMs comprise the basic experimental setup. Moreover, the NanoScope software used for this multimode is version 9.70. For an undisturbed operation, the multimode is positioned in the center of the glovebox on an Accurion Nano20 active anti-vibration isolation plate from Park Systems Corp, as depicted in **Figure 3.1.3b**.

Analogous to the older setup, the new one includes a Video-Only Optical Microscope (Model OMV-UNIV). In addition, a RE holder is attached to a stand next to the multimode, allowing the utilization of a standard RE. Due to the one-way use of the pipet tips mounted on the front of the holder, clean working conditions are ensured. Particular care must be taken to prevent gas bubbles inside the thin RE holder tube to guarantee an uninterrupted electrolyte junction to the EC-cell. In order to employ the multimode bipotentiostat, an additional cable (blue) connects the standard RE directly to the connector of the STM head. More information on the Bruker multimode is provided in the user manual^[248]. During the initial investigations, it turned out that even pushing or pulling out the gloves induces significant fluctuations in the internal gas pressure, resulting in bending the bottom of the glovebox. Consequently, a retrofitted metal stiffener directly underneath the glovebox's base plate prevents the resulting moving of the RE within the STM's EC-cell.

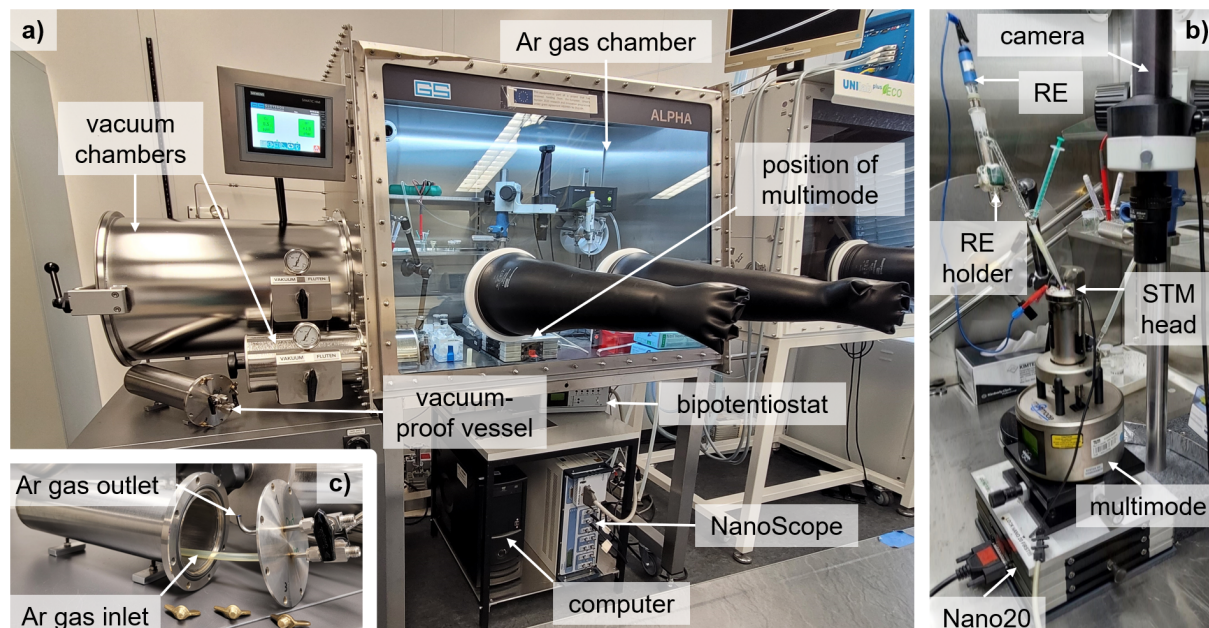


Figure 3.1.3. Pictures of the multimode setup in Ar atmosphere. **a)** Overview image of the new multimode setup inside the glovebox. **b)** shows the multimode standing on the Nano20 isolation plate within the glovebox during operation. The vacuum-proof vessel on the left side of **a)** fits into the glovebox's small vacuum chamber. **c)** Since Ar gas is heavier than air, the gas outlet is bent to the upper side of the vacuum-proof vessel. In contrast, the gas inlet is extended by a flexible tube to flush the vessel from the back side.

Moreover, an Ar gas-flushable vacuum-proof vessel presented in **Figure 3.1.3c** was designed to avoid damage to objects like pressure-sensitive devices and to prevent the electrolyte from boiling due to negative pressure inside the vacuum chamber during the transfer into the glovebox. In this way, moving the entire inductive heater cell, which was used for annealing the single crystals, into the glovebox is possible without its prior opening.

To conclude, with this further development of the multimode setup, it is now possible to systematically perform measurements on samples that must not have any contact with oxygen between the first annealing process and the final examination with the multimode device. An additional improvement by the new multimode setup yields the ability to directly purge the electrolyte within the glovebox by an additional Ar gas supply. Nevertheless, due to delays in the commissioning of the setup caused by functional and software-related saving errors and unexpected environmental interactions, the former multimode setup introduced in **Subchapter 3.1.2** was predominantly utilized for the measurements in this work.

3.2 Preparative Procedures

A meticulously prepared experiment is crucial to achieve reproducible and accurate results. For this reason, all components of any setup that came into contact with the electrolyte or the sample itself were regularly cleaned with Peroxymonosulfuric acid (H_2SO_5), also known as Caro's acid, and subsequently rinsed with hot ultrapure water (Evoqua Milli-Q, $18.2\text{M}\Omega\cdot\text{cm}$). Moreover, specific preparative procedures are required for each experiment, as discussed below.

3.2.1 Sample Preparations

Differentially shaped EC miniature cells were used depending on the sample's diameter and height. As illustrated in **Figure 3.2.1**, a Teflon™ ring presses the sample on a ferromagnetic metal base plate with four screws.

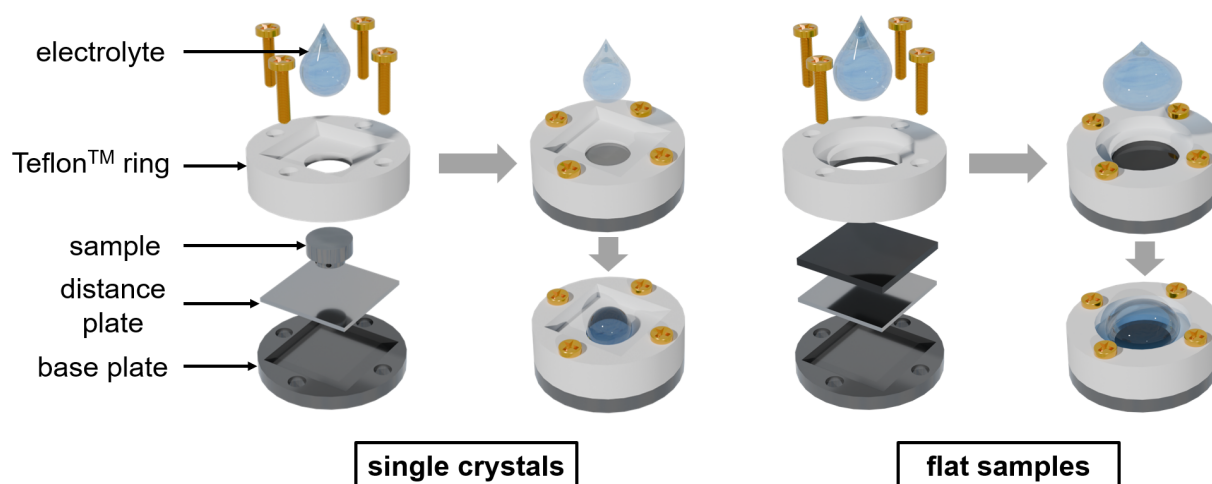


Figure 3.2.1. Schematic view of the individual parts of the STM sample holders on the left for single crystals and on the right for flat samples like HOPG or $\text{MnO}_2\text{NS}/\text{HOPG}$. A drop of electrolyte covers the exposed surface of the sample, which serves as WE.

In case of a gap between the sample and the base plate, an additional electrical conductive distance plate made from aluminum or HOPG was used. Through this construction of the sample holder, the STM tip can scan the exposed surface during standard STM measurements without significant sample shifts. A meticulous adjustment and uniform pressure distribution are required to achieve a leakage-proof interface between the sample and the Teflon™ ring. Several layers of

Parafilm® provide additional protection for the multimode device against electrolyte seepage on the sides of the EC-cell. If the sample-Teflon™ interface is sealed waterproof, a drop of electrolyte and an additional three-electrode setup allow the usage of the sample in EC-STM measurements (*cf.* **Figure 2.3.7**). The following paragraphs discuss the sample-related preparation procedures before the fixation in the sample holder.

Electrochemical cleaning of the Pd single crystals: Before each measurement, the oriented crystal facet of each Pd single crystal was electrochemically cleaned in 0.1M HClO₄. During this procedure, the sample was cycled between an electrochemical neutral potential on the double-layer and a relatively high OER potential using a CV setup (*cf.* **Figure 2.2.1** and **Subchapter 2.3.2**). In order to prevent high amounts of hydrogen from being absorbed into the bulk, the minimum applied potential was within the H_{UPD} region during this process. Due to the oxidation and reduction processes on the crystal surface, the sample gets freed from contaminations while only slightly roughening its surface ^[75]. A typical potential interval used for the electrochemical cleaning of the Pd single crystals was between 0.28V and 1.28V versus RHE. Despite the relatively gentle treatment compared to mechanical polishing, subsequent annealing is required before receiving atomically flat surfaces.

Oven annealing of Pd single crystals: The vulnerability of Pd to oxygen, especially at high temperatures, impedes the preparation of the Pd single crystals. At the beginning of the research on Pd, a high-temperature oven (Heraeus Instruments RO 7/50) was used to anneal the surface, thus creating atomically flat regions (*cf.* **Figure 3.2.2a**). During this process, the Pd single crystal with the measuring side facing upwards was heated for about one hour in a quartz tube to a temperature of approximately 950°C in a constant Ar stream (Argon 5.0, Westfalen, Germany) under oxygen exclusion. After three hours of annealing, the temperature was decreased to room temperature for about 18 hours under a constant Ar gas supply. To further protect the surface from oxygen, the crystal surface was covered by a drop of electrolyte inside the quartz tube using a pipette before exposure to air. At the final and most challenging preparatory step, the crystal was mounted into the sample holder while holding the drop of electrolyte on the sample surface. In case of losing this drop during this process, oxygen from the air reached the sample surface, and the entire annealing process was repeated.

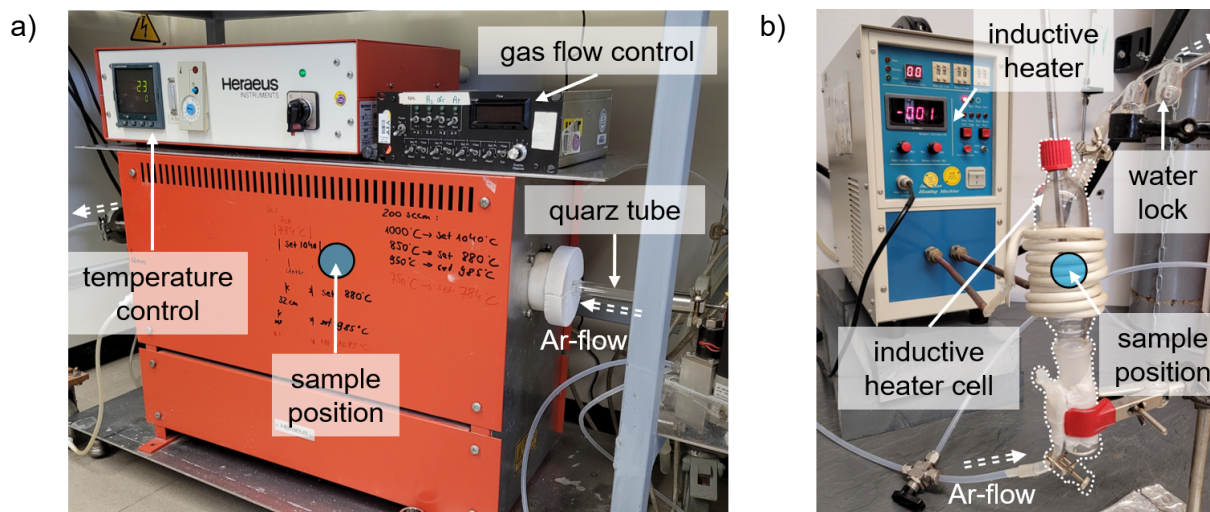


Figure 3.2.2. Annealing devices used for the Pd single crystals. **a)** High-temperature tube oven with controlled gas flow. **b)** Inductive heater setup. A water lock prevents air from backstreaming into the inductive heater cell. In both images, the dashed arrows demonstrate the direction of the Ar gas flow, while the blue cycles represent the positions of the sample during annealing.

Inductive heater annealing of Pd single crystals: An inductive heater cell was applied due to the duration-related drawbacks of oven annealing. As shown in **Figure 3.2.2b** by a white dashed line, here, a special quartz chamber, which was continuously flushed with Ar during the entire annealing process, was enclosed by an inductive heating coil. In the center of this inductive heater cell, the 5mm in diameter Pd crystal was fixed on a 0.5 mm thick Pd wire. The water-cooled high-frequency inductive heater (20–80 kHz, 15 KW–EQ-SP-15A, MTI, USA) has a maximum output power of 15kW^[249]. It was set to a heat current of 545A using a water-cooled copper coil of nine turns and an inner and outer diameter of 5cm and 6cm, respectively. After heating the sample for approximately 30s to a temperature between 1000°C and 1100°C, the annealing period was 60s for the first and 30s for the second and third rounds. In between each heating, a relaxing period of 5 minutes was inserted. Similar to the oven annealing, the surface of the Pd crystal was covered with a drop of electrolyte after it had been immersed in a small amount of electrolyte at the bottom of the inductive heating cell and subsequently installed into the EC-cell in an air atmosphere. After the commissioning of the Ar-filled glovebox, the covering with the electrolyte drop was omitted. Instead, the entire inductive heater vessel was transferred into the glovebox using the vacuum-proof vessel. Inside the Ar atmosphere, the sample was assembled without the risk of losing the electrolyte drop and thus destroying the surface by interactions with oxygen. This improvement

further significantly facilitated the handling of the Pd preparation, increasing the frequency of experiments.

Tape stripping on HOPG: Before using the raw HOPG samples as a support material, the surface was smoothed by carefully pulling off a thin layer using conventional adhesive tape. Due to the weak interactions between the individual graphene layers, large atomically flat surface areas of several micrometers are created, thus building the ideal support material for STM measurements.

MnO₂NS/HOPG preparation: The manufacturing of the MnO₂NS/HOPG sample was performed by our collaboration partners at the Osaka Research Institute of Industrial Science and Technology in Japan by first preparing a KMnO₄ powder, which was subsequently synthesized on a HOPG support. First, the KMnO₄ powder was heated for ten hours in the air at 800°C. After cooling, the powder was washed with ultrapure water. In the next phase, it was heated analogously for a second time for 20h. Afterward, a mixture of 200ml 1M HNO₃ and 1g of the resulting powder was continuously shaken at room temperature for 24h. Subsequently, the liquid was removed, replaced by fresh 1M HNO₃, and shaken again for the same duration. This step was repeated four times in total. Then, the solution was replaced by 200ml ultrapure water and 2.6g of (CH₃CH₂)₄NOH and further shaken at room temperature for ten days. By centrifuging the blend at 5000rpm and subsequently drying it in a vacuum, the MnO₂NS were obtained. The MnO₂NS were intermixed with BN and compressed into tablets to enable quality control treatments. In the second phase of manufacturing MnO₂NS/HOPG, the pellets were diluted to a solution containing 7mg·dm⁻³ MnO₂NS. After filling 250cm³ of this solution and 1cm³ of 10% (CH₃CH₂)₄NOH into a Langmuir-Blodgett trough, the blend relaxed for 30min at ambient conditions. The solution's surface pressure was increased to 17mN·m⁻¹ and held for 30min using a Wilhelmy plate tensiometer. Here, the barriers were moved with a velocity of 0.5mm·s⁻¹. After this procedure, the previously prepared HOPG was immersed into the blend and continuously lifted out with a velocity of 0.02mm·s⁻¹. This method allows the synthesis of the monolayered birnessite MnO₂ on the HOPG support, thus creating the MnO₂NS/HOPG sample.^[213] After each subsequent STM session, the employed MnO₂NS/HOPG samples were carefully cleaned with ultrapure water (Evoqua Milli-Q, 18.2MΩ·cm) and not further treated to preserve the MnO₂ sheets.

3.2.2 Electrolyte Preparations

All electrolytes used in this thesis were diluted with ultrapure water from an Evoqua Milli-Q water purification system with a resistivity of 18.2 M Ω -cm.

For the measurements on MnO₂NS/HOPG, 0.1M KOH was used as the electrolyte, which was mixed using 5,612 g potassium hydroxide pellets (Sigma Aldrich, 99.99%) and ultrapure water into a one-liter solution. Analogously, for one liter of 0.1M HClO₄ used in the Pd experiments, ultrapure water was mixed with 8,54 ml HClO₄ (Merck Suprapur®, 70%). For CV measurements in the Ar atmosphere, the electrolyte was purged with Ar gas (Argon 5.0, Westfalen, Germany) for at least 10 minutes to remove oxygen. Analogous, the electrolyte that was used in the reference holder and the STM device's miniature cell inside the Ar glovebox was purged beforehand by using an additional internal AR supply until the O₂-ppm value of the glovebox stabilized again. Since oxygen-free solutions absorb oxygen very quickly when exposed to air, the electrolytes used for measurements in an air atmosphere were not purged in advance.

3.2.3 STM Head Preparation

The STM head contains the STM tip, the CE, and the RE. These units represent the sensing elements of the multimode device. Consequently, accurately preparing the corresponding components before each experiment is crucial. **Figure 3.2.3a** presents one of the two structural identical STM heads used in this work. An overview of the preparation procedures for each component is shown in the following paragraphs.

Tip cutting and insulation: The STM tips used for this work were produced in-house by mechanical cutting. During production, a 0.25mm thick wire made of 80% Pt and 20% Ir (99.9+% purity, Goodfellow GmbH) was clamped in a pipe wrench and almost cut by a side cutter at an approximately 45-degree angle, as shown in **Figure 3.2.3b**. The remaining thin connection was torn apart by pulling, resulting in an atomically sharp tip at the fracture point. In addition, the Apiezon wax coating, which minimizes the occurrence of faradaic effects on the tip surface during EC-STM measurements, was created using a commercial soldering iron with a concave extension, as presented in **Figure 3.2.3c** ^[250].

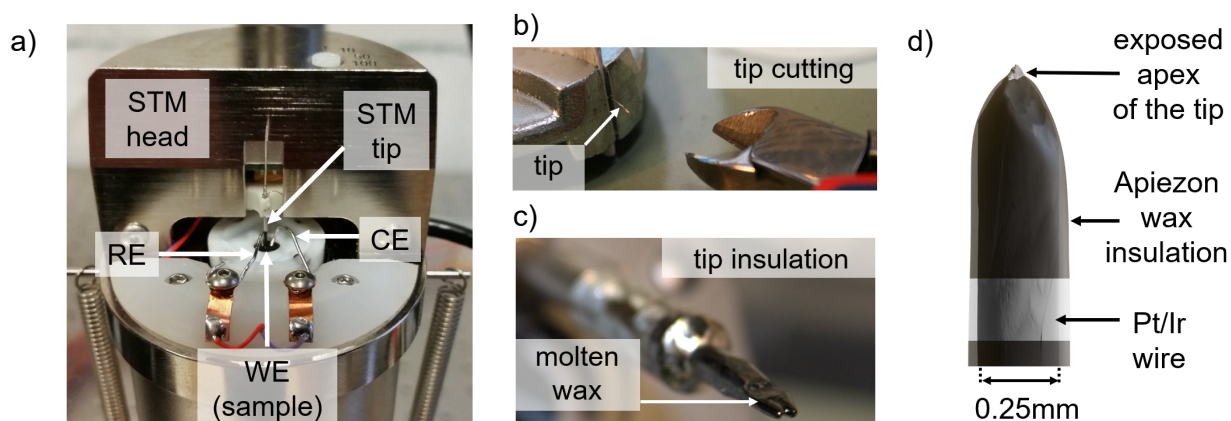


Figure 3.2.3. Overview of the STM head and the preparatory procedures. **a)** shows a typical STM head used for the STM measurements in this work. For a better view of the WE, RE, and CE, see the model in **Figure 2.3.7b**. **b)** A pipe wrench on the left of the image holds the wire while being cut by the side cutter shown on the right. **c)** soldering iron with molten wax on its front part, ready for tip insulation. **d)** Schematic overview of the tip apex and the insulating wax layer. Here, Leon Haase designed and implemented the STM tip model.

In this procedure, the uncoated tip apex was immersed four times into the molten wax drop to ensure complete coverage. For the last dipping, the tip was pierced through the droplet to increase the chance of an exposed metal apex. A schematic illustration of such an STM tip is presented in **Figure 3.2.3d**, while scanning electron microscopy (SEM) images of real raw and insulated STM tips are shown in **Figure 3.2.4a-f** and **Figure 3.2.4g-l**, respectively. These images demonstrate the structure of an STM tip and provide an impression of the small scales of the investigated areas in this research. In addition, they reveal the ability of the wax to coat the entire STM tip and provide an impression of the scales relevant to this research. A unique measurement captured during this doctorate is presented in **Figure 3.2.4 A1** in **Appendix D**, which shows the print of a recently crashed tip onto a flat HOPG surface. Coincidentally, the STM tip did not break during this collision, which enabled the measurement of the resulting crate with its excavation next to it. This rare image accidentally provided a further impression of the shape and size of an STM tip apex.

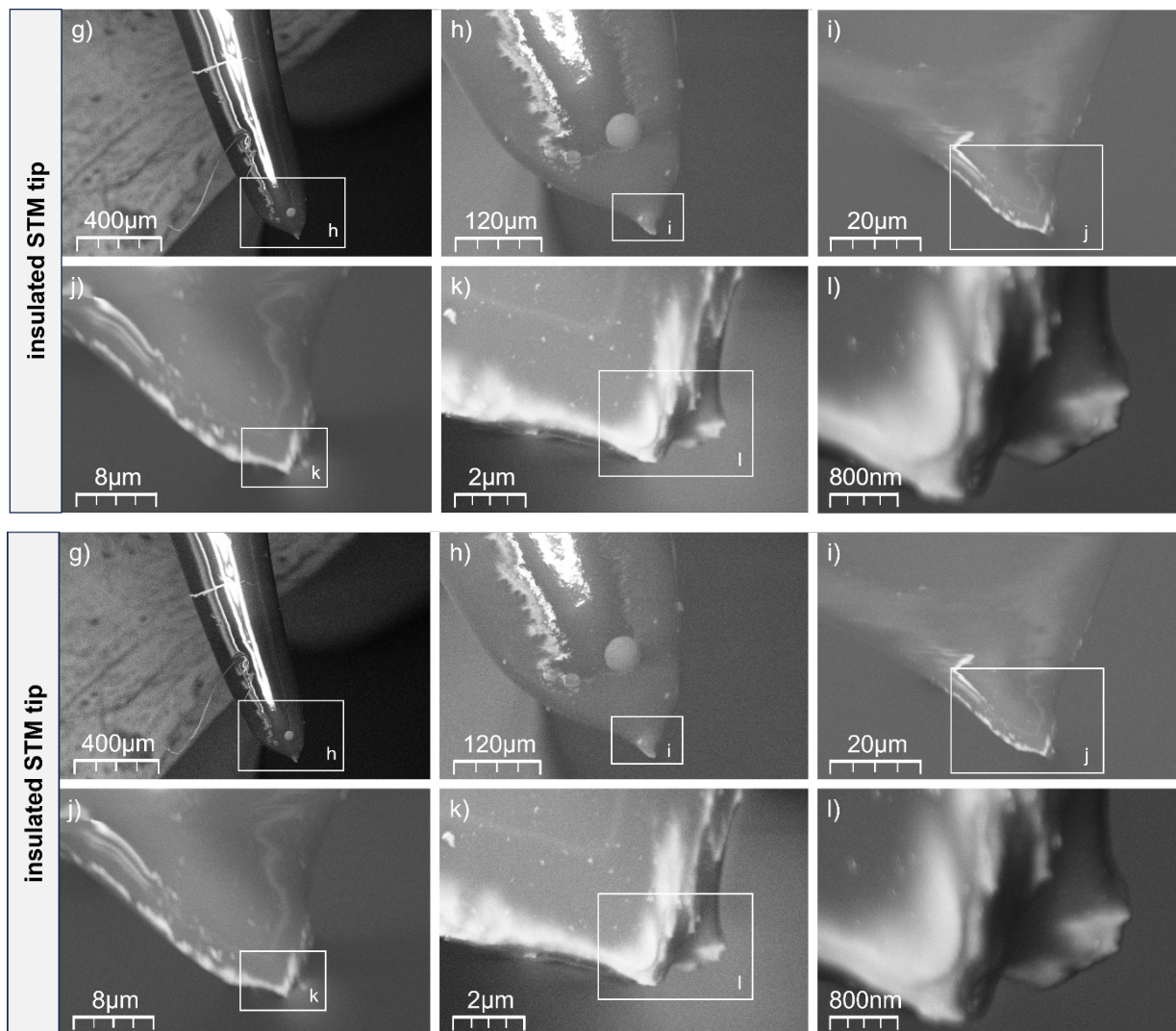


Figure 3.2.4. SEM image of STM tips. **a) - f)** Measurements of different magnifications show a freshly cut STM tip. The most magnified one in **f)** depicts three exposed structures on the top. Depending on the alignment of the tip relative to the sample, one of these apexes is expected to be the actual scanning tip. **g) - l)** Analogous SEM images of an Apiezon wax-insulated STM tip. The bright white regions, evident in **g)** to **j)**, are areas of charge accumulations that occur in non-conductive materials, such as wax. Despite the much more detailed surface structure in **l)**, which indicates an already thin wax layer, the magnification does not allow us to observe the uncovered apex of the tip.

Counter electrode preparation: The selection of the CE material complied with the WE (sample) material in order not to poison the sample surface with foreign elements due to dissolution. Consequently, for the experiments on MnO₂NS/HOPG, a 0.5mm in diameter graphite rod (99.95% purity, Goodfellow GmbH) served as the CE and was rinsed by ultrapure water (Evoqua Milli-Q,

18.2 M Ω ·cm) before each experiment. In contrast, for the measurements on Pd single crystals, a curled 0.25mm thick Pd wire (99.95% purity, MaTeck) was applied to maximize the CE surface within the electrolyte and avoid bubble formation. The latter was annealed by using a gas burner and subsequently rinsed with ultrapure water (Evoqua Milli-Q, 18.2 M Ω ·cm).

Reference electrode preparation: The Pt quasi-RE (QRE), also called pseudo-RE, used for the experiments on MnO₂NS/HOPG and partly for the Pd investigations consisted of a 0.5mm Pt wire (99.99% purity, MaTeck). As discussed in **Subchapter 3.3.2**, it was later replaced by a standardized RE. The preparation procedure for the Pt wire was the same as that for the Pd CE. When using a standard RE, the entire RE holder was filled with the identical electrolyte as used in the EC-STM experiments. The applied electrolyte within the RE holder was changed regularly, and the pipet tip and utilized injection were replaced to ensure a clean setup. For investigations using the multimode setup in an Ar atmosphere, the electrolyte was Ar-saturated inside the glovebox using the internal Ar supply as described in **Subchapter 3.1.3**.

3.3 Preparatory Considerations

Next to the physical preparations required before the experiments, some experience-based considerations also play a crucial role. This subchapter discusses the basic knowledge that is mandatory to perform n-EC-STM measurements correctly.

3.3.1 The STM Device's Miniature EC Cell

Compared to conventional setups, the electrochemical EC-STM cell with a diameter of about 0.48mm and 0.63mm for single crystals and chip-like samples is much smaller. As a result, it accommodates a significantly lower amount of electrolyte. Since the surface area of the electrolyte droplet compared to its volume is relatively large, it is essential to consider electrolyte composition changes by evaporation closely. Furthermore, due to the small drop volume, electrochemical reactions could further influence the electrolyte composition. For this reason, it is crucial to monitor the setup properties by, e.g., performing CVs during a measuring session or, in case of irregularities, replacing the electrolyte and, therefore, resetting the experimental conditions. It is important to note that the variation of the electrolyte concentration caused by evaporation during longer measuring sessions influences the pH value and, thus, the RE potential (*cf.* **Equation (1)**).

Nevertheless, despite this correlation, it does not significantly affect the n-EC-STM measurements since properly selected gain settings suppress the noise in less active areas, as further described in **Subchapter 3.3.3**. In addition, using a potential for reaction ‘Off’ in the double-layer region and only applying small overpotentials for reaction ‘On’ minimizes the effect of electrolyte composition changes by faradaic effects. All these measures are necessary to ensure constant experimental conditions and reproducibility of the experiments and yield a general challenge for EC-STM experiments using a miniature cell. No further miniature EC-cell-specific limitations are expected if these possible disturbing effects can be excluded.

3.3.2 The Utilization of a Standard RE at the EC-STM Setup

Due to the limited space in an EC-STM miniature cell, a common approach is to use a QRE, which could only consist of a thin wire immersed in the electrolyte ^[251,252]. In contrast to a standard RE, a QRE does not reach a thermodynamic equilibrium, which results in an undefined potential difference relative to a conventional one. In addition, the QRE's potential strongly depends on temperature, the pH value of the electrolyte, and its polarization during the experiment. ^[253–255] However, experience and the literature show that a Pt QRE has stable potentials for several hours but could have a slight potential shift when comparing CVs of the identical sample and setup on different sessions ^[256,257]. A representative measurement on Pd(111) using a Pt QRE is discussed in more detail in **Subchapter 4.1.1.2**. Despite the identical experimental conditions, a potential shift of about 70mV was detected at three individual measurements running on different days. Consequently, in this work, no potentials measured by a Pt QRE are converted to other scales, such as RHE, using **Equation (1)**. Despite these fluctuations, a Pt QRE is still a cost-efficient and appropriate solution for most EC-STM experiments and, therefore, has been used in previous research for decades ^[28,205,208,258,259]. Moreover, experience shows no evidence that electrolyte variations affected the n-EC-STM measurements within the typical duration of 16 minutes for a measurement with a scan size of 500nm. Nevertheless, as a precaution, comparing different regions within the data evaluation was only carried out within individual images and not across different measurements.

In order to record stable activity curves that could be used for further evaluation, CV measurements captured in standard EC-cells with a standard RE are additionally provided for each sample. These graphs are used for statements about activity and comparison between catalysts. In addition, to verify the activity trends and the quality of the sample, the corresponding

CVs recorded by the multimode using the Pt QRE are presented as well. As certain regions within a CV continuously merge into one another, the corresponding values for reactions 'On' and 'Off' are given as intervals rather than a specific point. This circumstance provides leeway for possible potentials that are suitable for n-EC-STM measurements. For this reason, using a Pt QRE is still a valid approach for most scenarios.

In addition, CVs were recorded prior to each experimental session to verify the respective daily potential region when using a Pt QRE. Even if slight potential shifts occur, these CVs reveal the double-layer position and the beginning of the desired reaction, which are essential to perform n-EC-STM experiments. In most cases, it was possible to use the same potentials for reactions 'On' and 'Off' even on different days without any adjustment due to the sufficient range of suitable potentials. A final confirmation of an appropriately chosen potential delivers the observed noise at the n-EC-STM images. As discussed in **Subchapter 3.3.3**, as long as the noise vanishes for reaction 'Off', an n-EC-STM experiment is feasible. In order to increase the reproducibility and the evaluation capabilities, as part of this work and discussed in **Subchapter 3.3.2**, a new RE holder was established to utilize all kinds of standard RE within the EC-STM cells in future experiments.

3.3.3 The Selection of Appropriate n-EC-STM Settings

When performing STM measurements, the final shape of the captured morphology generally depends on several factors and settings. Apart from tip and sample properties, different software settings drastically influence the shape of the detected structures^[260]. One of the most important values is the CS, which regulates the tip-sample distance and thus plays an essential role in the noise intensity and the image resolution. Furthermore, two further settings play a significant role: the proportional gain (PG) and the integral gain (IG), as explained below.^[190]

When measuring in the STM device's constant current mode, the tip moves over the surface while the sum of faradaic and tunneling current stays at a particular value, depending on the current setpoint input. The tunneling current increases when the tip reaches an exposed structure, such as an atomic step of the sample. Consequently, the STM unit's feedback loop instructs the piezoelectrics to lift the STM tip to retrieve the initial tunneling current. Depending on the set gain values, the intensity and shape of the tip moving varies. Proportional to the CS value, the PG regulates the intensity of the tip movement in the z-direction without knowing how big the step in front of the tip is. As a result, there is a delay in the tip's response, and therefore, it is likely that the actual required height is overshoot and a single-atomic step edge is mapped as, e.g., a two-atomic

hill on a single-atomic step. In order to reduce this effect, the IG value operates like a control system and corrects the pathway by calculating the average error and performing nonlinear adjustments. Consequently, controlling these gain features makes it possible to influence, *e.g.*, the shape of steps, even for basic STM measurements in air. Here, the goal is to reach well-defined and sharp steps that do not have an additional ridge at the edge. Experience shows that a ratio of three to two between PG and IG provides an appropriate representation of the surface. ^[190,185]

When performing n-EC-STM experiments, meticulously selected configurations are essential since the STM device must be able to record the surface morphology and the fine noise peaks simultaneously ^[213]. As explained in **Subchapter 2.3.3**, the measured tunneling current fluctuates when the STM tip scans an active surface site. From a simplified point of view, the way STM experiences active sites is similar to that of a very rough surface with several spikes. Since the working principle of how the multimode controls the tip-surface distance on active sites during n-EC-STM does not differentiate from how an STM device in air maps an atomic step, the shape of the noise peaks also strongly depends on the gain settings. Consequently, high gain values increase the observed height of the peaks and thus make electrochemical active areas more easily detectable. In order to identify the sample's most active sites, it is crucial to adjust the gain settings in a way that significant noise only appears on the most active structures while being suppressed in less active regions. In addition, the entire noise must disappear for the reaction 'Off' while the step edges should be pictured as unadulterated as possible without significant ridges at the edge. Besides the difficulties in sample preparation, balancing these requirements for each STM tip, electrolyte, reaction, and sample combination is one of the most challenging tasks when performing n-EC-STM measurements. Due to the measurement-specific adjustment of the gain settings and the resulting objective influence of the researcher's preferences regarding the height of noise peaks, a quantitative comparison across different STM measurements is unfeasible. The measurement settings used for all performed STM measurements in this work are listed in **Table A4.1** in **Appendix B**.

3.4 Data Evaluation

This subchapter presents different tools and evaluation techniques required to analyze the diverse nature of STM measurements, containing corrupted line scans, offset shifts in the z-direction at individual line scans, and noisy or very smooth surface areas. In this thesis, the CV, line scan, and

noise evaluation graphs were produced using the analysis and graphing software Origin® 2018b (64bit).

3.4.1 Image Processing and Filtering

As described in **Subchapter 2.3.3**, an STM image consists of several line scans, captured in the x-z-direction, that are merged into a colorized figure in the x-y-plane. Since the STM device cannot track the height of the sample and thus does not know the absolute height of the detected surface, it is forced to select a height offset for each line scan. Consequently, depending on the individual measurement, it is necessary to adjust this difference for several line scans to reconstruct the surface morphology. Next to Bruker's evaluation software NanoScope Analysis (version R1Sr2.157217), the freeware software WSxM 5.0 Develop (version 10.2), which was mainly used for the image processing in this thesis, offers a flattening tool for this purpose ^[261]. Depending on the intended use and illustrative purpose, the WSxM's options "Flatten" and "fit 2nd" were used for linear and area-related flattening, respectively. In addition, the tool "Remove lines" enables the averaging of individual line scans to delete corrupted line scans. This procedure is primarily required to visualize n-EC-STM measurements when the potential is changed between reaction 'On' and 'Off' and the tip retracts from the surface for one or two line scans. It is important to note that averaged and, thus, doubled line scans were excluded from any data evaluation in this thesis and mostly hidden by the white dashed lines used for marking the potential switch.

Another crucial application is the "2d FFT filter" tool, which removes artificial noise from the measurements using fast Fourier transformation (FFT). **Figure 3.4.1a** presents an atomically resolved STM image on a flat HOPG terrace in constant height mode. Interestingly, the scan size was switched from 5nm to 20nm and 10nm during the measurement. As a result, the regularly arranged orbitals shape an identical pattern in three extents. When transforming this dataset into the Fourier plane, as shown in **Figure 3.4.1b**, the individual scan sizes occupy specific symmetric positions containing the larger structures, such as the sample's morphology, in the center and the smaller and more detailed ones, e.g., noise peaks, in the outer regions. ^[262] Consequently, from inside to outside, the image exhibits the data set for the 5nm (white), 10nm (red), and 20nm (orange) scan size pattern, respectively.

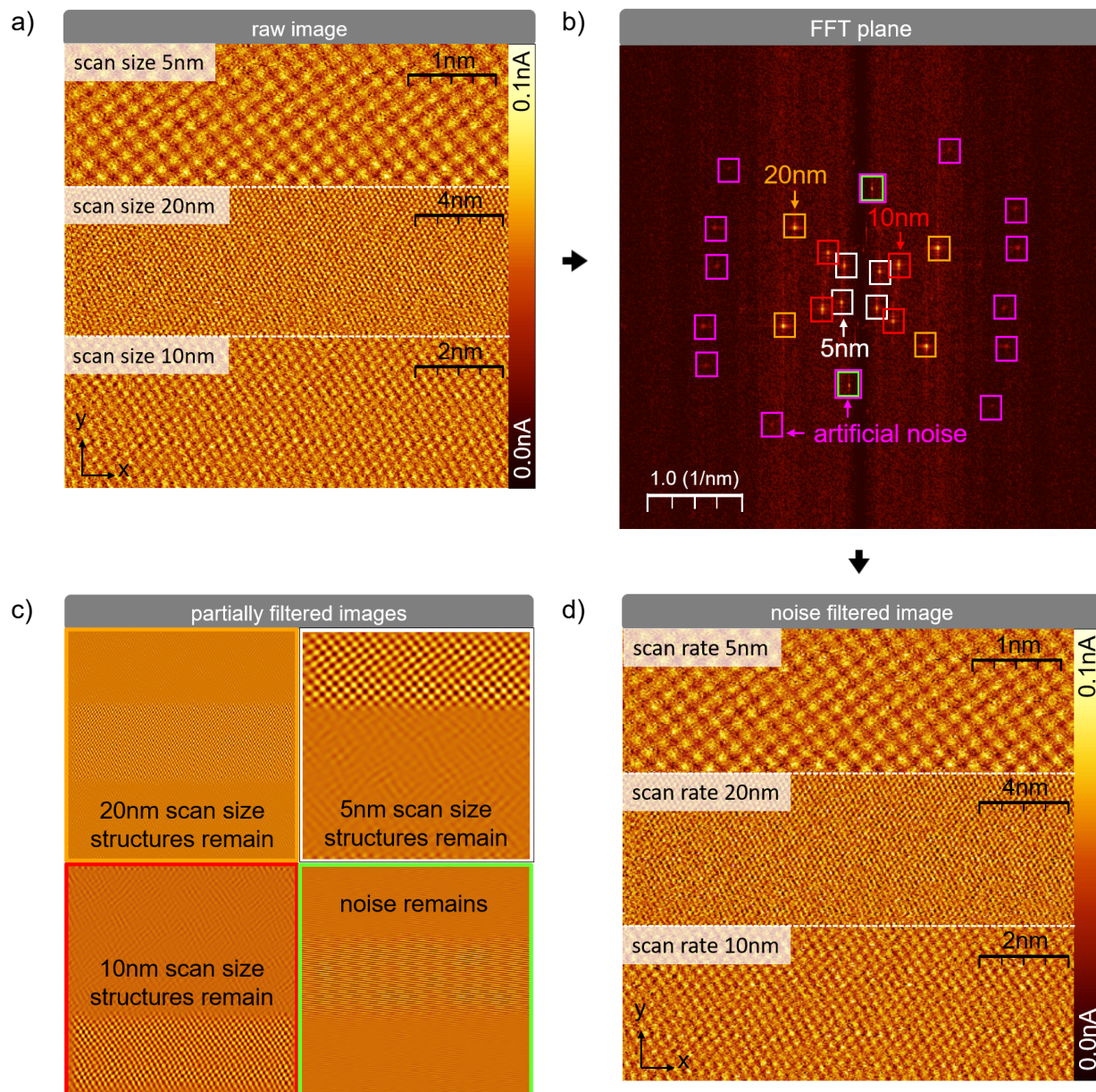


Figure 3.4.1. Example of FFT filtering on HOPG. The raw STM image in **a)** shows HOPG for three different scan sizes, while its FFT plane is visible in **b)**. The red background in **b)** represents nonperiodic structures, such as white noise. The absence of information is colorized in black. The image information saved in the specific data sets framed in **b)** is presented in **c)**. **d)** Artificial noise-filtered STM image.

Furthermore, only signals with a periodic characteristic, such as the 50Hz electrical grid noise, create white points in the FFT plane. Consequently, when filtering, the electrochemically induced noise from n-EC-STM measurements is unaffected due to its random height and occurrence. As a

result, it is a valid approach to filter the STM signal by using FFT to exclude artificial noise from the evaluation. In this example, three significant artificial noise frequencies, each for the individual scan sizes, highlighted in pink, and two additional ones framed in green, are visible on the outer side of the image, thus representing the most detailed periodic structures. After the inverse Fourier transformation and only passing specific colorized data sets, the individual image information of these spots becomes apparent, as presented in **Figure 3.4.1c**. For comparison, the artificial noise from the two green/pink marked dots in **Figure 3.4.1b** is visible in the bottom right part of this image. In contrast, when only the artificial noise data set (pink) is deleted, the entire surface structure remains, and the visibility of the HOPG pattern gets pronounced, as demonstrated in **Figure 3.4.1d**. For transparency and to verify that the filtering procedures applied in this thesis do not affect the results, the appendix provides the corresponding Fourier plans and deleted data sets for each filtered measurement.

3.4.2 Quantitative Evaluation

Due to the difficulty separating the electrochemically-induced noise from the irregularly shaped surface morphology, a computative evaluation of the faradaic processes captured by n-EC-STM is challenging. As a result, the quantitative interpretation of the observed noise behavior requires specific approaches depending on the observed surface structure, noise behavior, and analysis objective. It should be noted that the images and graphs presented in this subchapter do not show accurate measurements and serve as model surfaces. **Figure 3.4.2a** represents an n-EC-STM measurement under reaction conditions showing a hypothetical surface that consists of electrochemically inactive support (red area) and plateau material (orange area) while the step edges (yellow area) are relatively active. In addition, the upper part of the image illustrates a two-dimensional top view, while the lower part presents a three-dimensional perspective. The following paragraphs demonstrate the techniques applied in this thesis to reveal the actual surface morphology, the local noise behavior, and the most active sites.

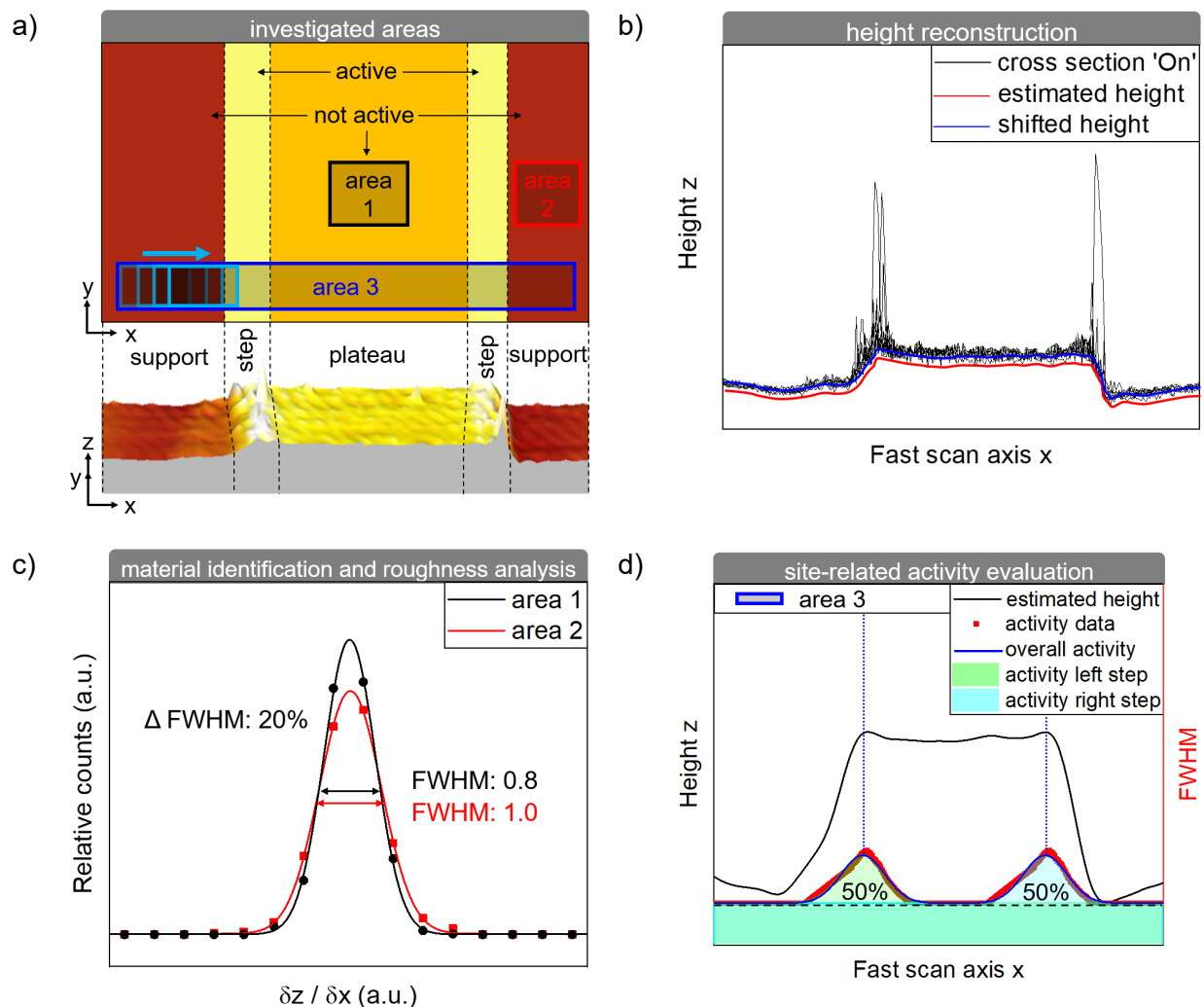


Figure 3.4.2. Overview of evaluation techniques. **a)** The model surface presents three investigated areas used to discuss the individual methods. The upper part presents a top view of a nanosheet (yellow) whose material differs from the one of the support material (red). The lower part provides a three-dimensional view. In this example, only the upper step edges are active. The entire example surface is illustrated for reaction 'On'. **b)** Schematic view of the height reconstruction process in area 3 in a). **c)** Roughness analysis and comparison of areas 1 and 2. **d)** Site-related activity evaluation. The black line corresponds to the height scale, while the other curves are shown in values of FWHM. The blue dotted vertical lines roughly allocate the maxima of the overall activity curve to the step edges.

Height reconstruction: Thermal shifts and the chance of losing the observed position make capturing the same area twice challenging. In addition, during the n-EC-STM measurements, parts of the sample are covered with noise peaks, thus hiding the actual surface morphology at this spot. Nevertheless, observing an entire section with a uniform shape makes the estimation of the actual

surface morphology possible, even if the entire area is superimposed with noise. Since white noise occurs randomly, the STM tip scans the actual surface morphology between the noise peaks. Consequently, when stacking multiple line scans on top of each other, as shown in **Figure 3.4.2b** as black lines, it is possible to estimate the shape of the surface. By connecting the lowest points for each x-value (red line), the morphology can be estimated for an adequate data set since the STM tip is never lower than the surface itself. To better present the estimated heights in this thesis, the Savitzky-Golay smoothing of the analysis software Origin® with a point of window value of 8 and polynomial order of 2 was additionally conducted. When shifting the red line to the top (blue line), an appropriate representation of the actual surface is proven, independent of the noise's height.

Material identification and noise analysis: It is helpful to evaluate the local surface roughness to compare the electrochemical activity between two individual areas and, therefore, learn about their material composition, e.g., areas 1 and 2 of the model surface. Since electrochemical noise is estimated to be white noise, the dataset of a very rough surface is comparable with that of a uniform active area. As presented in prior publications, this approach originates from the idea that rough regions have a higher slope diversity than flat ones ^[175,203–206,208,213]. Due to the constant scan velocity in the fast scan direction, the distance between the x-values is equal. As a result, it is possible to derive the height difference between neighboring data points according to this measurement-specific x-distance. The advantage of this derivation is the amplification of extremely small or huge height differences. By grouping the derived values into intervals (bins) with a specific range (bin size) and normalizing them against their total count, it is possible to plot them against their relative number (relative counts). **Figure 3.4.2c** presents such an evaluation for the fictive areas 1 and 2 illustrated in **Figure 3.4.2a**. Since the electrochemical noise has a random occurrence, the observed plot complies with a Gaussian distribution and thus can be represented by the full width at half maximum (FWHM). The derived slopes presented in this thesis are categorized into 30 bins with a bin size of 0.025. In addition, the mathematical function “numpy.gradient” of the Python library NumPy was applied to derive the height differences ^[263]. Additional information on the underlying principles can be found in the references ^[264–266]. It is important to note that due to the normalization of the number of counts, the dimensions of the analyzed areas used for the evaluation do not influence the results. Thus, comparing different-sized areas within a specific STM image is valid.

However, since the absolute heights of the relative counts depend on the sample's surface roughness, STM tip quality, and artificial noise, a direct comparison of the FWHM values between

different figures is generally not recommended. Nevertheless, these measurement-specific factors are eliminated when comparing the difference in FWHM within one image since the mentioned factors influence both FWHMs similarly and thus are largely canceled after subtraction. As illustrated in **Figure 3.4.2c**, the resulting $\Delta FWHM$ value represents the percentage deviation in relation to the larger FWHM:

$$\Delta FWHM = 100 - \left(\frac{FWHM_1}{FWHM_2} \cdot 100 \right) \text{ with } FWHM_1 < FWHM_2 \quad (3)$$

Here, the $FWHM_1$ and $FWHM_2$ correspond to the noise analysis of area 1 and area 2, while $FWHM_2$ is the larger value, respectively. To conclude, the $\Delta FWHM$ value provides a measure for the difference in roughness or activity. Thus, it could help to roughly compare, *e.g.*, how much higher the activity is on active sites compared to inactive ones across samples. In addition, it could serve to compare between different materials on hybrid samples. In the example of the model surface, a significant value of 20% for $\Delta FWHM$ between two non-active flat areas without defects and steps would consequently indicate different materials.

Site-related activity evaluation: If the positions of the active sites are not apparent from the n-EC-STM images in the first stage, the site-related activity evaluation could still help to unveil the noise behavior. This method evaluates an extended region across the entire measurement under reaction conditions (area 3) without a prior definition of specific structures like steps or plateaus. Instead, the area is divided into equally sized subareas that overlap (framed light blue regions), as presented in **Figure 3.4.2a**. The width of these areas used for the evaluations in this thesis was 6nm. Analogous to the calculations of the “material identification and noise analysis” for each subarea, the FWHM is calculated. Since each area provides next to the FWHM value information about the position within area 3, the individual FWHMs could be assigned to the surface structure. Combined with the estimated height profile (*cf.* **Subchapter 3.4.2**), and since the FWHM represents the activity intensity, it is possible to draw conclusions about the local surface activity as illustrated in **Figure 3.4.2d**.

Here, the red dots showcase the calculated values for the FWHM of each subarea, while the black line represents the estimated height. Interestingly, the course of these red dots can be reproduced very well by two Gaussian fits, presented in cyan and green. The reason for this accordance might originate from the continuous movement of the evaluated dataset (light blue squares in **Figure 3.4.2a**) used for the calculation of each red dot. The basic requirement for this kind of

analysis is that the distance between neighboring active areas is larger than these light blue squares. In other words, for small diameters of the light blue squares and sufficient large distances between evident active areas, the activity data always has a maximum neighbored by two minimums. From this consideration, one would expect a triangular-shaped course of the activity data points. However, since the interface between noisy and less noisy areas is a rather seamless transition when being considered on small scales, which originates in the working principle of STM and is influenced by the gain settings (see **Subchapter 2.3.3** and **Subchapter 3.3.3**), the course of the activity data is bell-curved and thus almost Gauss distributed. Consequently, this approach is rather unsuitable for other model surfaces, such as large active terraces, but works very well on locally restricted active sites.

The sum of the cyan and green graphs is plotted in dark blue and yields a measure of the position-related activity. Moreover, the area below this graph corresponds to the total activity of the investigated area. Consequently, the integrals of two individual curves (cyan and green) are proportional to the activity on the corresponding steps. Since, on this model surface, both steps are equally active, the ratio of both steps is 50%. Due to the extent of the light blue square and the possible influence of neighbored less apparent active regions on the fitting, the maximum of the overall activity could not be precisely assigned to a certain x-position but allows a rather rough allocation to distinct surface morphology (dark blue dotted line in **Figure 3.4.2d**). In brief, this evaluation method enables an extended investigation of the partial activity on active sites with limited local expansion.

4 Results and Discussions

This chapter presents the most relevant findings obtained during this doctorate. As demonstrated in the following, the n-EC-STM technique played a crucial role in identifying the active sites on different Pd single crystals and MnO₂NS on an HOPG support. All experimental settings and essential parameters used for the STM and CV measurements are provided in **Table A4.1** and **Table A4.2** in **Appendix B**, respectively. Moreover, a list of the calculated FWHMs of each Gauss fit used for the noise evaluation for Pd and MnO₂NS/HOPG can be found in **Table A4.3** and **Table A4.4**, respectively. A detailed discussion of the techniques, including the preparation of the samples, theoretical considerations, and working principles, are provided in **Subchapter 2.3** and **Chapter 3**. It is important to note that **Chapter 4** is mainly based on particular research projects that have been published during this doctorate. Consequently, for clarity, the references are shown at the beginning of each subchapter instead of referring to each paragraph separately unless other literature is explicitly cited.

4.1 Palladium Investigations

This subchapter discusses the identification of active sites at selected Pd(hkl) single crystals during proton reduction. The ability to absorb hydrogen into its bulk is an exciting feature of Pd, making it an attractive candidate as a HER catalyst. To further understand the surface processes occurring during HER, this subchapter discusses the nature of active sites from an experiential and computational point of view. Apart from the presented CV and n-EC-STM measurements, which were conducted at the chair's laboratory, the DFT calculations were executed by Apinya Ngoipala under the supervision of Dr. Matthias Vandichel from the University of Limerick (Faculty of Science & Engineering Department of Chemical Science). It is important to note that due to the initial functional errors and unexpected location-related interactions that disturbed the STM measurements of the new Bruker multimode setup inside the Ar-glovebox, most of the STM measurements were performed using the older Veeco multimode introduced in **Subchapter 3.1.2**.

Furthermore, the findings presented in this subchapter are based on the following publications and portray their major findings. The additive ⁽⁺⁾ indicates the first authors, while * refers to the corresponding authors of the publication.

- Schmidt T.O.,⁽⁺⁾ Ngoipala A.,⁽⁺⁾ Arevalo R.L., Watzele S.A., Lipin R., Kluge R.M., Hou S., Haid R.W., Senyshyn A., Gubanova E.L.,* Bandarenka A.S.,* Vandichel M.* *Elucidation of structure-activity relations in proton electroreduction at Pd surfaces. Theoretical and experimental study.* Small **2022**, 18, 2202410.
- Gubanova E.,⁽⁺⁾* Schmidt T.O.,⁽⁺⁾ Watzele S., Alexandrov V.,* Bandarenka A.S.* *Structure-dependent electrical double layer capacitances of the basal plane Pd(hkl) electrodes in HClO₄.* J. Phys. Chem. C **2022**, 126, 11414-11420.
- Schmidt T.O.,⁽⁺⁾ Haid R.W., Gubanova E.L., Kluge R.M.,* Bandarenka A.S.* *Electrochemical scanning tunneling microscopy as a tool for the detection of active electrocatalytic sites.* Topics in Catalysis **2023**, 66, 1270-1279.

4.1.1 General Assessments on Pd(111), Pd(110), and Pd(100)

As discussed at the beginning of this thesis, the three Pd surface facets (111), (110), and (100) were selected to gain a representative benchmark. In the first phase of this project, published in Schmidt *et al.*, the quality of the annealing process was verified by performing systematic STM and CV measurements, presented in the following ^[175].

4.1.1.1 Morphologic Initial Investigations

As discussed in **Subchapter 3.2.1**, the crystal is expected to have a smooth surface at an atomic level after the annealing process. In order to verify if this smoothness has reached the desired level, preliminary investigations were performed. As published in Gubanova *et al.*, **Figure 4.1.1a, b, and c** illustrate a 280nm to 260nm large atomically flat area of the Pd(111), Pd(110), and Pd(100) surfaces in air-saturated 0.1M HClO₄, respectively ^[267]. In these measurements, a potential within the double-layer region, as discussed below in **Subchapter 4.1.1.2**, was applied to prevent surface alteration due to electrochemical reactions.

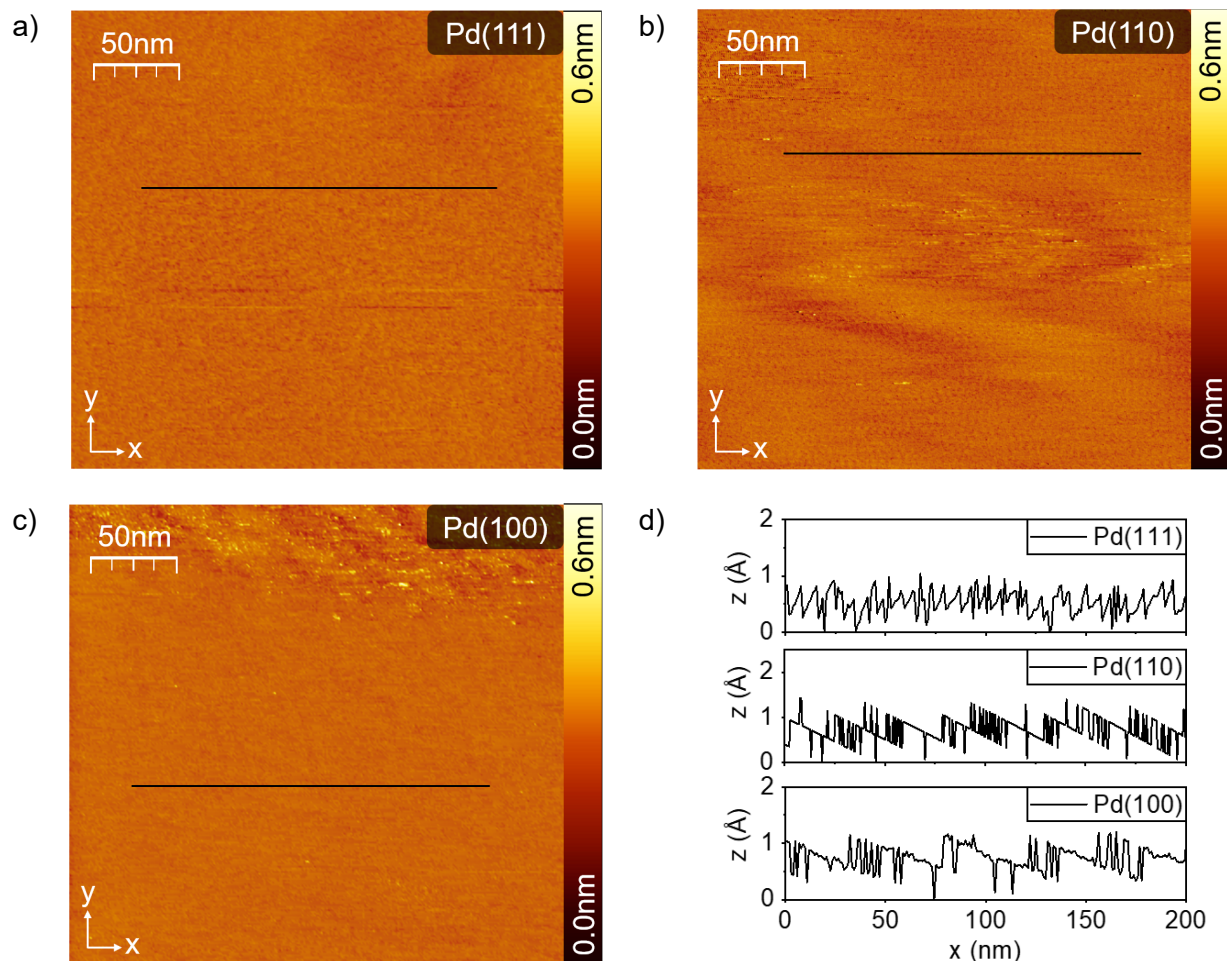


Figure 4.1.1. STM measurements in 0.1M HClO_4 in air atmosphere. The atomically flat surfaces of **a)** Pd(111), **b)** Pd(110), and **c)** Pd(100) were captured directly after annealing. The black highlights situated in the slow scan axis (x -direction) present the positions of the line scans demonstrated in **d)**. Data of all figures published in reference ^[267].

Moreover, these images show the pristine surface before any electrochemical measurements. The color bar on the right suggests the maximum height differences within these images, which is in the range of Angstrom. Furthermore, the black colored lines indicate the positions of the line scans demonstrated in **Figure 4.1.1d**. Here, a roughness of less than 1Å on an extension atomically flat area of about 200nm is visible on all investigated single crystals. These images demonstrate the ability of the oven applied here to produce an outstanding smooth surface on Pd. Nevertheless, the majority of the crystals appeared to have a roughness of approximately the height of a single Pd atom, as visible in the middle section of **Figure 4.1.1b** and on the top part of **Figure 4.1.1c** (cf. **Subchapter 2.4.1**). More information and additional figures on this finding for the different

crystal facets are provided in **Figure 4.1.1 A1** in **Appendix C**. In addition, this image presents an analog measurement on Pd(111) captured using the successor STM setup, including a multimode device inside an Ar-glovebox (see **Subchapter 3.1.3**). Here, a roughness similar to the setup in the air atmosphere could be seen. It is important to note that, as mentioned in **Subchapter 3.2.1**, the subsequent use of an inductive heater achieved a comparable high-quality surface preparation at a minimum expenditure of time. Moreover, large-scale SEM images present a uniform planar surface for the primary single crystals investigated in this work, Pd(111) and Pd(100), as illustrated in **Figure 4.1.1 A2** in **Appendix C**.

4.1.1.2 Electrochemical Initial Investigations

The utilization of CVs provides a powerful tool for investigating the electrochemical properties of a catalyst. Next to the unique shape of the crystal facet-dependent current-voltage relation, the published manuscript provided information about the absorption of H into the Pd bulk ^[175]. The measurements illustrated in **Figure 4.1.2a, b, and c** present the first cycles recorded on freshly annealed Pd(111), Pd(110), and Pd(100) in Ar-saturated 0.1M HClO₄ within an Ar- atmosphere, respectively. This data was captured in a conventional EC-cell that has an electrolyte volumetric capacity of several tens of milliliters (*cf.* **Subchapter 3.3.1**). The potential applied at the beginning of the CV was set to 0.57V versus RHE to ensure a low electrochemical initial activity. For each crystallographic plane, the detected characteristic peaks match the observations of other literature on single crystalline Pd ^[174,268]. Thus, next to the local validation of the annealing quality shown before by using STM, these data confirm a well-aligned surface on a large scale. Moreover, as described in **Subchapter 2.3.2**, all crystal facets showed a lower integrated area below the anodic scan compared to the cathodic scan. This difference suggests an H-absorption on all surfaces, even in the first cycle. Here, following **Equation (2)**, Pd(110) shows the highest value, approximately 31%, followed by Pd(100) and Pd(111). This finding underlines the high absorption ability of Pd. As reported in different literature, the initially detected characteristic peak within the first cycle starts to disappear already in the second one. This phenomenon was also detected in this work, whereby stable CVs were found after approximately 30 cycles (*cf.* **Figure 4.1.2 A1**).

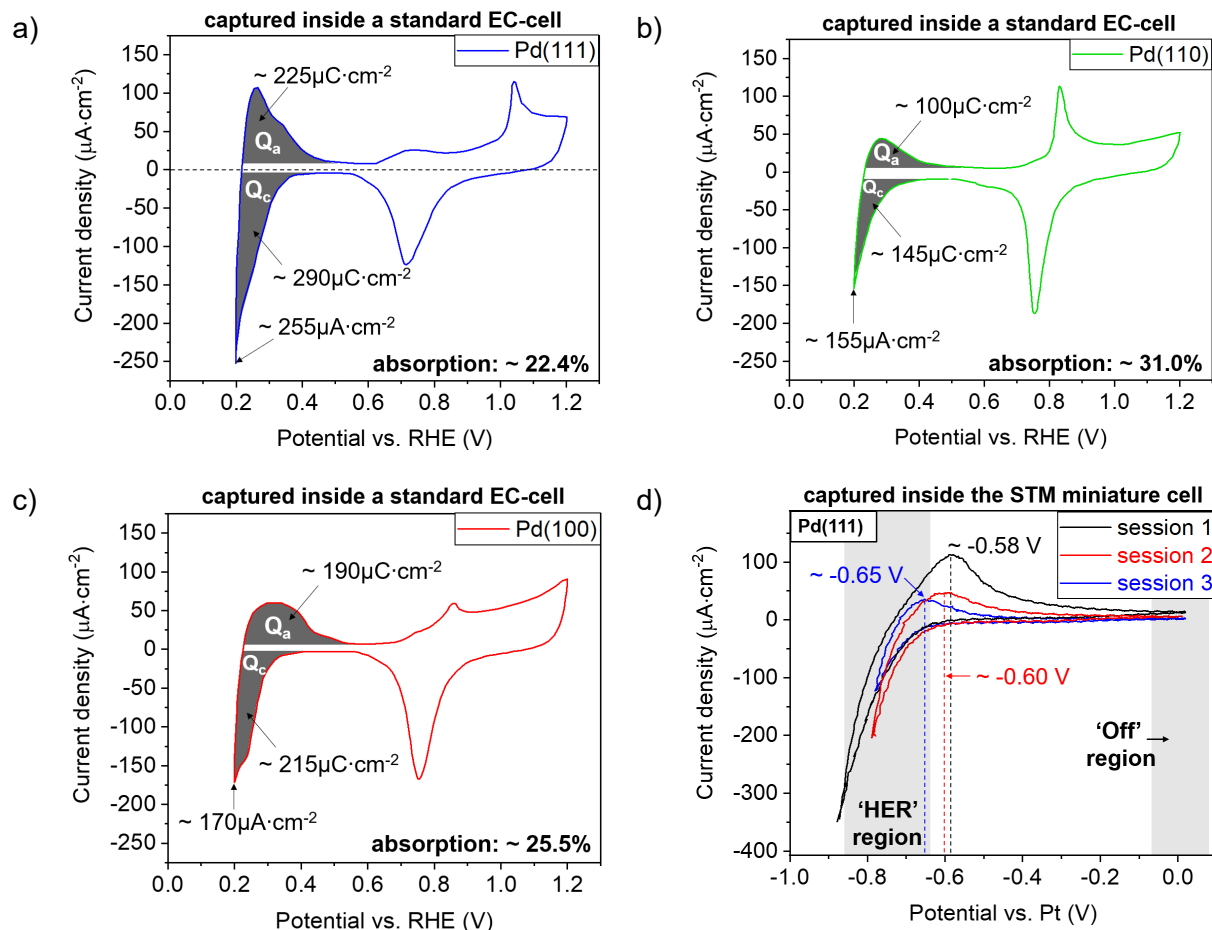


Figure 4.1.2. Representative CV measurements on different Pd single crystal facets. **a)**, **b)**, and **c)** show the first cycles on freshly annealed Pd(hkl) surfaces in Ar-saturated 0.1M HClO_4 within an Ar-atmosphere. The values for the estimated absorbed hydrogen are calculated using **Equation (2)**. **d)** CV measurements of stable cycles on freshly annealed Pd(111), captured on different sessions in air-saturated 0.1M HClO_4 within the STM device's miniature cell in the air-atmosphere. The marked potentials present the maximum of the anodic scan, which differs for the individual sessions. Data of all figures published in reference ^[175], representation inspired by reference ^[175].

Based on the absence of gas bubble formations at low potentials, in measurements in the standard EC-cell, the H_{UPD} region could be allocated to a rough potential interval between 0.2V and 0.4V versus RHE for all crystal facets. Consequently, it is sufficient to identify the potential ranges for the proton reduction taking place ('HER') and the minimized catalytic activity ('Off') against a Pt QRE on one of the Pd surfaces. **Figure 4.1.2d** shows three representative cycles captured on three different days on Pd(111), captured in the EC-STMs miniature EC-cell. As discussed before in

Subchapter 3.3.2, due to the usage of a Pt QRE, the characteristic peaks shift up to 70 mV between the different measuring sessions. Despite these fluctuations, a rough interval within the H_{UPD} region could be confined for the applied potentials between -0.7V and -0.8V versus Pt used in the EC-STM measurements for 'HER' (left-sided gray area). Furthermore, due to the sufficient width of the double-layer, a reasonable interval within the electrocatalytic range was reached when applying a potential of 0V versus Pt for reaction 'Off'. However, in each measurement session, the suitability of the potentials was verified by the presence or absence of the noise during the n-EC-STM measurements for these two potential intervals, respectively. More information and specific considerations when working with the STM device's miniature cell are provided in **Subchapter 3.3.1**.

Further interesting insights into the activity of the different Pd crystal facets were achieved by performing LSV within H_2 -saturated 0.1M $HClO_4$ (cf. **Subchapter 2.3.2**). **Figure 4.1.3** summarizes the detected absolute current values in logarithmic scales against the potential versus RHE within the H_{UPD} region. Shinagawa *et al.* elucidated a correlation between values of $30mV \cdot dec^{-1}$, $40mV \cdot dec^{-1}$, and $120mV \cdot dec^{-1}$ for the Tafel slopes and the Tafel, Heyrovsky and Volmer steps as the RDS respectively, during HER (see **Subchapter 2.2.2**)^[162]. Since the slopes s_{Tafel} for Pd(111), Pd(110), and Pd(100) of $150mV \cdot dec^{-1}$, $150mV \cdot dec^{-1}$, and $80mV \cdot dec^{-1}$, respectively, do not correspond to these expected relationships, a direct deduction of the RDS is not possible. Nevertheless, interestingly, the values for the s_{Tafel} of Pd(111) and Pd(110) are equal, which indicates a similarity in the active sites being decisive on these surfaces. In addition, the Tafel plots in **Figure 4.1.3** show the biggest value for j_0 for Pd(111) and the smallest for Pd(100). Thus, these two surfaces are expected to have the highest and lowest electrochemical activity, respectively, as discussed in **Subchapter 2.3.2**. This finding supports the assumption of differences in the electrochemical processes on these crystallographic facets. Consequently, to divide the capacities and obtain the highest amount of information on the HER processes on Pd, the performed n-EC-STM investigations focused on Pd(111) and Pd(100).

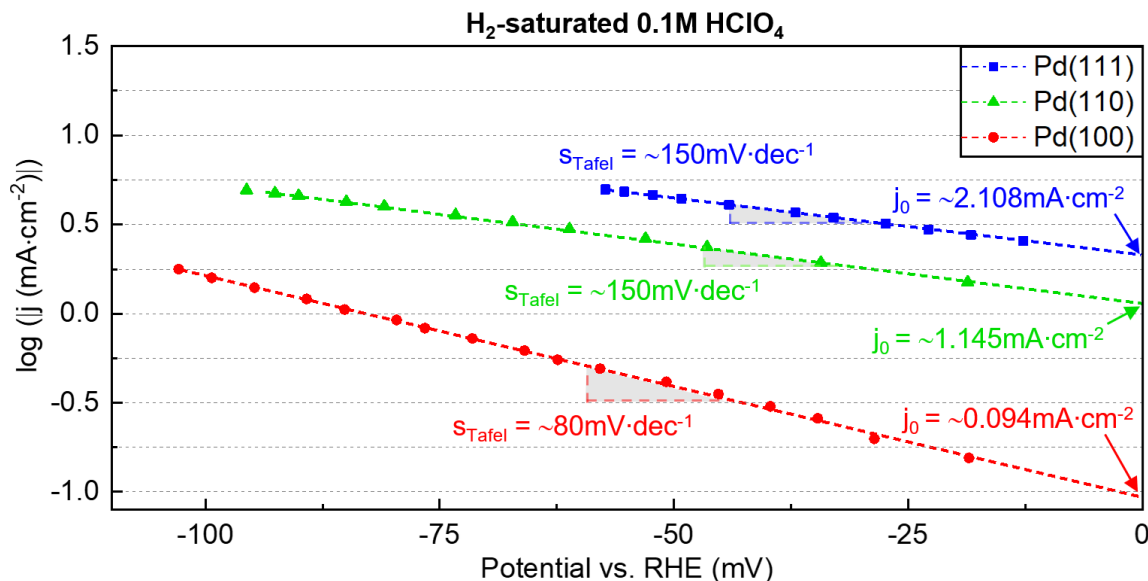


Figure 4.1.3. Tafel plots for Pd single crystals with different crystallographic facets captured at a scan rate of $50\text{mV}\cdot\text{s}^{-1}$ in H_2 -saturated 0.1M HClO_4 . The rectangles, triangles, and circles show the actual measured values for Pd(111), Pd(110), and Pd(100), respectively, while the dashed lines illustrate the extension of the linear region to 0V versus RHE. The identified values for s_{Tafel} are $150\text{mV}\cdot\text{dec}^{-1}$ for both Pd(111) and Pd(110), while it is significantly lower for Pd(100). This circumstance indicates a difference in active sites between Pd(111) and Pd(100). In addition, the trend for j_0 , with Pd(111) showing the highest and Pd(100) the lowest value, indicates significant differences in the active sites between these two crystals. Data published in reference ^[175], representation inspired by reference ^[175].

4.1.2 Active Site Identification on Recently Annealed Pd

Due to the possibility of gaining insights into the nature of active sites on catalyst materials on the nanoscale by using n-EC-STM (cf. **Subchapter 2.3.3**), this technique was selected for the subsequent investigations on freshly annealed Pd. The initial findings suggested Pd(111) and Pd(100) as suitable candidates for these measurements and documented the quality of the annealed crystalline surfaces. According to the published manuscript, the following subchapters experimentally reveal the nature of active sites and complement these observations with computational assessments ^[175].

4.1.2.1 Annealed Pd (111)

The first investigated sample was the Pd(111) crystal, which was revealed as the most active system in the CV experiments. An ideal region for the investigation provides a stair-like structure separating two atomically flat terraces, as illustrated in **Figure 4.1.4a**. Here, as typical for n-EC-STM measurements, the potential was changed during the measurement in order to receive information about the local activity. The white dashed line marks the potential switch, while white dotted lines sketch the contours of the individual step edges (I-IV). In the upper part, the image's high peaks reveal an increased activity, especially on steps I and II for 'HER', which disappears on the lower part for the reaction 'Off'.

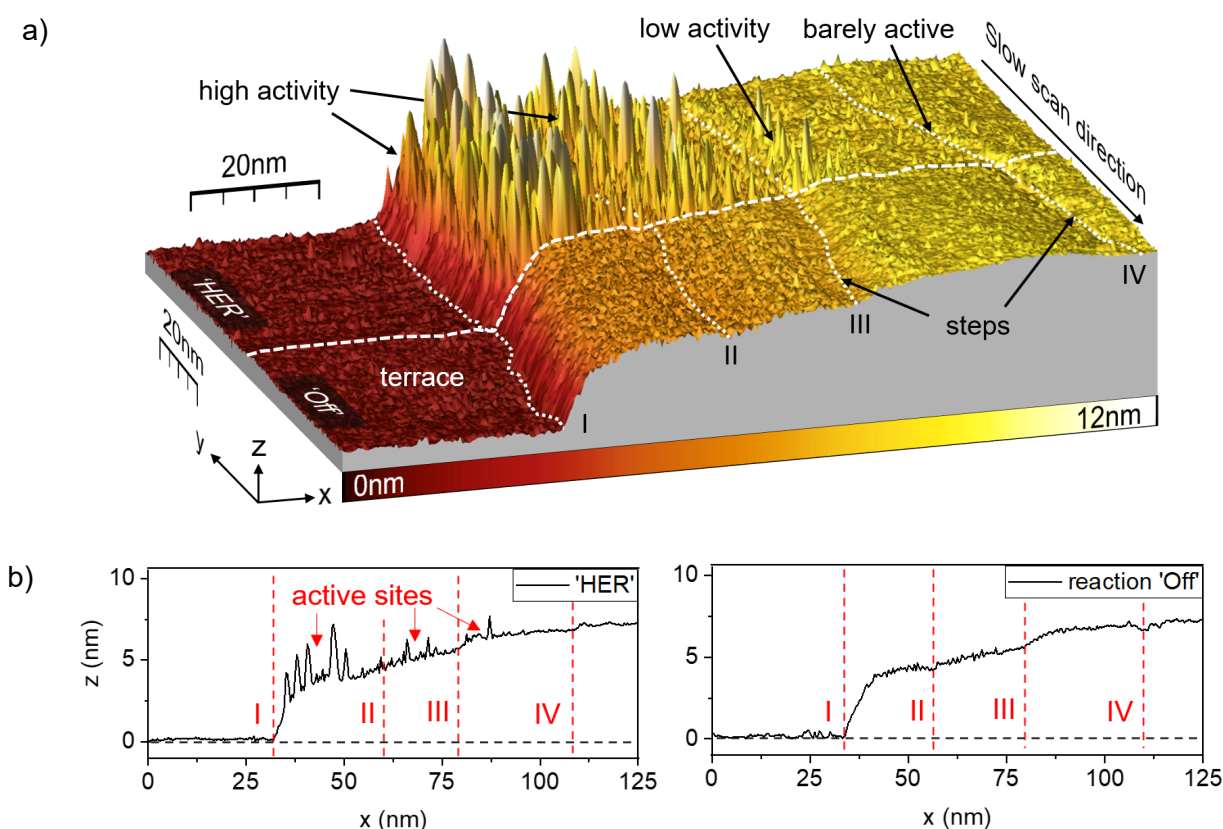


Figure 4.1.4. Freshly annealed Pd(111), investigated in 0.1M HClO₄ by n-EC-STM. **a)** Three-dimensional image of a stair-like structure separating two atomically flat areas. The upper half of the image was recorded for 'HER', while the lower half was captured for reaction 'Off'. A white dashed line highlights the potential switch while the dotted white line marks the course of steps I to IV. **b)** Representative line scans for 'HER' (left side) and reaction 'Off' (right side), which illustrate the extent of the noise and the actual morphology of the structure, respectively. Data of all figures published in reference ^[175].

In contrast, the red-colored flat terrace on the image's left side and step IV seem rather inactive (*cf.* **Figure 4.1.4b**). However, to identify the actual active sites, a more detailed noise evaluation of the individual sections of the step is required (for more information, see **Subchapter 3.4.2**).

In order to understand which parts of the stair-like structure show the highest activity, first of all, each step is divided into two areas: its lower and upper half (areas 1-6). These areas' positions are framed in **Figure 4.1.5a**, which provides a two-dimensional view with its upper half for 'HER' and its lower one for reaction 'Off'. The corresponding data set was extracted and evaluated for each region according to the noise analysis introduced in **Subchapter 3.4.2**. Before the computation of the individual FWHM, all sections were leveled using the flattening tool of the evaluation software WSxM to eliminate adulterations by the height differences of the steps, as described in **Figure 4.1.5. A1**. When counting the amount of the derivatives of the captured slopes for each point within each area, a Gaussian distribution is visible (solid lines in **Figure 4.1.5b, c, and d**). Interestingly, the upper parts of steps I to III (areas 2, 4, and 6) show a clear activity trend: Step I (red) has the highest activity since the FWHM is the largest one of the analyzed steps, followed by step II (green) (*cf.* **Figure 4.1.5b**). A FWHM difference of about 16% between these two steps is observed. Even higher is the difference between steps II and III, which is about 24%. This graph underpins the first impression that steps I and II are the most active steps. Consequently, the observed activity trend on the step edges follows $I > II > III > IV$.

However, regarding the height of the left step (I) of approximately 4nm and the much smaller heights of the other ones (II: ~0.7nm, III: ~1.1nm, IV: ~0.4nm), the height of the steps does not directly correlate with the trend in the activity of the individual steps. For comparison, at a theoretically assumed height of 0.223nm of a Pd(111) monolayer, the individual steps would correspond to 18, 3, 5, and 2 layers, respectively ^[234–238]. Another analysis shown in **Figure 4.1.5c** compares the noise between each step's upper and lower regions. Here, it becomes clear that step I is the most active step, with a Δ FWHM value of about 65%. In contrast, the less active step III only shows a difference of approximately 22%. The reason for the small difference of only 9% in the second step edge originates from the merging of the noise from the upper part of step I and the lower half of step II. As a result, the FWHM of the lower part of step II is much larger than it would be without the presence of step I. Consequently, the evaluation of step II is less representative.

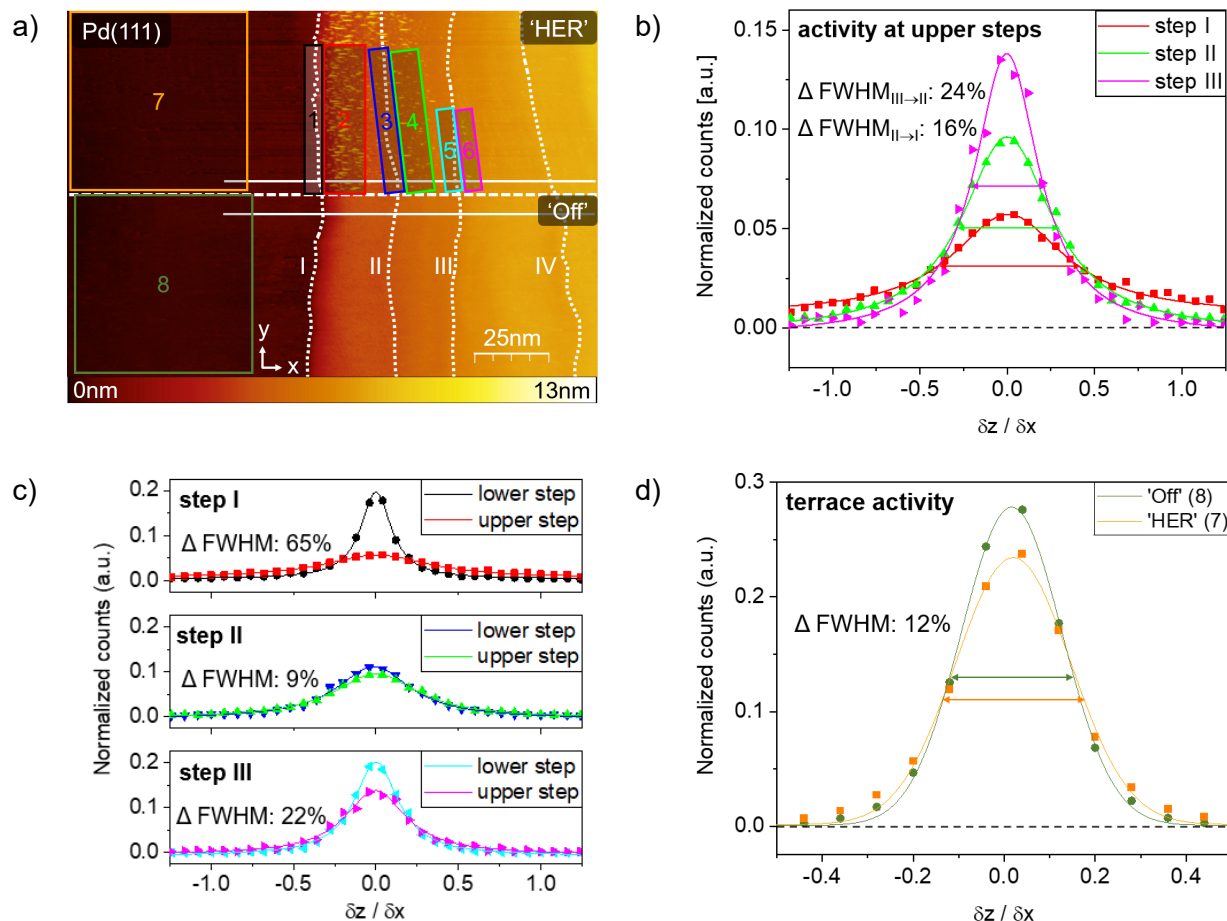


Figure 4.1.5. Noise evaluation on freshly annealed Pd(111). **a)** Two-dimensional view of **Figure 4.1.4a** with highlighted positions for the areas used for the noise evaluation (areas 1-8). The white dotted vertical lines represent the course of the steps, while the white dashed horizontal line depicts the border between 'HER' and reaction 'Off'. The horizontal white solid lines show the line scans' positions in Figure 4.1.4b. **b)** Noise analysis of the upper parts of steps I to III (areas 2, 4, and 6) for 'HER'. **c)** Comparison of the upper and lower section of each step edge (areas 1-6) with respect to the color code used in a). **d)** Evaluation of the terrace activity for 'HER' (area 7) and reaction 'Off' (area 8). A Gaussian fit was used to evaluate the data points in all presented diagrams. Data of all figures published in reference ^[175].

However, the evaluation shows for all steps that the upper part is more active than the lower one, which indicates the location of the active site on Pd(111), independent from the step height, on top of the step edges. Despite, when observing **Figure 4.1.4a and b**, the first impressions suggesting that the terrace might be rather inactive, a significant difference in the FWHM of approximately 12% is observed when comparing the terrace for 'HER' (position 7, orange) and reaction 'Off' (position 8, dark green), illustrated in **Figure 4.1.5d**. This rather surprising finding again underlines

the necessity of quantitative noise analysis of the STM measurements. In addition, it is reasonable that the high activity on the step edges of Pd(111) combined with the noticeable activity all over the terraces might cause the high activity of Pd(111) during the experiments in H₂-saturated 0.1M HClO₄ (see discussion of **Figure 4.1.3**). Consequently, already from these experiments, one could conclude that the activity on step edges, terraces, or both might be lower for Pd(110) and Pd(100).

Another remarkable finding is that even active steps are not necessarily entirely active. This was already visible for step III, which only shows a high activity in its lower half. More drastic is the absence of high noise on monoatomic step IV, which seems to be similar to the activity of the surrounding terrace. This difference in local activity on individual step edges is more obvious in **Figure 4.1.6a and b**, which show a three-dimensional and a two-dimensional image of another position on the Pd(111) crystal, respectively. Here, the upper and the lower parts are captured under 'HER' conditions, while the middle section represents the surface for reaction 'Off', separated by a white dashed line. Also, the step edges are visualized using dotted lines. While the three-dimensional view illustrates the intensity of the noise on the active sites for certain steps, the two-dimensional view emphasizes the active and less active positions more in detail. For the latter, the regions of the step edges where an apparent high noise is visible are highlighted as black dotted lines, while the white ones represent areas without significant noise peaks. This perspective indicates a non-trivial explanation for the occurrence of noise on Pd(111) steps: While step I is mostly active in the upper 'HER' region and does not show any noise peaks for reaction 'Off', only two-thirds of the step within the lower 'HER' region is significantly active. In contrast, step II is almost entirely active in the lower 'HER' region but remains less active in the upper one. Furthermore, the active step V is split into steps III and IV close to the 'Off' region. However, about two-thirds of step III shows significant noise within the lower 'HER' region, while step IV does not. A possible reason for this unintuitive noise behavior might originate from the height difference of the individual steps and, thus, their distinct GCN, as explained in **Subchapter 2.1.5**. As elucidated in Gubanov *et al.*, DFT calculations on Pd(111), Pd(110), and Pd(100) revealed that the adsorption of water molecules, which is a crucial process in water splitting, was significantly influenced by the characteristics of the surface ^[267,269]. This statement is based on the linear correlation found between the GCN and the H₂O binding energies on the different surface facets.

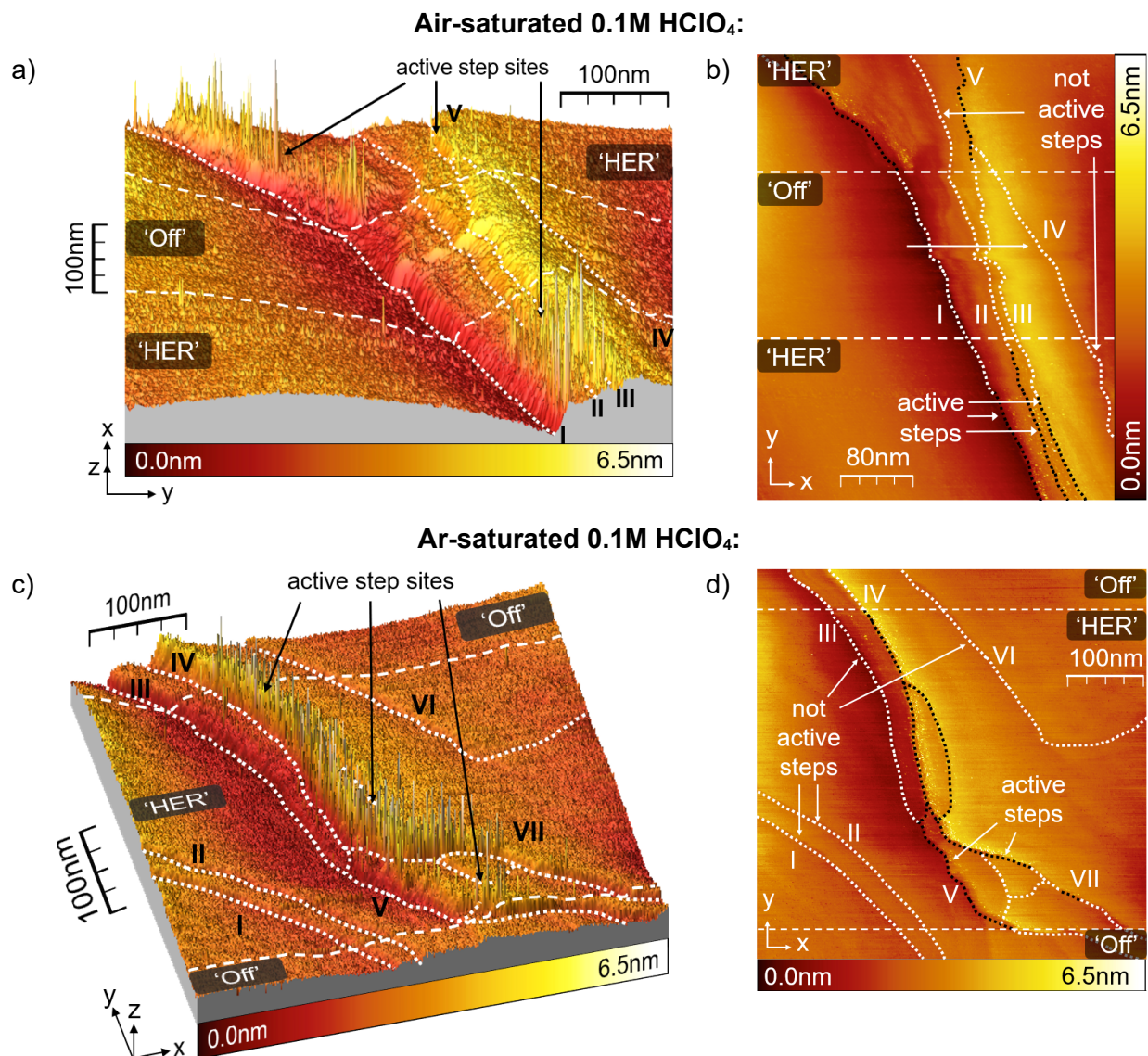


Figure 4.1.6. Comparison of two measurements on freshly annealed Pd(111) in **a)** air-saturated 0.1M HClO₄ in an air-atmosphere and **c)** in Ar-saturated 0.1M HClO₄ in an Ar-atmosphere. White dashed lines highlight the positions of the potential switches, and dotted lines mark the step edges. The corresponding two-dimensional views in **b)** and **d)** emphasize step regions with significant noise as black dotted lines. In contrast, the white dotted lines map the regions for reaction 'Off' and 'HER' where no or only a slight noise behavior appears. Interestingly, entire steps like step IV in **b)** or steps I, II, and VI in **d)** do not show any outstanding noise, while some steps like step III in **b)** and step VII in **d)** are only partly significantly active. Both samples were prepared using the inductive heater described in **Subchapter 3.2.1**. Data of **a)** and **b)** published in reference ^[175].

Furthermore, it is shown that the GCN depends on the number of neighboring atoms and possible strain effects within the crystal lattice.^[267,270] As discussed in the subsequent **Subchapter 4.1.3**, especially the latter has a significant influence on the HER activity of Pd. Due to the challenge of gaining atomically resolved STM images on Pd at room temperature, the actual morphology on the observed step edges in **Figure 4.1.6** remains unclear. However, it is plausible that the non-trivial distribution of noise on the step edges might originate from a variation in the GCN on its individual sections since strain effects, defects, and a jagged course of the step edges are presumable.

As discussed in detail in **Subchapter 3.1.3**, as part of this work, a new STM setup was built inside an Ar-glovebox in order to exclude the origin of unpredicted noise behavior by O₂-based processes. Nevertheless, **Figure 4.1.6c and d** present an analogous measurement to **Figure 4.1.6a and b** with a similar unintuitive noise behavior on freshly annealed Pd(111) in Ar-saturated 0.1M HClO₄ in an Ar-atmosphere. Here, several step edges have active and non-active sections within the 'HER' region, as shown in the three-dimensional and two-dimensional views, respectively. On the one hand, due to the identical noise behavior, this additional measurement indicates the proton reduction as the actual reaction observed in the experiments outside the glovebox, thus underpinning the validity of the findings. On the other hand, oxygen or effects from the ORR could be excluded as the origin for the unintuitive noise behavior. However, further understanding the reason for the unequally distributed noise on Pd(111) step edges requires additional investigations and could be part of future research projects.

4.1.2.2 Annealed Pd (100)

The second Pd single crystal investigated by the n-EC-STM technique in this study is Pd(100). The experiments were performed directly after the annealing procedure, described in **Subchapter 3.2.1**. Similar to the study on Pd(111), here, the area investigated shows an atomically flat terrace, separated by a step edge of a height of about 3.4nm, as presented in **Figure 4.1.7a**. Under 'HER' conditions (in the front and back sides of the three-dimensional image), on the step edge large noise peaks arise, which disappear for reaction 'Off' (middle section). Moreover, a lower noise behavior on the very flat terrace sites indicates electrochemical activity all over the surface.

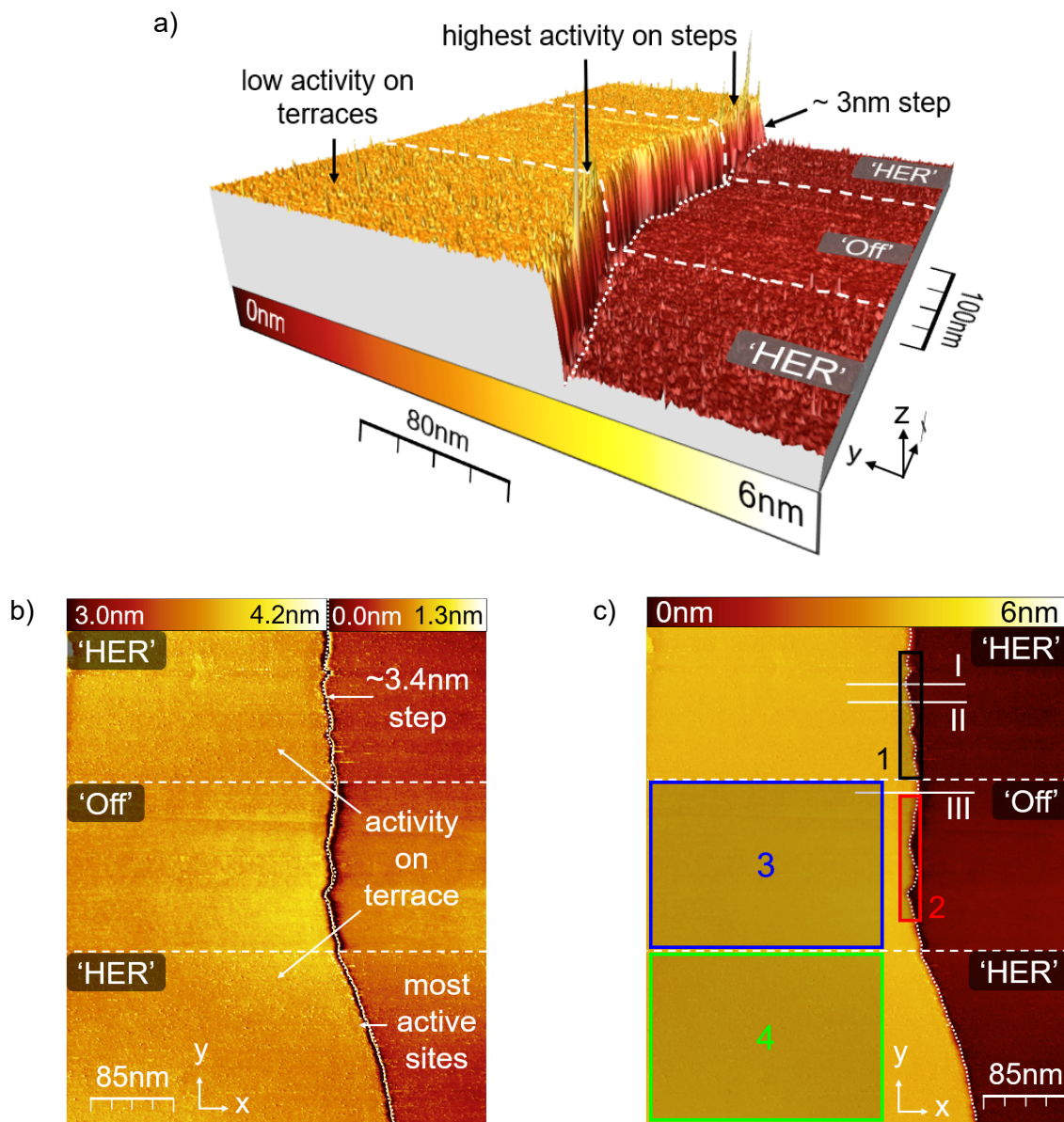


Figure 4.1.7. *n*-EC-STM measurement in 0.1M HClO₄ of freshly annealed Pd(100). **a)** The orange-colored upper terrace on the left gets separated by an approximately 3.4nm high step from the red-colored lower terrace on the right. The white dashed line marks the position of the potential switch between 'HER' and reaction 'Off', while the white dotted line highlights the course of the step. **b)** A recolored two-dimensional view was merged with single images of the upper and lower terraces to eliminate the height difference of the step for better visibility using two individual color bars. **c)** Classical two-dimensional view of a) demonstrating the height of the step. The marked areas used for the noise evaluation are in **Figure 4.1.8a and b**, while the solid white lines indicate the positions of the line scans in **Figure 4.1.8d**. Data of all figures published in reference ^[175].

The two-dimensional view in **Figure 4.1.7b** emphasizes this increased terrace activity. Here, individual color bars illustrate the upper (left side) and lower terrace (right side) for better visualization. Their low intervals of 1.2nm and 1.3nm demonstrate the low height difference on the terraces and enable the observation of the terrace activity. For comparison, **Figure 4.1.7c** provides the classical two-dimensional view with one color bar, including the highlighted positions for the subsequent noise analysis (areas 1-4) according to **Subchapter 3.4.2**. Due to the relatively low noise on the terrace, the difference between 'HER' and reaction 'Off' is no longer visible. An additional example in **Figure 4.1.7 A1** in **Appendix C** shows a comparable n-EC-STM measurement on Pd(100) while highlighting the dependency of the used magnification and the visibility of the noise peaks. Consequently, this figure underpins the need for a comprehensive noise evaluation, even in unexpected areas.

As presented in **Figure 4.1.8a**, the evaluation of the step noise reveals a significant difference between the FWHMs for 'HER' (black) and reaction 'Off' (red) of about 41%. In contrast, the analogous investigation on the terrace (green and blue, respectively) showcases a much lower value for ΔFWHM of approximately 14%, as demonstrated in **Figure 4.1.8b**. This data underpins the initial impression that, similar to Pd(111), the step edge is the most active site on Pd(100), followed by the terrace. The individual extracted areas used for the noise evaluation and a list of all values for the FWHM are provided in **Figure 4.1.8 A1 (Appendix C)** and **Table A4.3 (Appendix B)**, respectively.

Furthermore, similar to the observations on freshly annealed Pd(111), the noise on the step edge does not arise on the entire step. However, instead of entire regions without significant activity on steps, on Pd(100), the noise on the step edges seems more sporadic but frequent, as illustrated in **Figure 4.1.8c**. Here, the waterfall plot shows an exemplary extract of the step edge under 'HER' conditions. The line scans with high peaks on the steps are highlighted in red, while the black ones show a similar activity all over the line scan. Moreover, **Figure 4.1.8d** illustrates representative line scans that underline this difference for two different positions for 'HER' (red and black) and reaction 'Off' (blue).

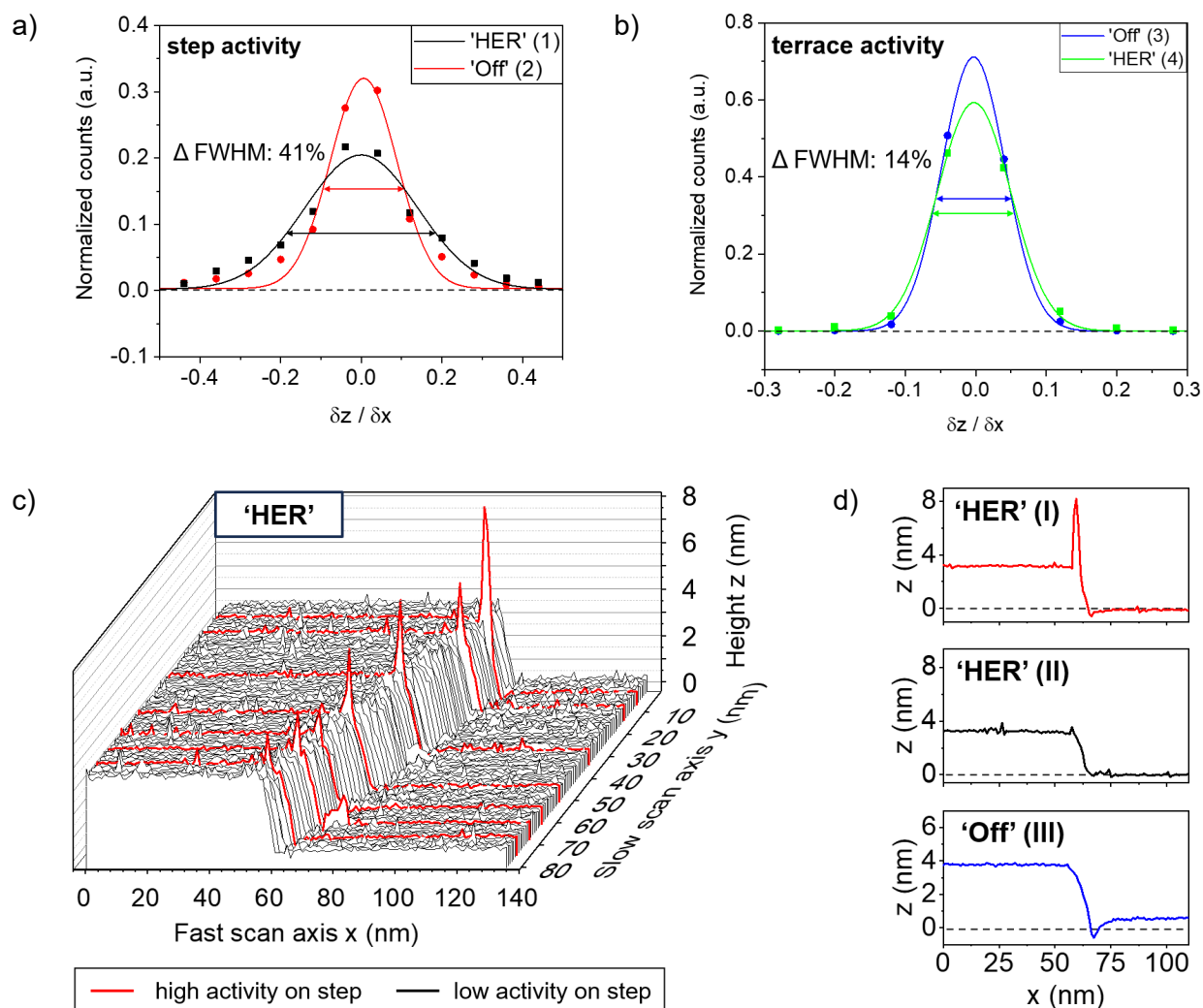


Figure 4.1.8. Noise analysis on freshly annealed Pd(100). **a)** Diagram of the normalized counts versus the derived slopes of the step regions highlighted in **Figure 4.1.7c**. The FWHM of the Gaussian fits for 'HER' is significantly broader than for reaction 'Off'. **b)** Analogous evaluation for the terrace. **c)** Waterfall plot, presenting 81 consecutive line scans for 'HER'. Line scans with outstanding noise on the step edge are highlighted in red, indicating a sporadic noise behavior. **d)** Selected line scans marked in **Figure 4.1.7c** showing representative height profiles. Data of all figures published in reference ^[175].

An explanation for this observation could originate from a relatively low reaction rate. As discussed in **Subchapter 2.3.2**, the current density of a specific potential on different CV measurements provides information about the relative reaction rate. When comparing the current densities captured at a potential of 0.2V versus RHE at the CV measurements in **Figure 4.1.2**, a significantly lower current density of $\sim 170 \mu\text{A}\cdot\text{cm}^{-2}$ for Pd(100) compared to Pd(111) ($\sim 255 \mu\text{A}\cdot\text{cm}^{-2}$) was

detected. As a result, it appears plausible that due to the relatively low number of reactions occurring when the STM tip scans the surface over an active step site, the disturbance within the tunneling barrier does not sufficiently affect the tunneling current to exceed the threshold of the gain setting (*cf.* **Subchapter 2.3.3**). Consequently, the tip would not retract from the surface, and no noise would be detected. As explained in **Subchapter 3.3.3**, appropriate gain settings could partly regulate the noise intensity. However, if the gain settings were too low to visualize the noise on the step edge, it would also be too low to unveil the noise on the terrace. Since this is not the case, a relatively low distortion in the tunneling gap between the STM tip and the sample, which likely originates from the low reaction rate, might cause sporadic noise on the step sites.

4.1.2.3 DFT-Based Activity Analysis

The following discussion focuses on the insights into the previously, by n-EC-STM observed proton reduction activity on ideal Pd surfaces from a computational perspective, implemented by the University of Limerick and published in Schmidt *et al.* ^[175]. A discussion of the underlying considerations is provided in **Subchapter 2.3.4**. For the calculations, the DFT experts assumed a simulated applied potential of 0V versus SHE at realistic conditions with 1atm ambient pressure and a temperature of 300K. Moreover, as previously discussed, low H-Pd ratios of 1:4 for Pd(111) and Pd(100), 1:6 for Pd(211), and 1:8 for Pd(110) were assumed for the calculation in this chapter (*cf.* **Figure 2.3.9 A1b**). Consequently, selecting these conditions simulates a theoretical system that is as similar as possible to those of the CV and STM experiments. For comparison, the calculations for high coverages with a one-to-one ratio are presented in reference ^[175]. However, this would be less representative due to the low expected H load on the Pd surface when operating in the H_{UPD} region during the EC-STM experiments (*cf.* **Subchapter 2.2.1**).

The DFT calculations presented in **Figure 4.1.9** focus on the Volmer step, where the H atom gets adsorbed onto the Pd surface (see **Subchapter 2.2.2**). Here, the investigated ΔG_{H^*} provides a measure for the expected HER activity of the observed systems due to its correlation with the adsorption and binding energy (see **Subchapter 2.1.4**) ^[161]. Since all presented ΔG_{H^*} are negative, spontaneous adsorption is thermodynamically favored ^[271]. Nevertheless, the lower the absolute value of ΔG_{H^*} , the smaller the possibility of poisoning the surface. The DFT results demonstrate a trend in decreasing absolute ΔG_{H^*} for an increasing number of PdH sublayers for all surface facets except for Pd(100) (red). For the latter, a similar value of around -0.45eV was calculated for all observed scenarios.

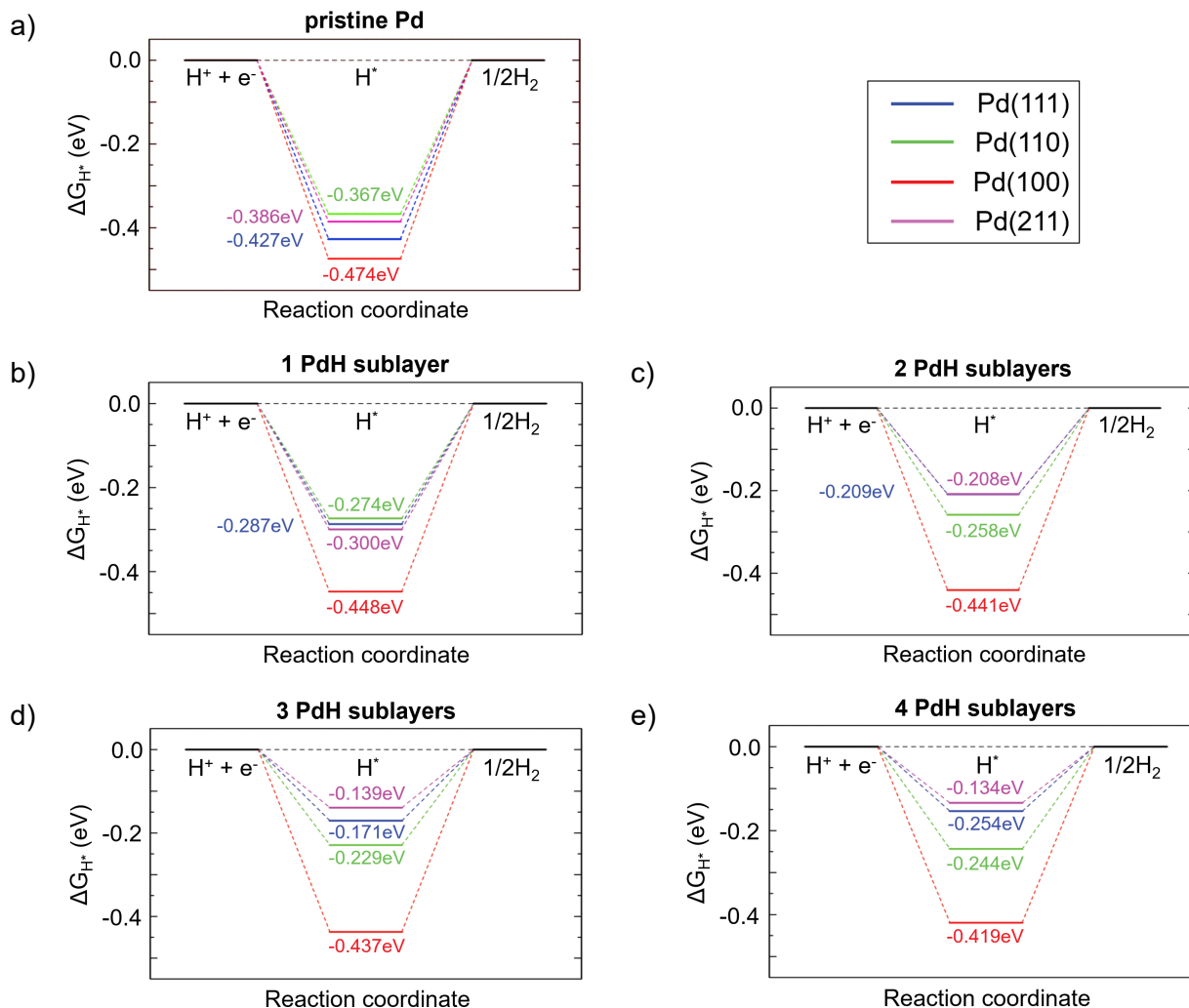


Figure 4.1.9. Summary of calculated changes in Gibbs free energy for the Volmer reduction during HER for relatively low H-Pd ratios. **a) - e)** illustrate the different values for ΔG_{H^+} for 0 to 4 PdH sublayers directly underneath the surface of the Pd(111) (blue), Pd(110) (green), Pd(100) (red), and Pd(211) (purple) crystals. Figures adapted from reference ^[175] and licensed under CC BY 4.0 ^[87].

However, the Pd(211) (purple) and Pd(111) (blue) facets' absolute value of ΔG_{H^+} decreases approximately by a factor of three and by two for Pd(110) (green). As a result, for two or more PdH sublayers, Pd(211) and Pd(111) revealed the lowest absolute ΔG_{H^+} . Consequently, a significant increase in activity could be expected for these crystal facets and postulate them as the most promising ones in this study (see volcano plot in **Figure 4.1.9 A1** in **Appendix C**). This finding agrees with the previously presented Tafel plots and EC-STM measurements, which also found Pd(111) to be very active. (**Figure 4.1.2a**, **Figure 4.1.3**, and **Figure 4.1.4a**). Furthermore, as demonstrated in **Subchapter 4.1.2.1** and **Subchapter 4.1.2.2**, both the Pd(100) and Pd(111)

facets reveal the highest activity on step sites. Considering that the (211)-orientation has a “step-like” nature, the predicted HER activity by the DFT calculations agrees with the experimental observations showing an increased activity on step edges.

4.1.3 Active Site Identification on Annealed Subsequent Cycled Pd

As previously presented in **Subchapter 4.1.1.2** and **Subchapter 4.1.2.3**, hydrogen absorption plays a crucial role in proton reduction on Pd. This influence is illustrated in particular by the fact that the CV of a freshly annealed Pd single crystal differs from that of a multiple-cycled one. As a result, the subsequent publicized study focused on freshly annealed Pd single crystals and crystals that were cycled until a stable CV was reached, as presented in the following ^[175].

4.1.3.1 Annealed and Cycled Pd(111)

Instead of atomically flat terraces separated by multilayered steps as mainly seen on freshly annealed Pd, the preliminary STM investigations in air-saturated 0.1M HClO₄ in an air atmosphere on cycled Pd(111) (Pd(111)_c) for reaction ‘Off’ revealed a hilly morphology across the entire surface, shown in **Figure 4.1.10a**. This measurement is assumed to show an intermediate state between a freshly annealed, atomically flat surface and a hilly surface after cycling. Besides the undulating structures visible in the front of the three-dimensional image, the surface morphology in the back remained relatively flat. This difference gets even more apparent when observing the two-dimensional perspective illustrated in **Figure 4.1.10b**. Here, parts of the hills created by electrochemical cycling seem to be arranged along the ridge of the prominent elevations.

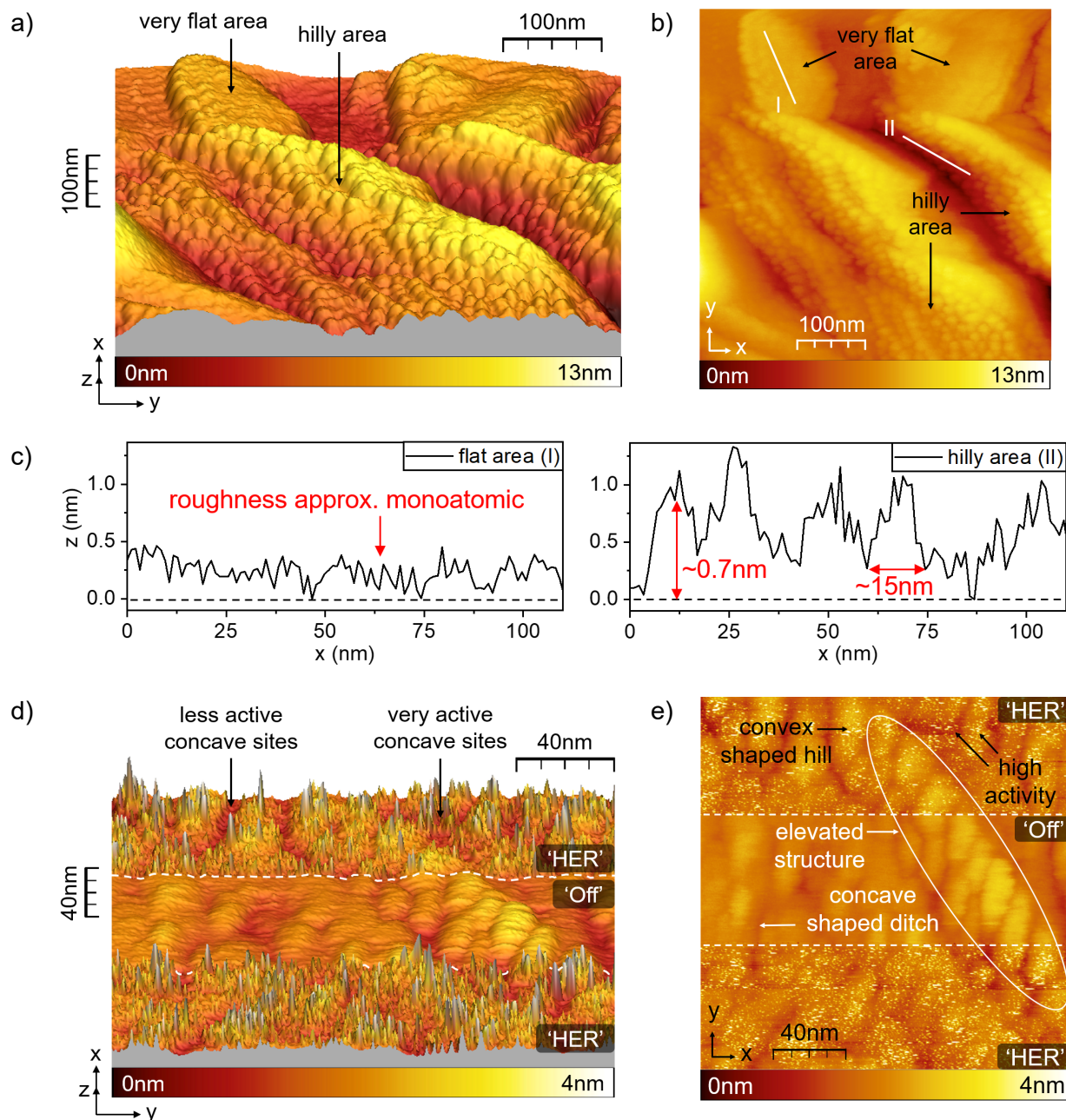


Figure 4.1.10. EC-STM measurements on Pd(111)_c. **a)** and **b)** illustrate an EC-STM image for reaction 'Off', showing an estimated intermediate state between a freshly annealed and a hilly surface after electrochemical cycling in three-dimensional and two-dimensional, respectively. **c)** Line scans of a very flat (left side) and a hilly structure (right side) at positions I and II, highlighted in b). **d)** and **e)** present the noise behavior in a three-dimensional and two-dimensional perspective of an n-EC-STM measurement on Pd(111)_c, respectively. Data of all figures published in reference ^[175].

The solid white lines highlight the positions of the line scans presented in **Figure 4.1.10c**. A very flat surface was found at position I with a roughness corresponding approximately to a monolayer of Pd ($\sim 0.223\text{nm}$), while position II represents an undulating area ^[234–238]. For the latter, a typical diameter of about 15nm and a height of approximately 0.7nm were found in this measurement. However, the variation in the height and diameter of these hills seems to be comprehensive, as elucidated in **Figure 4.1.10 A1** in **Appendix C**.

Interestingly, when observing the n-EC-STM measurement in **Figure 4.1.10d**, the noise behavior on Pd(111)_c also seems to differ from that on Pd(111). Here, the convex-shaped parts of the mounds appear to be very active throughout, while the concave-shaped ditches in between show both high and low activity. In addition, as depicted in **Figure 4.1.10e**, the elevated structure, which crosses the image vertically at a 45-angle from the top mid to the right, does not show any outstanding noise. Regarding the findings on freshly annealed Pd(111), where the step-like structures revealed a remarkable noise behavior, this observation indicates a change in the nature of the noise. An additional measurement showing the same phenomenon is provided in **Figure 4.1.10 A2** in **Appendix C**.

A more detailed evaluation of the noise behavior on Pd(111)_c could be achieved when separating the concave and the convex regions, as illustrated in **Figure 4.1.11**. The splitting was executed using the WSxM tool “flooding”, which allows the exclusion of all data points with a height above or below a selected threshold. Consequently, this feature facilitates an individual evaluation of the measurement's concave (blue regions) and convex (orange-red regions) sections. Similar to previously shown color bars, both selected scales used in these figures display lower topographies in dark and higher ones in bright colors. Consequently, high noise peaks are shown as white dots for concave and convex regions. In the upper half of the image, under ‘HER’ conditions, all concave areas feature noise peaks, while the concave regions demonstrate sections with both low and high activity. In contrast, when the reaction was turned ‘Off’ in the lower half, the entire noise disappeared.

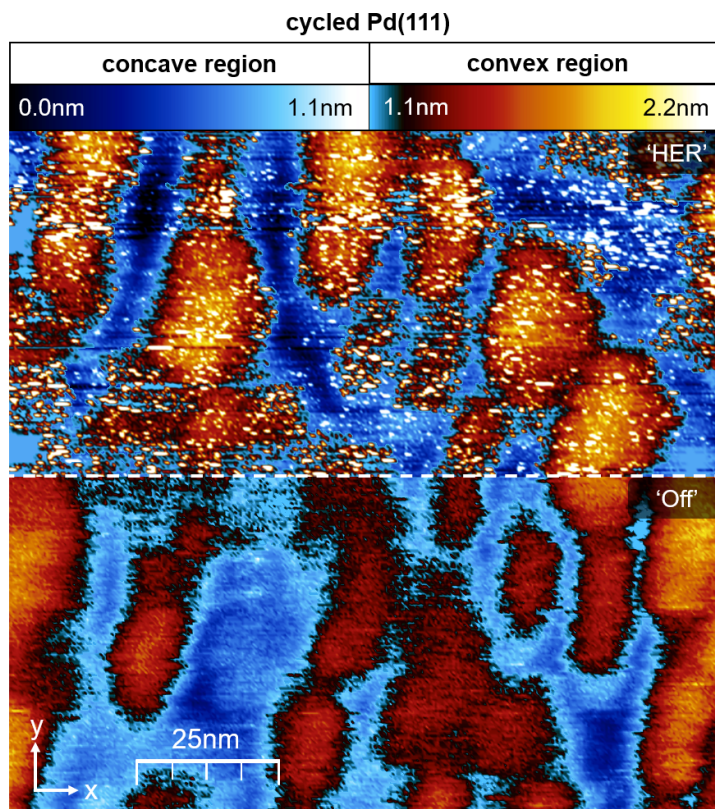


Figure 4.1.11. *n*-EC-STM measurement on Pd(111)_c in air-saturated 0.1M HClO₄ with individual color bars for concave-shaped (blue shades) and convex-shaped (orange-red shades) structures. The white dashed solid horizontal line marks the position of the potential switch from 'HER' (upper half) to reaction 'Off' (lower half). The white dots at 'HER' represent high noise peaks. An overview of the individual areas is provided in **Figure 4.1.11 A1** and **Figure 4.1.11 A2** for 'HER' and reaction 'Off', respectively. The separation of the concave and convex areas shown in this image is also the basis for the subsequent noise analysis. Data published in reference ^[175].

During the subsequent noise analysis, a discrepancy of 7% was found for the FWHMs at concave and convex sites, as presented in **Figure 4.1.12a** for 'HER'. In contrast, for reaction 'Off' (*cf.* **Figure 4.1.12b**), a value of 13% was calculated. The latter shows that even the actual crystal surface exhibits a general roughness difference in concave and convex areas. However, regarding the preliminary findings of very active convex areas and both less and more active concave regions, the small value for Δ FWHM of 7% for 'HER' is not surprising: This circumstance might originate from the much larger height of the noise peaks compared to the general surface roughness. In other words, the local surface unevenness on active sites gets superimposed by the noise peaks when the STM tip scans the sample at reaction conditions. Since the

electrochemical-induced noise is expected to be white noise, the average tunneling current captured on active concave or active convex sites will not differ.

Consequently, in the hypothetical case that the entire surface would be similarly active, the value for ΔFWHM would diverge towards zero. Thus, the reason for the non-zero value of 7% might therefore lie in the sometimes active and sometimes inactive concave areas. However, this value might vary depending on the number of the less active concave regions within the selected section used for the evaluation. From this point of view and regarding the relatively low value for ΔFWHM of 7%, it is nevertheless reasonable to classify the surface of $\text{Pd}(111)_c$ as predominantly active.

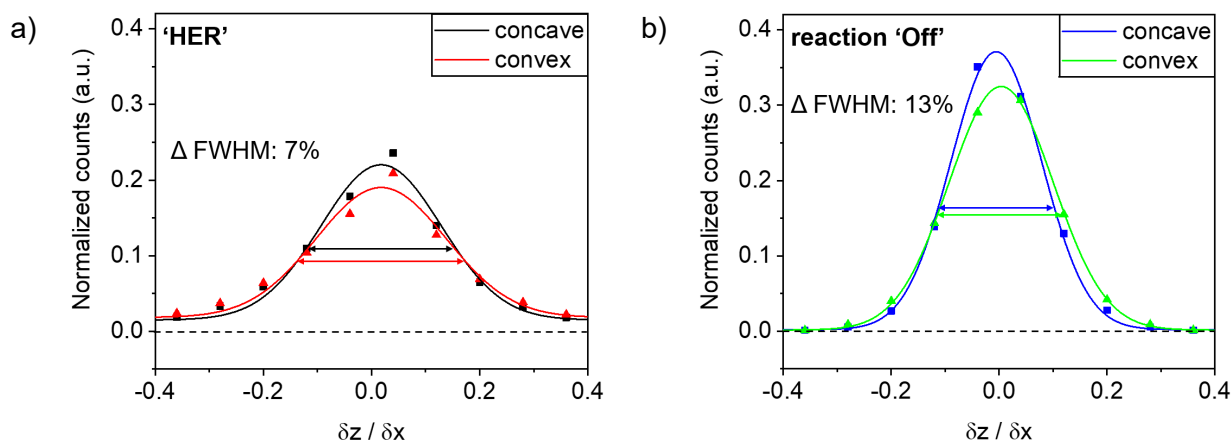


Figure 4.1.12. Noise analysis comparing the FWHMs of the concave and convex structures for **a)** 'HER' and **b)** reaction 'Off'. As elucidated in **Subchapter 3.4.2**, a higher distribution of the derived slopes results in a broader FWHM and lower amplitude, thus indicating a higher local roughness. Since electrochemical noise is expected to be white noise for areas captured under reaction conditions, this type of analysis is a measure of the activity. Moreover, for this reason, all graphs are approximated by Gaussian fits. Data of both figures published in reference ^[175].

4.1.3.2 Annealed and Cycled Pd(100)

Analogous to the measurements on freshly annealed Pd, this subchapter presents the results on cycled Pd(100), termed $\text{Pd}(100)_c$. Similar to $\text{Pd}(111)_c$, a hilly morphology covers the entire crystal surface on $\text{Pd}(100)_c$, as identified in the n-EC-STM measurement in **Figure 4.1.13a**. Visible in the upper and lower thirds of the image, captured under 'HER' conditions, significant noise peaks appear all over the surface. In the middle section for reaction 'Off', the noise disappears, revealing the hilly topography. As visible in the two-dimensional view in **Figure 4.1.13b**, in contrast to the freshly annealed Pd where step edges represented the most active sites, the noise on cycled

Pd(100) (Pd(100)_c) does not show a significant behavior on elevations. An additional n-EC-STM measurement presented in **Figure 4.1.13 A1** of **Appendix C** illustrates a large-scale measurement of a similar surface. Next to a similar hilly surface, here, multiatomic steps of several nanometers are visible, showing no outstanding noise behavior. Moreover, as discussed in **Figure 4.1.13 A2** (**Appendix C**), the dimensions of the hilly structure on Pd(100)_c with a diameter between 10nm to 25nm and height up to 1nm resemble those on Pd(111)_c. Also, from the first impression of these pictures, the convex structures seem to be more active than the concave ones.

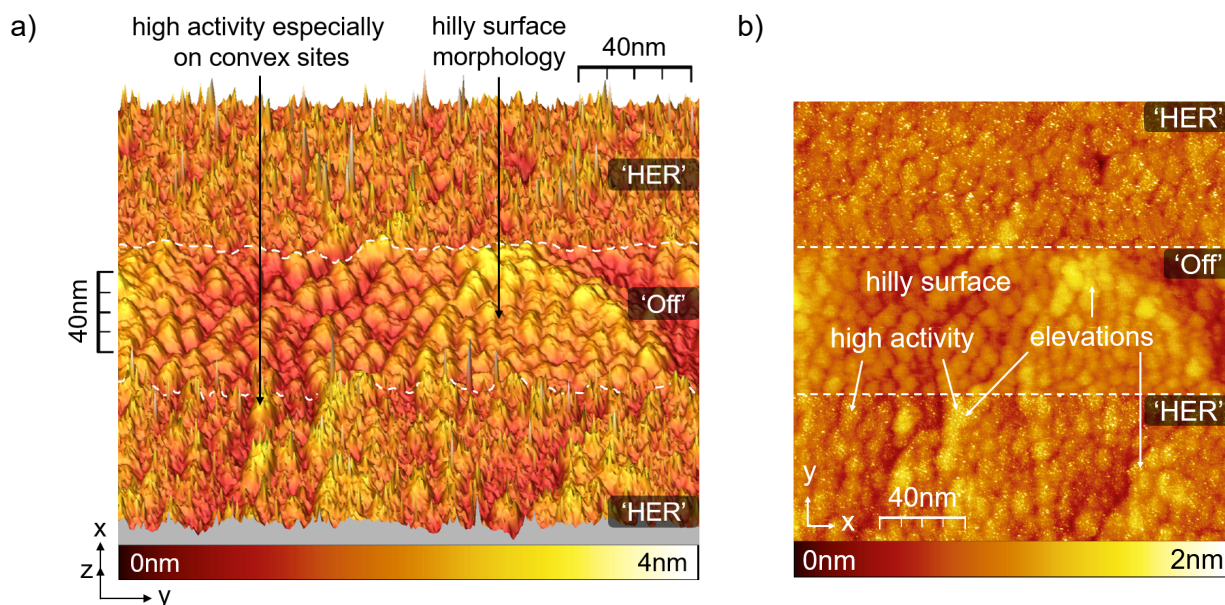


Figure 4.1.13. n-EC-STM measurement of Pd(111)_c captured in air-saturated 0.1M HClO₄. **a)** and **b)** demonstrate the identical image in three-dimensional and two-dimensional perspectives, respectively. White dashed lines separate the 'HER' regions in the image's upper and lower thirds, showing significant activity. The middle section images the hilly surface for reaction 'Off'. At the elevated hills, no exceptional noise is visible. Data of both figures published in reference ^[175].

This suspicion is substantiated by examining **Figure 4.1.14**, which presents an analogous separation of concave and convex areas as illustrated in **Figure 4.1.11** for Pd(111)_c. Here, the blue-colored concave regions clearly differentiate from the orange-red-tinged convex structures. The solid white dashed line separates the upper half of the image, presenting the surface under 'HER' conditions and the lower one for reaction 'Off'. Interestingly, the concave region screens

only small sections that exhibit white peaks and, therefore, a high noise level. In contrast, many white dots cover most of the convex region.

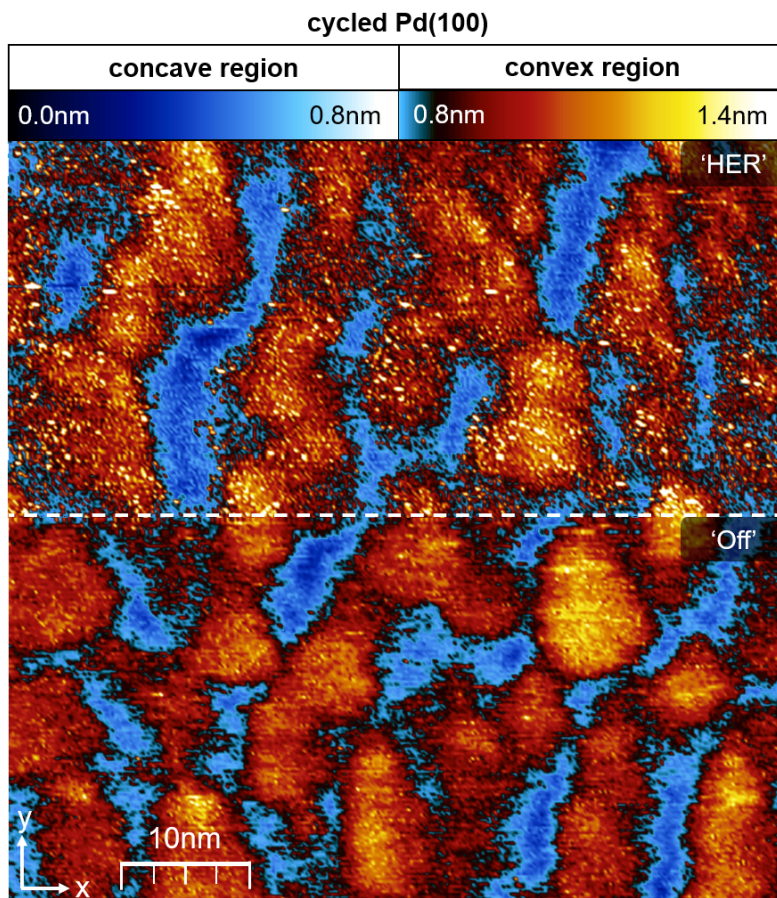


Figure 4.1.14. Recolored *n*-EC-STM measurement recorded in air-saturated 0.1M HClO₄, displaying the concave and convex regions in different colors. Here, analogous to **Figure 4.1.11**, the customized color bars highlight significant noise peaks as white dots in both areas. Notably, even for 'HER' in the upper half of the image, the blue-tinged areas barely exhibit noise features. In contrast, the convex orange-red colored regions appear to be very active. The individual areas, separated by the WSxM tool "flooding", are shown in **Figure 4.1.14 A1** and **Figure 4.1.14 A2** for 'HER' and reaction 'Off', respectively. In addition, it is important to note that this image was FFT-filtered using WSxM 5.0 Develop 9.4, as demonstrated in **Figure 4.1.14 A3** ^[261]. Data published in reference ^[175].

The subsequent noise analysis presented in **Figure 4.1.15** underlines this initial observation. The comparison of the concave and convex areas under reaction conditions (*cf.* **Figure 4.1.15a**) revealed a discrepancy of approximately 27%. As mentioned before, due to the extent of the noise peaks' heights relative to the surface's roughness, a value close to zero for $\Delta FWHM$ would be

expected for a hypothetical entirely active surface. Consequently, the substantial value of 27% indicates a significant increased activity on convex structures.

Furthermore, analogous to the investigations on Pd(111)_c, the concave areas on Pd(100)_c exhibit less surface roughness than convex ones even for reaction 'Off', as visualized in **Figure 4.1.15b**. Here, $\Delta FWHM$ is about 18%, indicating a substantially larger roughness on convex regions even for reaction 'Off'. Due to the challenge of resolving the Pd surface at room temperature in high resolution, one could only speculate about the origin of this discrepancy detected on both crystal facets.

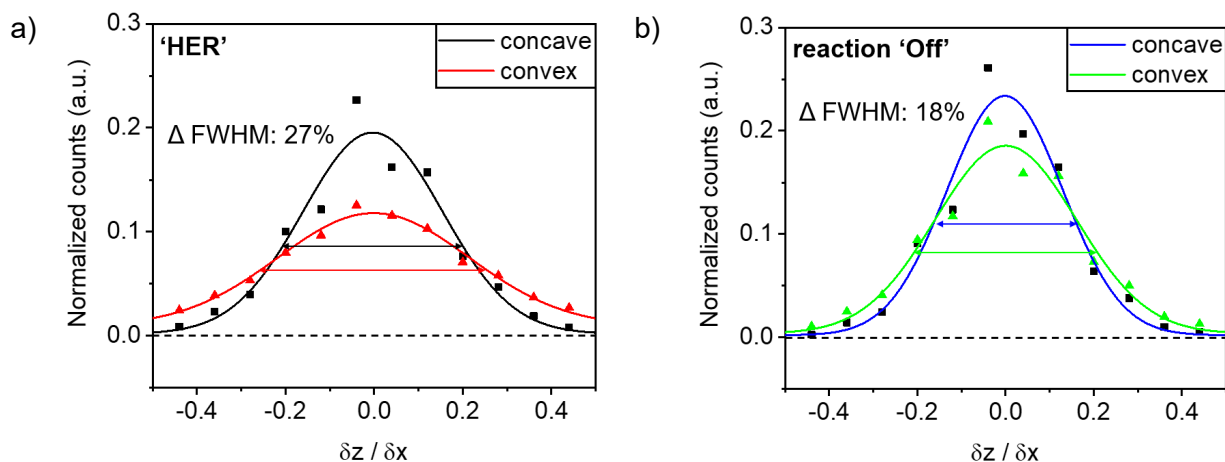


Figure 4.1.15. Noise analysis on Pd(100)_c representing the discrepancies in FWHM between the concave and convex structures for **a)** 'HER' and **b)** reaction 'Off'. For 'HER', the lower amplitude and the much higher FWHM for convex sites, which explain the relatively high value of 27% for $\Delta FWHM$, indicate a significantly increased activity on convex structures in comparison to concave ones. The individual FWHM values for the Pd evaluation are provided in **Table A4.3** in **Appendix B**. Data of both figures published in reference ^[175].

4.1.3.3 DFT Discussion and the Impact of Compressive Strain

As discussed in **Subchapter 2.3.4** and reference ^[175], the initial computational investigations indicated an increase in volume caused by H-absorption. The accompanying DFT calculations show that this additional space demand results in compressive strain and is expected to occur from the additional space required to form PdH within the spatially limited crystal lattice. Consequently, after the relaxation of the crystal, the surface might form a similar hilly surface as seen before in the STM measurements on cycled single crystals. Based on these considerations, the DFT calculations investigated the influence of H-absorption on the Pd(111), Pd(100), Pd(110),

and Pd(211) single crystals, as visible in **Figure 4.1.16a, b, c, and d**, respectively. It was found that this compressive areal strain further lowers the absolute value of ΔG_{H} for higher numbers of formed PdH sublayers, thus increasing the HER activity according to the Sabatier principle (see **Subchapter 2.1.4**). The correlation between strain effects caused by hydrogen absorption in Pd and an increasing HER activity is also well known in the literature ^[44]. It is important to note that the absolute values for ΔG_{H^+} and the relative value for the compression of the lattice correlate with the number of PdH sublayers. Next to the outstanding small absolute values of Pd(111) and Pd(211) for ΔG_{H^+} , these crystal facets also reveal the highest compressive strain for higher PdH contents. As illustrated in the volcano plot in **Figure 4.1.9 A1 (Appendix C)**, Pd(211) might have a slightly better HER performance than Pd(111). In contrast, Pd(100), which indicated only a minor increase in ΔG_{H^+} , also has a much lower compressive strain gain than the other crystallographic planes and thus ranks lowest in terms of HER activity for higher H loading.

Furthermore, a possible quantum chemical explanation was suggested, which also begins with the idea that H and Pd form PdH after H intercalation into the Pd crystal. Caused by the resulting compressive strain, the d-orbitals of the Pd atoms within the lattice get forced to overlap with the ones of their neighbors. As a result, the adsorbing H atoms tend to bind to a greater extent in H-s–Pd-d antibonding orbitals, where they are only weakly bound to the Pd atoms. This circumstance leads to a lower absolute value of ΔG_{H^+} for higher numbers of PdH sublayers within the Pd crystal surface, which predicts an increased HER activity after H-absorption.

However, the DFT investigations did not include any relaxation processes in their model, which, in reality, would likely occur after H-absorption. Thus, it is plausible that, when exceeding a specific strain threshold, the surface would locally bend under the burden of the strain, hence creating a hilly structure as observed in the STM experiments. In this case, the concave regions would be subjected to compressive stress, while the convex areas would be under tensile strain. As a result, the distances between the Pd atoms might slightly change according to the corresponding forces. On the one hand, next to the occurrence of a hilly morphology after relaxation, the potentially modified electrochemical properties might also explain the diverse noise behaviors observed by STM on concave regions on Pd(111)_c and Pd(100)_c.

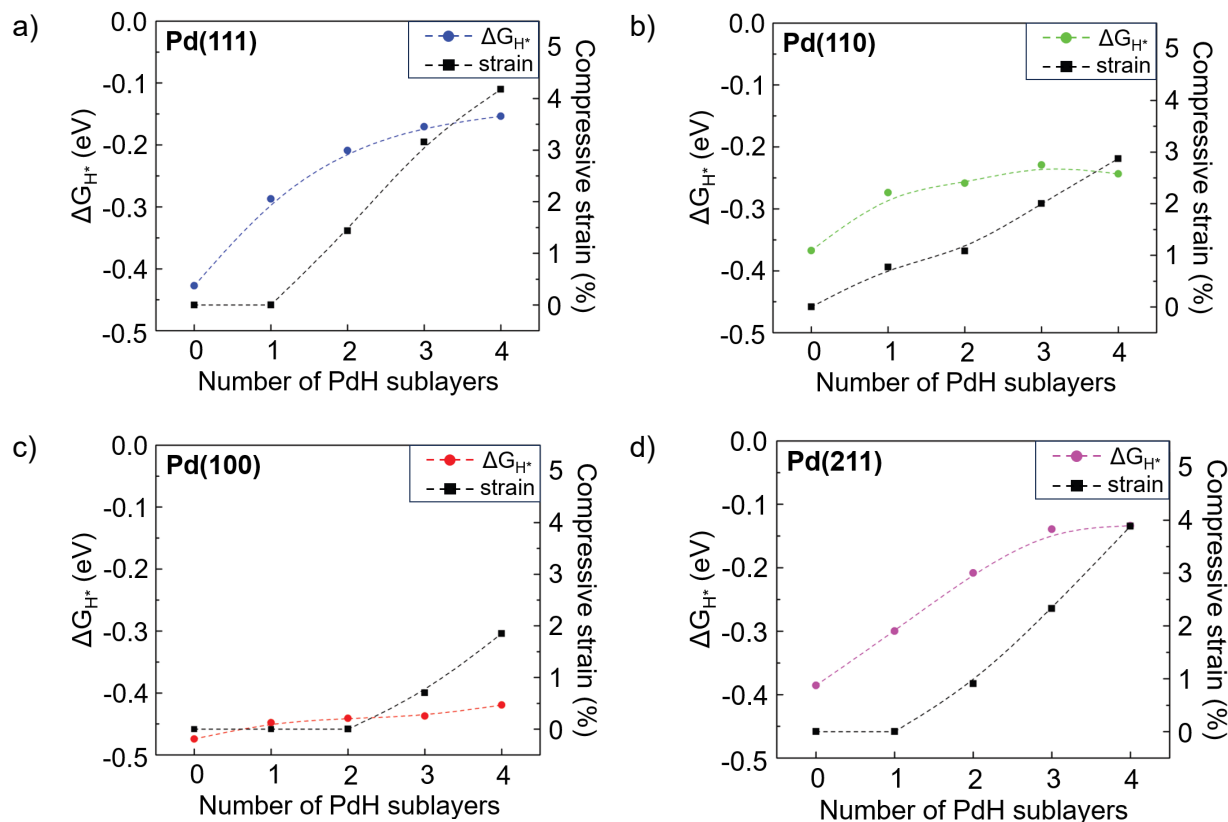


Figure 4.1.16. Computationally determined correlation between the change in Gibbs free energy (colored) and the compressive strain (black) caused by H-absorption for different numbers of PdH top sublayers. **a)**, **b)**, **c)**, and **d)** show this depending on Pd (111), Pd(110), Pd(100), and Pd(211), respectively. A trend towards increased activity and strain is visible for all single crystal facets with rising numbers of PdH sublayers. Images adapted from reference ^[175] and licensed under CC BY 4.0 ^[87].

On the other hand, it is plausible that a significant bending might create defects in the crystal surface at convex curved regions. As a result, if multiple very thin ditches cover the surface, it is evident that the STM signal would also detect a slightly higher roughness in these areas. This circumstance might explain the high values for $\Delta FWHM$ of 13% and 18% found in the STM measurements for reaction 'Off' on Pd(111)_c and Pd(100)_c, respectively (cf. **Figure 4.1.12b** and **Figure 4.1.15b**). However, to verify this hypothesis, high-resolution images of the convex areas would be required, which prove or disprove the presence of such ditches. Since experience shows that reaching an atomic resolution on single crystalline Pd is unattainable at room temperature, a future project could involve STM investigations on electrochemical cycled Pd in a vacuum at temperatures close to 0K.

4.1.4 Summary and Prospects

The findings presented in this chapter comprise combined experimental and theoretical insights into the processes occurring on Pd single crystals during HER in 0.1M HClO₄, as shown in the final publication ^[175]. All applied experimental and theoretical approaches individually identified the Pd(111) crystal facet as the most active among Pd(111), Pd(110), and Pd(100). Moreover, the DFT investigations state that Pd(211) has similar high activity as Pd(111) after forming a minimum of two Pd sublayers after hydrogen absorption. Regarding the step-like characteristic of the Pd(211) crystallographic facet, this insight agrees with the STM experiments on atomically flat Pd single crystals. These measurements revealed outstanding activity on the upper step edges on freshly annealed single crystalline Pd(111). However, some Pd(111) steps showcased a lack of activity in certain sections, while others were completely inactive. Apart from the hypothesis that unsuitable GCN could cause this low activity on several step sites, neither the STM nor the DFT investigations have located the origin of this phenomenon. In contrast, during the STM experiments on atomically flat single crystalline Pd(100), the noise on the steps was more sporadic but frequent, which might explain its lower overall activity observed in the CV experiments.

Furthermore, the DFT calculations identified a considerable compressive strain induced by PdH-formation within the subsurface of the bulk after hydrogen absorption, which enhances the crystals' activity. A presumable resulting surface relaxation might cause the experimentally observed hilly morphology on Pd(111)_c and Pd(100)_c after electrochemical cycling. In addition, the n-EC-STM experiments on both samples revealed a change in noise behavior away from the outstanding activity on step edges towards an overall active surface. However, the reason for the lower activity of concave regions on Pd(100)_c compared to convex ones found in these measurements remains unclear and requires further examination. In contrast, on Pd(111)_c, the concave and convex areas are roughly similar active. Apart from these findings, an increased roughness was determined on both crystals in the convex-shaped areas for reaction 'Off'. An explanation for this circumstance might provide the presence of defects created by bending the surface due to the compressive strain. This phenomenon of Pd cracking when interacting with hydrogen is also known from Pd sensors and is described in the literature ^[38,272–274]. However, further high-resolution investigations of the surface before and after hydrogen absorption are necessary to verify this hypothesis.

Based on these findings, a potential nanoparticle containing a high ratio of Pd(211) and Pd(111) crystal facets was designed, as illustrated in **Figure 4.1.17**. Regarding its extent between 6.7nm to 7.0nm, which approximately complies with the smallest diameters of hills found on Pd(111)_c and

Pd(100)_c during the STM experiments, it is likely that strain effects do not play a crucial role on this particle. Nevertheless, the proposed nanoparticle might feature a significant electrochemical activity even without the assumed activity boost due to surface strain. Thus, this particle would be a promising candidate for future electrochemical surface studies with Pd-based nanomaterials.

Due to the ability of Pd to absorb hydrogen and its resulting complexity as a HER catalyst, its study poses a great challenge, making it beyond the scope of this work to uncover all the details of the processes involved. However, precisely this wealth of capabilities and unexplored interrelationships make Pd such an interesting HER material and hold significant potential for further discoveries and future applications.

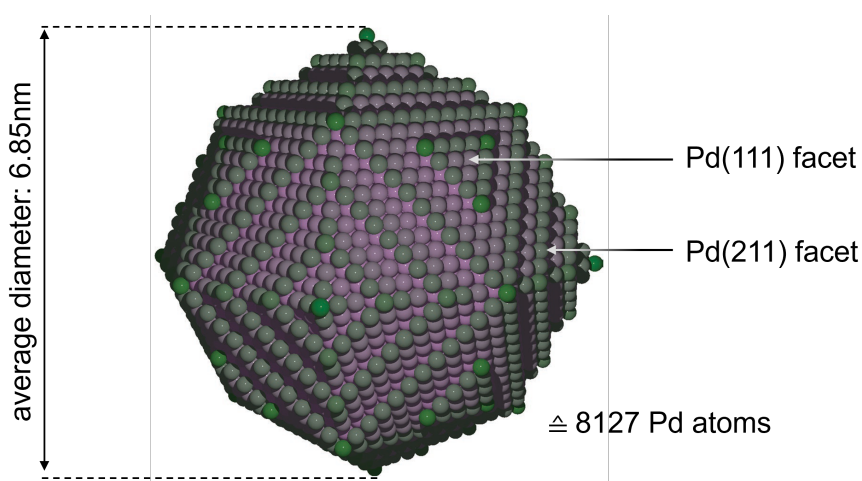


Figure 4.1.17. Modeled nanoparticle with large areas of Pd(211) and Pd(111) crystal facets consisting of 8127 Pd atoms. The individual colors indicate atoms with identical GCNs. This example particle is assumed to have a high HER activity based on the findings from the collaborative project. Adapted from reference ^[175] and licensed under CC BY 4.0 ^[87].

4.2 MnO₂NS/HOPG Investigations

This chapter deals with the state-of-the-art catalyst material MnO₂NS/HOPG, which consists of MnO₂ nanosheets synthesized on a flat HOPG support. It will be shown that even HOPG with poor electrochemical activity can reach notable OER activity when it is combined with a suitable hybrid material. The presented findings build an excellent basis for seeking novel electrocatalysts consisting of common elements. On the investigated MnO₂NS/HOPG sample, schematically illustrated in **Figure 4.2.1**, most of the surface consists of pure HOPG terraces, separated by single and multiple atomic steps with a length of several hundreds of micrometers. Scattered MnO₂ nanosheets with a diameter of several hundred nanometers are located on top of these terraces.

As already mentioned in the introduction, the idea of performing the oxygen evolution on these elements is not new. In nature, the Mn-based oxygen-evolving complex of PS II in leaves is essential in producing atmospheric oxygen. More precisely, the water oxidizes on the Mn₄CaO₅ cluster during organic photosynthesis. The working principle of this biological catalyst is still not completely understood ^[275]. However, significant progress has been made in recent decades, demonstrating the natural version's high potential. ^[66,276,277] For this reason, there is a great effort to investigate novel electrocatalysts based on the natural blueprint, such as MnO_x-based systems. ^[278,279]

With this in mind, it is engaging to investigate the processes taking place on the much simpler but related sample material MnO₂NS/HOPG. Electrochemical approaches and in-EC-STM measurements, in combination with theoretical considerations, elucidate the processes taking place during the OER on this material. The first subchapters provide a detailed overview of the catalyst's electrochemical properties and the surface's morphology in an air environment. Moreover, the findings gained are underpinned by investigations on pure HOPG and clearly showcase the improvements made by additionally synthesizing MnO₂NS. Subsequent STM measurements in 0.1M KOH electrolyte show the actual nature of active sites and clarify the origin of the sample's increased activity.

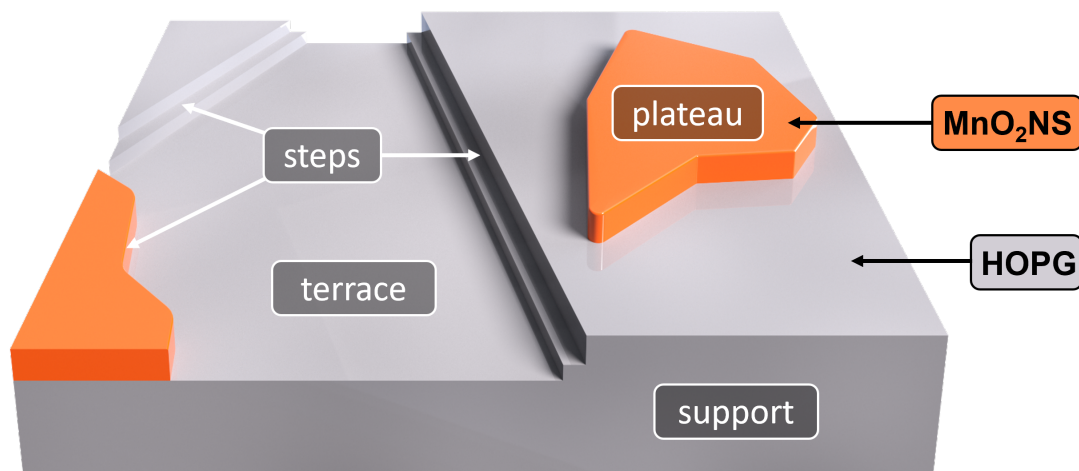


Figure 4.2.1. Schematic model of the $\text{MnO}_2\text{NS}/\text{HOPG}$ surface. The grey HOPG, with its characteristic flat terraces and long steps of different heights, builds the carbon basis of the sample. Its synergies with the orange-colored MnO_2NS are the focus of this investigation. The model surface was designed by Leon Haase. Inspired by ^[213].

Furthermore, in collaboration with André Wark under the lead of Prof. Egill Skúlason at the University of Iceland (Faculty of Chemical Engineering, Mechanical Engineering and Computer Science), which calculated the detailed reaction pathways on different positions on the sample using DFT, new impressions beyond the limits of STM enlighten the STM results from a new perspective. Thus, the final analysis in this chapter is based on the following publications:

- Schmidt T.O.,⁽⁺⁾ Wark A.,⁽⁺⁾ Haid R.W., Kluge R.M., Suzuki S., Kamiya K., Bandarenka A.S.*, Maruyama J.*, Skúlason E.* *Elucidating the active sites and synergies in water splitting on manganese oxide nanosheets on graphite support*. *Advanced Energy Materials* **2023**, 13, 2302039.
- Haid R.W.,⁽⁺⁾ Kluge R.M.,⁽⁺⁾ Schmidt T.O., Bandarenka A.S. *In-situ detection of active sites for carbon-based bifunctional oxygen reduction and evolution catalysis*. *Electrochimica Acta* **2021**, 382, 138285.
- Wark A.,⁽⁺⁾ Schmidt T.O.,⁽⁺⁾ Haid R.W., Kluge R.M., Suzuki S., Siroma Z., Skúlason E.*, Bandarenka A.S.*, Maruyama J.*, *The role of manganese oxide nanosheets in pyrolyzed carbonaceous supports for water oxidation (submitted)*

4.2.1 General Investigations

To achieve unbiased results, before the n-EC-STM measurements, the untreated sample was analyzed electrochemically and morphologically. The collected preparatory findings and considerations presented in the published manuscript allow a comparison to the original state of the sample at any time during the investigation process ^[213]. Moreover, as demonstrated in the following subchapters, they provide a first insight into the sample's characteristics, such as roughness, repeating structures, and the size and shape of the nanosheets.

4.2.1.1 HOPG as Support Material

A previous study investigated the electrochemical properties and noise behavior of pristine HOPG in 0.1M KOH ^[118]. As presented in **Figure 4.2.2a**, the CV measurements with a scan rate of 50mV·s⁻¹ show a low current at a potential of 0mV versus a Pt QRE electrode, which was used as reaction 'Off'. Furthermore, the waterfall plot in **Figure 4.2.2b** showcases representative extracts for different ORR and OER potentials on the example of a 2nm step edge, which roughly corresponds to 6 graphene layers of approximately 0.34nm each ^[242]. Interestingly, the terrace shows significant activity for increasing OER potentials as well. As discussed in **Subchapter 3.3.3**, the correlation between the first occurrence of the noise on specific structures and the set potential must be treated very carefully due to the measurement session-specific gain settings and tip properties. Nevertheless, these measurements clearly demonstrate the activity trend, revealing the most active sites on step edges for ORR and OER, followed by the terrace for OER at higher potentials.

It is important to note that this prominent noise on step edges occurred on a step of several graphene layers and could be less pronounced on single ones, as shown in **Figure 4.2.2c**. This image captured in 0.1M KOH for a potential of 600mV versus Pt showcases a sheet-like HOPG structure with a two-layered (I) and a single-layered (II) step on the left side. In contrast, both two steps on the right side (III and IV) are single-layered. The missing single atomic step might be underneath the sheet, which could be surmised by an elevated stripe in the upper left part on top of the sheet. While the right-sided steps III and IV demonstrate exceptional noise compared to the terraces, the bottom side of step II from the left side does not show this pronounced behavior despite all these steps being single HOPG layers.

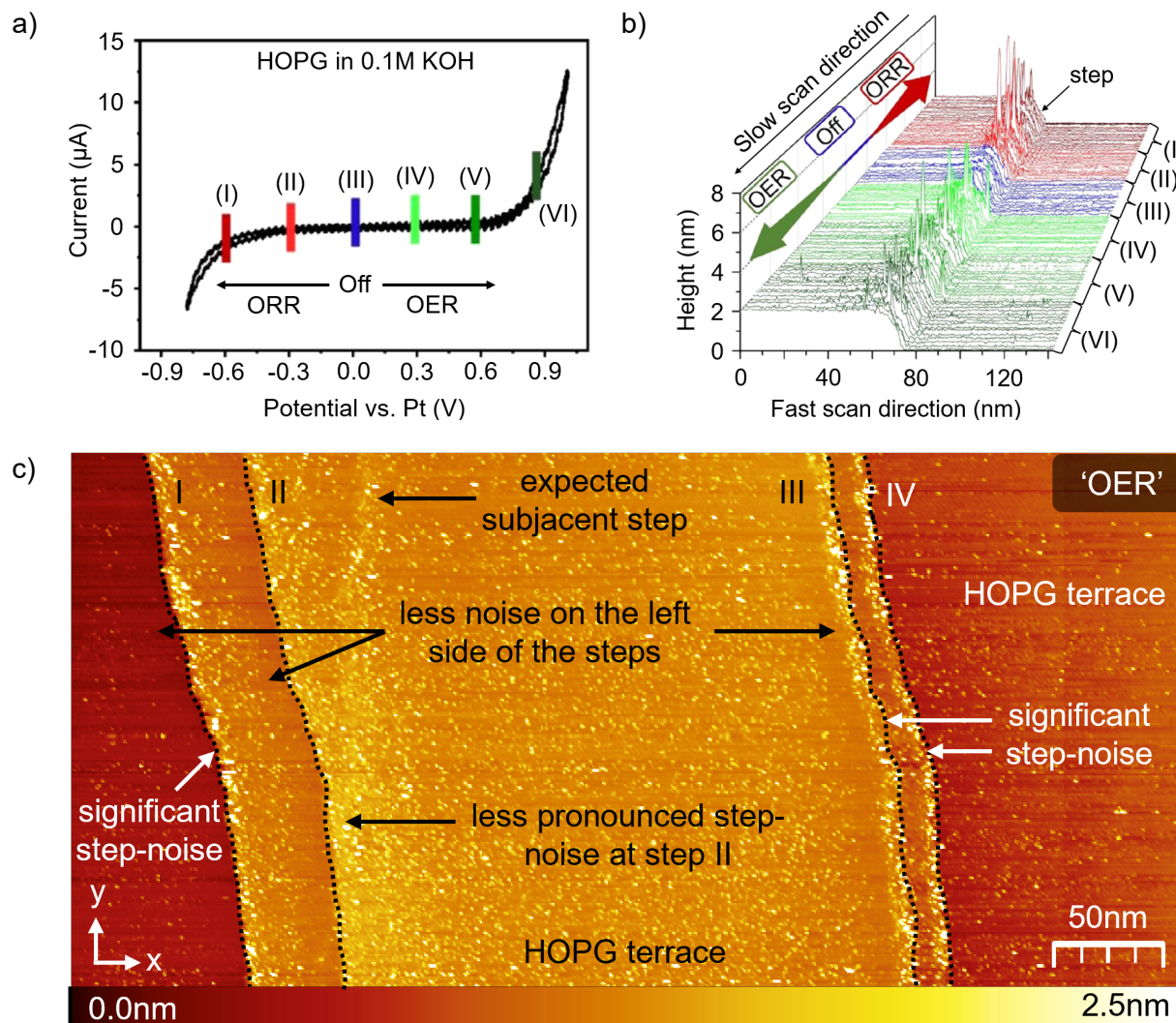


Figure 4.2.2. Electrochemical activity investigation on pristine HOPG in 0.1M KOH. **a)** CV measurement showing the positions of the applied potentials shown in **b)**. **b)** Waterfall plot illustrating the noise behavior for different ORR and OER potentials. **c)** n-EC-STM measurement captured at 600mV versus Pt. The outstanding noise on the step edges reveals it as the most active site, followed by the terrace. It is important to note that the second step from the left (II) does not reveal this exceptional noise on the bottom side but indicates a similar activity as the terraces. Figures **a)** and **b)** are adapted with permission from reference ^[118]. Copyright 2021 Elsevier Ltd, all rights reserved. Data of **c)** published in reference ^[118].

A possible reason for this might be a timing-dependent circumstance in combination with specific gain settings similar to the observations on Pd(100) in **Subchapter 4.1.2.2**: Due to the high scanning velocity of about one $\mu\text{m}\cdot\text{s}^{-1}$ during the measurement, the STM tip only records a short

time window on each sample position. In other words, it represents a unique moment. Consequently, since chemical reactions appear randomly on specific sites, there is a probability that a locally decreased disturbance of the tunneling barrier occurs during scanning. Thus, the tip does not retract as far as expected on the edge site, even though an above-average number of chemical reactions occur at this location. At specific gain values, it is therefore conceivable that the threshold for a prominent tip retraction is not exceeded, and consequently, a comparable noise behavior as on the terrace appears.

Another possible explanation for the lower noise behavior on the single-layered step II could be that the expected presence of the subjacent step close to the step edge coincidentally results in a local GCN, which might be relatively unfavorable for the reaction kinetics. However, due to insufficient data from such combinations, verifying or refuting this hypothesis is unfeasible and could be a topic of subsequent research projects.

However, this measurement on HOPG in 0.1M KOH for 600mV versus Pt localizes the main active sites on the step edges, with a lower activity on the terraces. At the same time, under unknown circumstances, the step edges at pure HOPG exhibit a comparable noise behavior to that of the terraces, which agrees with the measurements on the support material of the MnO₂NS/HOPG sample as shown below (*cf.* **Subchapter 4.2.2.1**).

4.2.1.2 Morphologic Initial Investigations

Since the impact of electrochemical reactions on the sample morphology is not clear before the measurement, it is crucial to have a comparison of the inert sample surface in case of inconsistencies. To identify unexpected processes, such as a dissolution of the nanosheets by, e.g., water presence, and to verify the surface quality measurements in air were performed before the n-EC-STM experiments.

In the first preliminary STM investigation, the sample was found to be composed mainly of pristine HOPG with rarely scattered MnO₂NS on top. This circumstance complicated the detection of nanosheets and made a successful recording of an n-EC-STM image at the MnO₂NS-HOPG interface challenging. Nevertheless, a significant advantage of a low MnO₂ coverage is that the probability of accumulating several nanosheets is also relatively low. In the case of stacked nanosheets, besides the limited measuring height of STM, it is challenging to distinguish between the stepped support material and one of the actual nanostructures. Consequently, detecting a single sheet lying freely on the support material is similarly demanding as finding one when the

MnO₂ coverage is very low. Therefore, medium to small nanosheet coverage yields the optimum coverage for the investigations of hybrid materials.

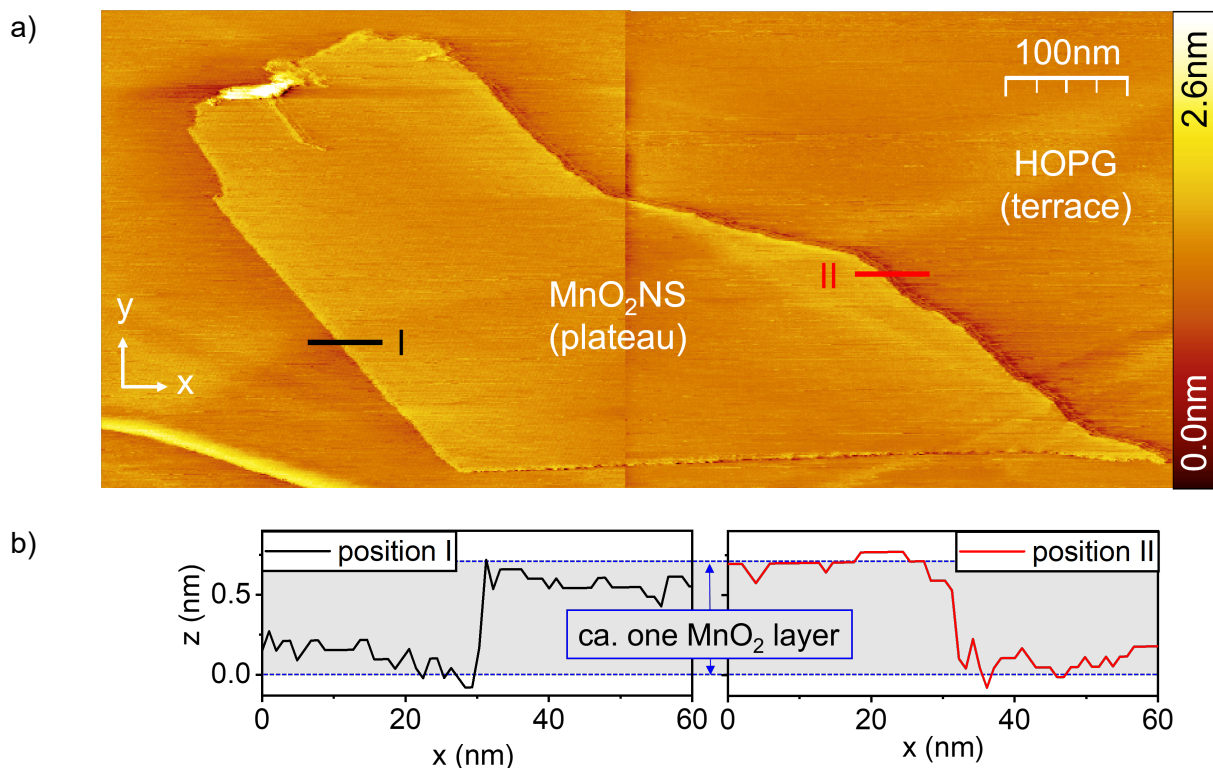


Figure 4.2.3. Initial investigation of MnO₂NS/HOPG in air atmosphere before the electrochemical experiments. **a)** The overview-STM image was merged out of two individual measurements. The extension and atypical shape for HOPG indicate MnO₂ as the sheet material on an HOPG support. **b)** The line scans representing the morphology of the sheet edges at positions I and II reveal a rough height of about 0.7nm, corresponding to the theoretical height of a single-layered MnO₂NS^[280]. Data of both figures published in reference^[213].

Figure 4.2.3a shows an STM measurement on MnO₂NS/HOPG captured in an air atmosphere and assembled from two subsequent measurements. The captured nanosheet has a length of approximately 800nm and a diameter of about 250nm. The two line scans illustrated in **Figure 4.2.3b** show the height profile at the edge positions I and II. Here, the grey area represents a nanosheet layer's height of 0.7nm, as stated in other literature, and agrees well with the observed line scans^[280,281]. This height agrees with the step altitude of the detected sheet on both sides. Along with the fact that the detected structure forms a protruding surface of several hundreds of nm, these findings indicate MnO₂ as the sheet material.^[280] In contrast, experience

shows that HOPG typically shapes large atomically flat terraces separated by steps of different heights with a length of several micrometers. From the preliminary investigations on MnO₂NS/HOPG, this HOPG-like morphology was visible at the large and flat surface beneath the sheet. However, since STM generally does not provide information about the captured material composition, in this case, a reliable element-specific assignment is not possible without further investigation.

4.2.1.3 Electrochemical Initial Investigations

As part of this collaborative project, Jun Maruyama from the Research Division of Environmental Technology (Osaka Research Institute of Industrial Science and Technology, Japan) performed the first electrochemical investigations on MnO₂NS/HOPG in Ar-saturated 0.1M KOH using an electrochemical analyzer (660B, ALS) (*cf.* **Table A4.2**)^[213]. The results show that compared to pure HOPG, the observed potential sweep presented for MnO₂NS/HOPG in **Figure 4.2.4a** reveals a significantly more substantial current increase within the OER region. Its exponential rise starts approximately at 1.6V versus RHE (red curve) and shows faster growth than pure HOPG (black curve). Consequently, it demonstrates an enhanced activity caused by the presence of MnO₂. In addition, compared to other OER catalysts, such as IrO₂ or RuO₂, this graph demonstrates the relatively poor catalytic OER activity of pristine HOPG^[245,246].

The same activity trend was detected at the subsequent anodic potential sweeps using the EC-STM universal bipotentiostat with a scan rate of 50mV·s⁻¹, shown in **Figure 4.2.4b**. As elucidated in **Subchapter 3.3.2**, direct comparison of the individual graphs at specific potentials is challenging due to possible daily potential shifts caused by the Pt QRE. Nevertheless, the plot shows similar current-voltage behavior for MnO₂NS/HOPG (black) compared to pure HOPG (red), as observed in the electrochemical analyzer: Similar as for potentials lower than 1.6V in **Figure 4.2.4a**, here, a comparably increased slope is visible at the linear interval for potentials lower than 500mV. In addition, the OER current rise is much more pronounced for higher potentials in the exponential region compared to pure HOPG, analogous to the measurements captured using the electrochemical analyzer. Consequently, despite concerns about the stability of the Pt QRE, the potential sweep measurements clearly verify the presence of MnO₂ on the sample just before the n-EC-STM experiments.

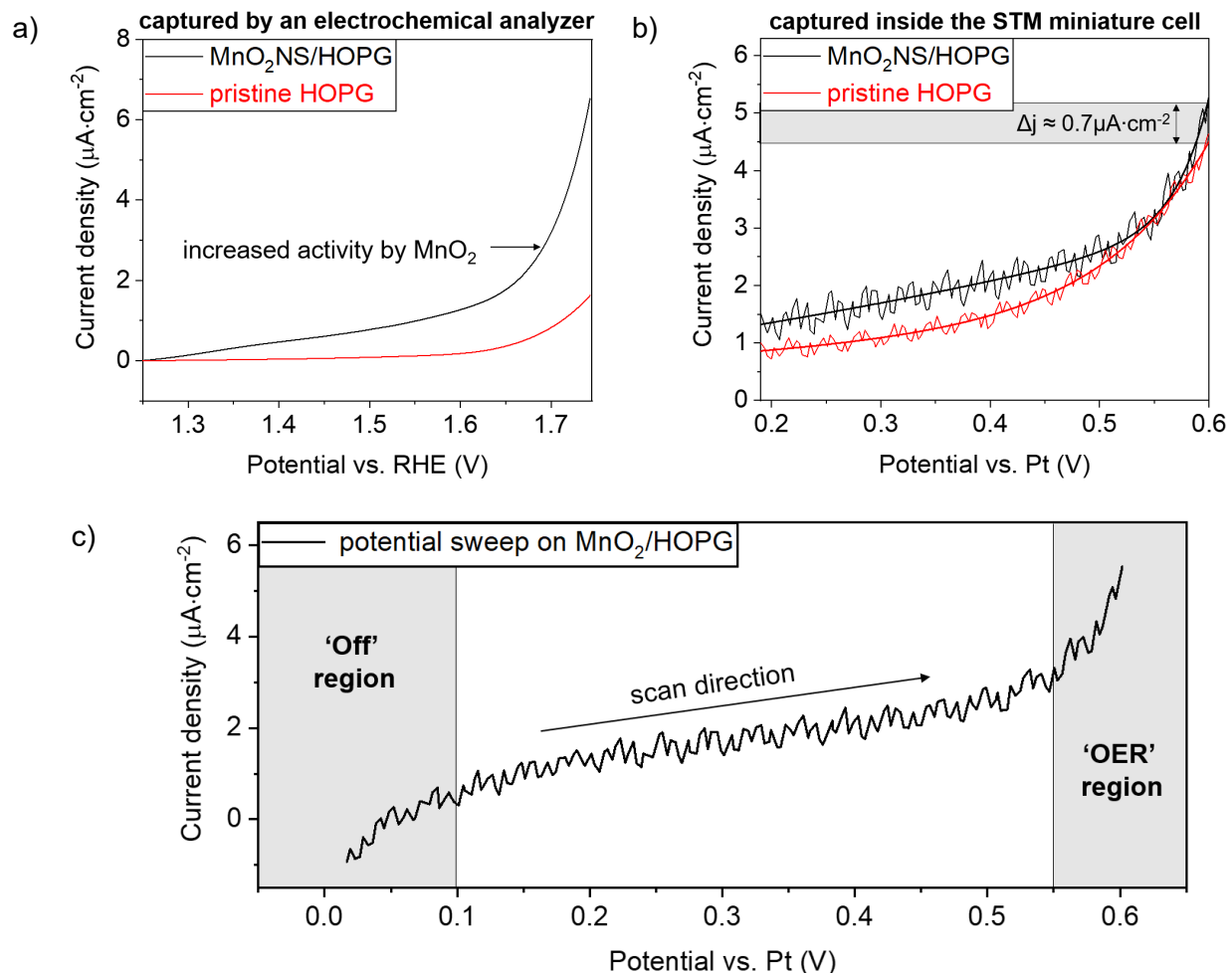


Figure 4.2.4. Voltammetry measurements on MnO₂NS/HOPG and pure HOPG in 0.1M KOH. **a)** Linear potential sweeps, captured by an electrochemical analyzer against a Hg/HgO (0.1M KOH) RE in combination with a carbon CE (EC-CC1-060T, ElectroChem) in Ar-saturated 0.1M KOH (Ultrapur, Kanto Chemical). The measurements were captured for a scan rate of $10\text{mV}\cdot\text{s}^{-1}$ at room temperature. **b)** Comparison of positive potential sweeps for MnO₂NS/HOPG and pristine HOPG using the multimode's universal bipotentiostat and a scan rate of $50\text{mV}\cdot\text{s}^{-1}$ in air-saturated 0.1M KOH, verifying the presence of MnO₂ on the sample. **c)** Analogous measurement to b, captured directly before the measurements within the EC-STM cell, representing the potential ranges for 'OER' and reaction 'Off'. Data of a) and the pristine HOPG curve in b) published in reference ^[213], representation of b) and c) inspired by reference ^[213].

Furthermore, the voltammetry measurement in **Figure 4.2.4c**, also captured at a scan rate of $50\text{mV}\cdot\text{s}^{-1}$, provides information about the expected appropriate potential ranges for the n-EC-STM measurements. Here, the anodic potential sweep reveals a significant current increase at potentials higher than 600mV versus Pt. In contrast, a minimum current is achieved for potentials

close to 50mV versus Pt. Keeping this in mind and combined with a substantial noise behavior during the n-EC-STM measurements at 600mV versus Pt, which completely vanished at 0mV versus Pt, these potentials were selected for 'OER' and reaction 'Off', respectively.

4.2.2 Active Site Identification and n-EC-STM Measurements

At the subsequent n-EC-STM measurements in 0.1M KOH emphasized in the published manuscript, a MnO₂NS with a high electrochemical activity was detected and further analyzed ^[213]. For these measurements, the STM device's gain values were configured so that possible noise on the underlying structures was suppressed for 'OER' at 600mV versus Pt to highlight the most active sites. For reaction 'Off', a potential of 0mV versus Pt was selected, as discussed before. This subchapter discusses a detailed validation of MnO₂NS as the sheet material and HOPG as subjacent support, followed by stability considerations.

Despite the difficulty of finding the rare MnO₂NS on the HOPG support, a single-layered MnO₂NS was successfully detected by using n-EC-STM. The investigated part of the sheet has a length of 250nm and a rough width of about 50nm, as visible in **Figure 4.2.5a**. On the left side of the image, under 'OER' conditions, high noise features occur on the edges of the sheet. For better visibility, this image was filtered by using WSxM's FFT tool, as discussed in **Subchapter 3.4.1** and **Figure 4.2.5 A1** in **Appendix D**. Moreover, a slight roughness on the sheet's plateau appears while the surrounding HOPG terrace remains primarily inactive. For comparison, separated by a white dotted line, the reaction was switched 'Off' on the right side of the image. Here, all noise features vanish entirely due to appropriately selected gain settings. As represented by the left line scan for 'OER' in **Figure 4.2.5b**, huge noise peaks extend on the upper step edges of the sheet while the rest of the surface appears inactive. The line scan on the right shows the sheet, representing the sheet morphology. The detected sheet height of approximately 0.7nm corresponds to a single layer of MnO₂ (*cf.* **Subchapter 2.4.2**), thus providing a first indication of MnO₂ as sheet material ^[280]. Nevertheless, it is insufficient to define the nanosheet material only on this assumption since two layers of HOPG have a similar theoretical height of 0,68nm ^[242].

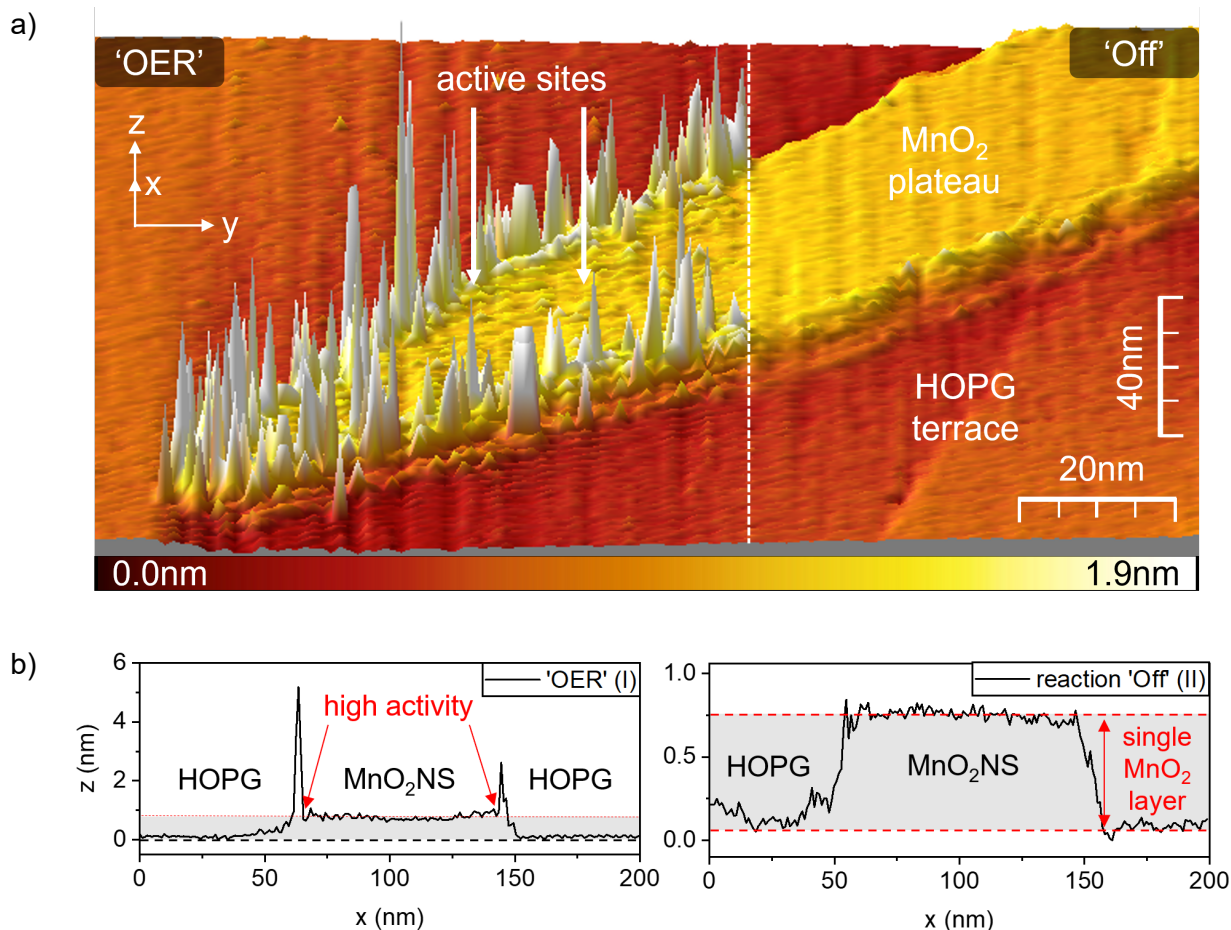


Figure 4.2.5. *n*-EC-STM measurement on $\text{MnO}_2\text{NS}/\text{HOPG}$ in 0.1M KOH. **a)** Three-dimensional view of an estimated MnO_2NS (yellow) with huge noise peaks (white) on the left half for 'OER'. The orange-red-colored underlying surface is supposed to be HOPG. **b)** Line scans for 'OER' and reaction 'Off'. The grey bar has a height of 0.7nm and represents a single layer of MnO_2 . The individual line scan positions are provided in **Figure 4.2.6a** as white solid lines (I and II). Data of both figures published in reference ^[213], representation inspired by reference ^[213].

4.2.2.1 Assignment of the Nanosheet Material

When performing *n*-EC-STM measurements on hybrid materials, it is challenging to identify the observed surfaces. This difficulty results in STM being generally unsuitable for distinguishing between different substances. Nevertheless, under certain conditions, a classification is possible anyway. For example, crystalline surfaces could be assigned by investigating their atomic structure. Unfortunately, on most crystals, only experimental setups operating at ultralow temperatures under vacuum conditions could achieve such high resolution. However, this

approach is not applicable to measurements in aqueous electrolytes due to ice formation at low temperatures.

Despite the possibility of reaching atomic resolution on HOPG, as shown in **Figure 4.2.5 A2** in **Appendix D** and the literature, in this measurement session, it was impossible to distinguish the sheet and support material in this way ^[29,118,282,283]. After capturing the n-EC-STM images at this promising sample spot, the STM tip lost its ability to resolve the surface when operating in constant height mode, which is preferred to measure at atomic resolution. A reason for this might be a tip crash and the resulting decrease in quality. However, when using the n-EC-STM technique, the detected noise provides information about the local activity and, by comparing characteristic morphologies, enables a conclusion on the observed material.

Figure 4.2.6a presents the identical measurement as **Figure 4.2.5a** in a two-dimensional view. The white dotted line in the middle of the image marks the position where the potential was switched from 'OER' to the reaction 'Off'. The underlying principle to identify the sheet material is based on the different noise behaviors of individual materials and, thus, surface roughness variations. Therefore, the four highlighted positions (b1 to b4) on the yellow-colored sheet plateau and the red/orange-colored terrace for each, 'OER' and reaction 'Off', were compared. As discussed in **Subchapter 3.4.2**, the normalized counts of the slopes provide a measure for the local activity due to the Gaussian distribution of electrochemically produced noise. The characteristic peak shape and, thus, the intensity of the noise characterizes the FWHM. Consequently, when comparing two areas, one would expect a similar FWHM at positions within the same potential area of identical sheet materials. In contrast, different materials would result in a pronounced discrepancy between the observed noise behavior, thus indicating different materials. The upper graph in **Figure 4.2.6b** compares the NS plateau (b1) and the underlying surface (b2) under reaction conditions. Following **Equation (3)**, the deviation of the FWHM on these positions is about 47%, thus representing a significant difference. In contrast, for reaction 'Off' (b3 and b4) demonstrated in the graph below, a much lower Δ FWHM of about 3% is detected. These different Δ FWHM at varied potentials inevitably lead to an unequal noise behavior at the nanosheet plateau and the underlying surface, thus indicating different materials. Since the sample only consists of MnO₂ and HOPG and previous electrochemical considerations in **Subchapter 4.2.1.3**, stating that MnO₂ increases the activity, the sheet material could clearly be identified as MnO₂.

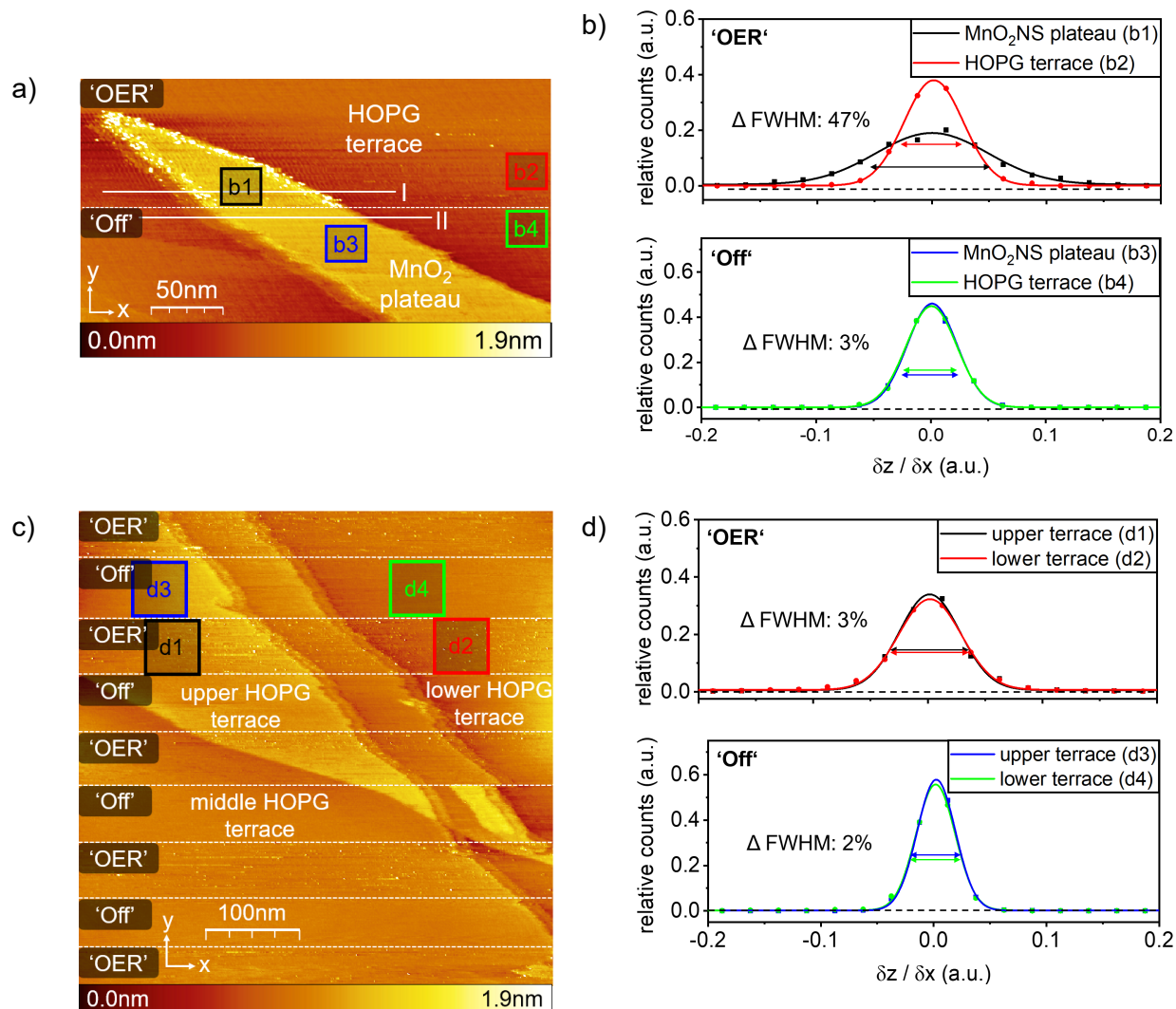


Figure 4.2.6. n-EC-STM measurements on different positions on MnO₂NS/HOPG captured in 0.1M KOH. **a)** MnO₂NS on an HOPG support for 'OER' and reaction 'Off' separated by a white dotted line. The solid white lines show the positions of the line scans illustrated in **Figure 4.2.5b**, while the framed regions represent the areas used for the subsequent analysis. **b)** Roughness analysis on selected areas marked in **a)**, indicating a different nanosheet material than the support material. **c), d)** Analogous analysis process as illustrated in **a)** and **b)** on the HOPG support, identifying the observed sheet material as pure HOPG. Data of **a)** and **c)** published in reference ^[213], representation of **b)** and **d)** inspired by ^[213].

For comparison, **Figure 4.2.6c** illustrates an example of a similar-looking nanosheet with the same material as the underlying surface. This image shows an area of pure HOPG without any MnO₂ on the MnO₂NS/HOPG surface. Similar to **Figure 4.2.6a**, the potential change between 'OER' and reaction 'Off' is marked by white dotted lines. However, in contrast, an apparent noise stretches all

over the terraces. This noise behavior is similar to the observations on pure HOPG at step II in **Figure 4.2.2**, seen in **Subchapter 4.2.1.2**. As discussed in **Subchapter 3.3.3**, the distinct visualized intensity of the noise mainly results in the selected gain settings and thus makes a direct comparison of individual measurements unfeasible. However, to analyze this measurement, **Figure 4.2.6d** presents the noise evaluation for the highlighted areas (d1 to d4). The upper graph compares the two areas atop the nanosheet (d1) and the neighbored terrace (d2) under 'OER' conditions. In addition, the lower graph shows the equivalent positions for reaction 'Off' (d3 and d4). As expected, in contrast to **Figure 4.2.6b**, both graphs reveal a low Δ FWHM of 3% for 'OER' and 2% for reaction 'Off'. As elucidated before, this observation proves that the sheet material behaves fundamentally comparable to the surrounding terrace, thus confirming the materials' equality.

It is important to note that both steps, separating the upper and lower terrace, are two single HOPG-layered steps instead of two double HOPG layers. This assumption is supported by the line scan illustrated in **Figure 4.2.6 A1** in **Appendix D**, which represents the height profile of **Figure 4.2.6c** (*cf.* **Figure 4.2.6 A4b**, at position III). The two-level shape of these steps might result from a double-tip since the height of the artifact of about 0.2nm is too small for actual atomic structures on the surface (*cf.* **Subchapter 2.3.3**). Owing to the height differences between the lower, middle, and upper terrace close to the theoretical value for a single layer of HOPG (0.34nm), MnO₂ could be excluded from the possible candidates, thus indicating HOPG as the observed material ^[242,280]. These findings again underline the assignment of the nanosheet material to MnO₂ in **Figure 4.2.5a**.

Moreover, when comparing the noise behavior in **Figure 4.2.6c** to the one on pure HOPG presented in **Figure 4.2.2**, the initial impression could suggest that the HOPG steps do not exhibit outstanding noise. Still, even if the difference is marginal, as characteristic for HOPG in 0.1M KOH, the steps in **Figure 4.2.6c** remain the most active sites. This statement is demonstrated at three step edges highlighted in **Figure 4.2.6 A5** and **Figure 4.2.6 A6** (**Appendix D**) using the site-related activity evaluation (*cf.* **Subchapter 3.4.2**). At all observed positions, the step edges exhibit increased activity and thus once more underpin the consistency of the n-EC-STM results.

For transparency, next to a list of all individual FWHM values for each Gaussian fit in **Table A4.4** (**Appendix B**), the highlighted areas b1 to b4 and d1 to d4 are provided in **Appendix D** in **Figure 4.2.6 A2** and **Figure 4.2.6 A3**. Furthermore, the FFT filtering process of **Figure 4.2.6c** is shown in **Figure 4.2.6 A4a**, while all areas used for the activity evaluation are presented in **Figure 4.2.6 A4b**.

4.2.2.2 Extended Noise Analysis and Activity Allocation

A more detailed understanding of the electrochemical behavior at the MnO₂NS requires an extended analysis of the collected data. **Figure 4.2.7a** shows an n-EC-STM measurement of the same nanosheet with a turned scanning angle. During capturing this image, the potential was switched between 'OER' and 'Off' several times, starting on the left side. Here, similar to **Figure 4.2.5a** high noise peaks are visible predominantly on the steps, followed by smaller ones on the sheet's plateau. Next to this outstanding activity, this measurement demonstrates the stability of the sample during the measurement. The comparison of two line scans in the 'Off' region (positions I and II in **Figure 4.2.7b**) before and after applying an 'OER' potential is depicted in **Figure 4.2.7c**, illustrating the preservation of the nanosheet shape during the experiment. Despite the funnel shape of the sheet, the representative line scans show an almost accordance in height, size, and shape. Consequently, far-reaching influences on the surface morphology of the locally investigated areas caused by electrochemical reactions during the measurements are unexpected. Analogous to the other EC-STM images, the presented data were carefully FFT-filtered, as visualized in **Figure 4.2.7. A1a**, supplied in **Appendix D**.

More detailed knowledge about the local noise behavior delivers the application of the site-related activity evaluation introduced in **Subchapter 3.4.2**. The investigated black-framed area 1, as highlighted in **Figure 4.2.7b**, provides a suitable area for this evaluation due to its parallel sheet edges to the slow scan axis. The computed results of this evaluation are summarized in **Figure 4.2.8**. Here, the black line illustrates the estimated height of the nanosheet of the investigated area under reaction conditions. This simulated graph is very similar in size and shape to the actual line scans for reaction 'Off' (cf. **Figure 4.2.7. A1b**).

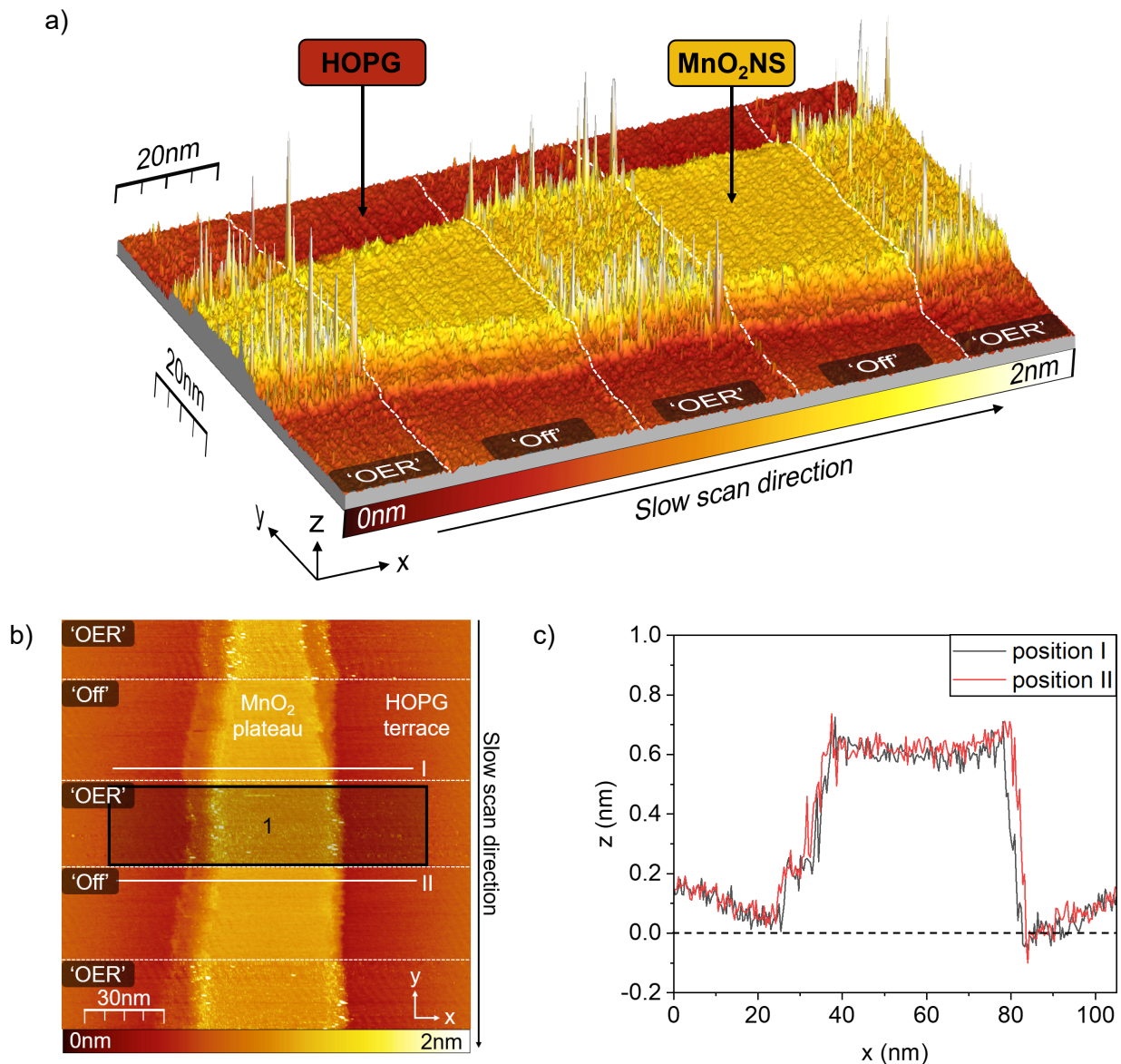


Figure 4.2.7. Additional *n*-EC-STM measurement of the nanosheet is illustrated in **Figure 4.2.5**, recorded in 0.1M KOH. **a)** Three-dimensional perspective presenting high noise peaks predominantly on the step edges and the MnO_2NS plateau. **b)** Two-dimensional view of **a)** with drawn-in line scans (white) and the area used for the evaluation in **Figure 4.2.8** (black). **c)** Mostly identical line scans on positions before and after the OER potential were applied to the sample, underlining the stability of the surface structures. Data of all figures published in reference ^[213].

The previous investigations showed that the sheets' activity could be broken down into three primary sources of activity: the left step, the sheets plateau, and the right step. Interestingly, the

course of activity data (red-colored dots) in **Figure 4.2.8** for the site-related FWHM could be nicely approximated by the sum of three Gaussian fits (blue curve), analogous to the model surface in **Subchapter 3.4.2**. Consequently, the blue curve represents the overall activity within the observed region. In addition, due to the locally restricted activity, mainly on the step edges, a rough estimation of the individual contribution of each active site is possible. Since the blue curve corresponds to the sum of the green, cyan, and magenta curves, the areas below the respective curves must also match the area below the blue one. As a result, the green, cyan, and magenta areas yield the activity ratio of the individual sites. However, since the curves' breadth depends on the set analysis width of 6nm used for the FWHM calculation, the observed proportion must be seen as a rough estimation instead of an absolute value. Nevertheless, despite the much bigger size of the terrace, this approximation assigns only 43% of the overall activity to the MnO₂NS plateau, while 57% remains on the much smaller step edges. Probably caused by the double apex on the STM tip, as discussed before, the noise on the left step might be measured twice, thus explaining the increased ratio of 34% on the left step.

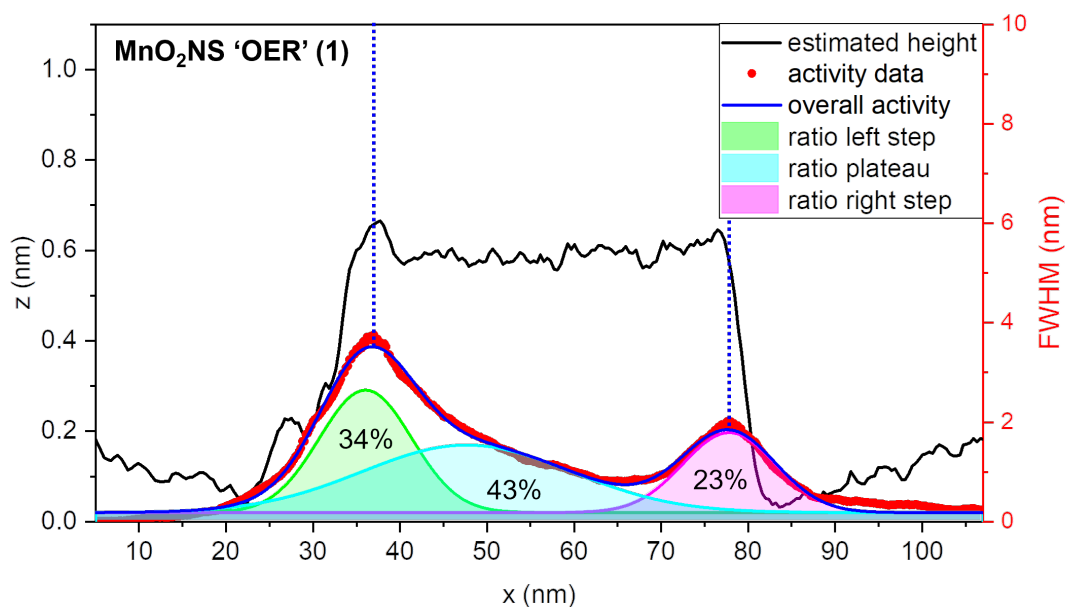


Figure 4.2.8. Site-related activity evaluation for the middle 'OER' section, highlighted in **Figure 4.2.7b** (area 1). The black curve represents the approximate height profile of the sheet in this region. Moreover, the calculated FWHM values (red dots) are fitted by the blue curve, which coincides well with the sum of the individual Gaussian fits for the step edges (green, magenta) and the one for the plateau (cyan). As a guide for the eyes, the dotted blue lines compare the cross-section of the sheet with the positions of the highest calculated activity for the left and right steps, respectively.

Since the twice-measured step is located on the left side of the NS, it is plausible that the decisive double-tip might be on the right side of the STM tip. In addition, since the distance between these double-tips is expected to be approximately 5nm (*cf.* **Figure 4.2.7. A1b** and **Subchapter 2.3.3**), which is about half of the extent of the active site detected on the NS step edges, which is about 10nm, also the noisy region increases by approximately 50% (*cf.* extends of noisy areas in **Figure 4.2.7. A1c**). This estimation is well suited to the finding that the ratio of the left step (34%) is about 50% larger than that of the right one (23%). This artificially enhanced activity on the left step might also cause the delocalization of the maximum cyan curve to the left side. Due to the asymmetric activity on the step edges, the Gaussian fit on the plateau might be artificially shifted to the more active one. This phenomenon of double-captured noise when acquiring the STM data demonstrates the strong influence of the tip shape on the n-EC-STM measurements and underlines the requirement for a meticulous discussion of the results. Moreover, this example shows that a quantitative statistic analysis tool is of fundamental importance for any n-EC-STM analysis process.

In addition, the evaluation in **Figure 4.2.8** reveals the highest activity directly on the step edges. The blue-dotted vertical extensions of the overall activity suggest that the most active sites are likely on top of the nanosheet at the edges. However, due to the large scan size of this measurement and thus the limited resolution, secure identification of the precise origin of the noise is not possible. Furthermore, a slight deviation between the fitted overall activity (blue) and the activity data on the right-sided terrace, next to the nanosheet, is visible. This discrepancy results from a slight activity increase on this part of the terrace. A possible reason for this could be a marginal defective HOPG surface, which was not further evaluated in this study due to the large scan size of the STM image. Still, as evident in **Figure 4.2.7a**, the HOPG terraces remain mostly inactive compared to the MnO₂NS. In order to bring light to the detailed electrocatalytic activity of the individual materials, the following paragraph evaluates and compares the most characteristic surface sites.

For this evaluation, the roughness analysis introduced in **Subchapter 3.4.2** is applied to the MnO₂NS-HOPG interface, the MnO₂NS plateau, and the HOPG terrace, respectively. The individual positions of the investigated areas are highlighted in **Figure 4.2.9a**, which provides a two-dimensional view of **Figure 4.2.5a**. Starting with the roughness analysis on two comparable step regions for 'OER' (cyan) and reaction 'Off' (pink), the discrepancy ΔFWHM reveals 49%, which, as expected, states a massive roughness increase caused by the electrochemical reactions

(cf. **Figure 4.2.9b**). Moreover, an analogous evaluation in **Figure 4.2.9c** compares different positions on top of the MnO₂NS plateau (black and blue) and exhibits a value of 55% for $\Delta FWHM$.

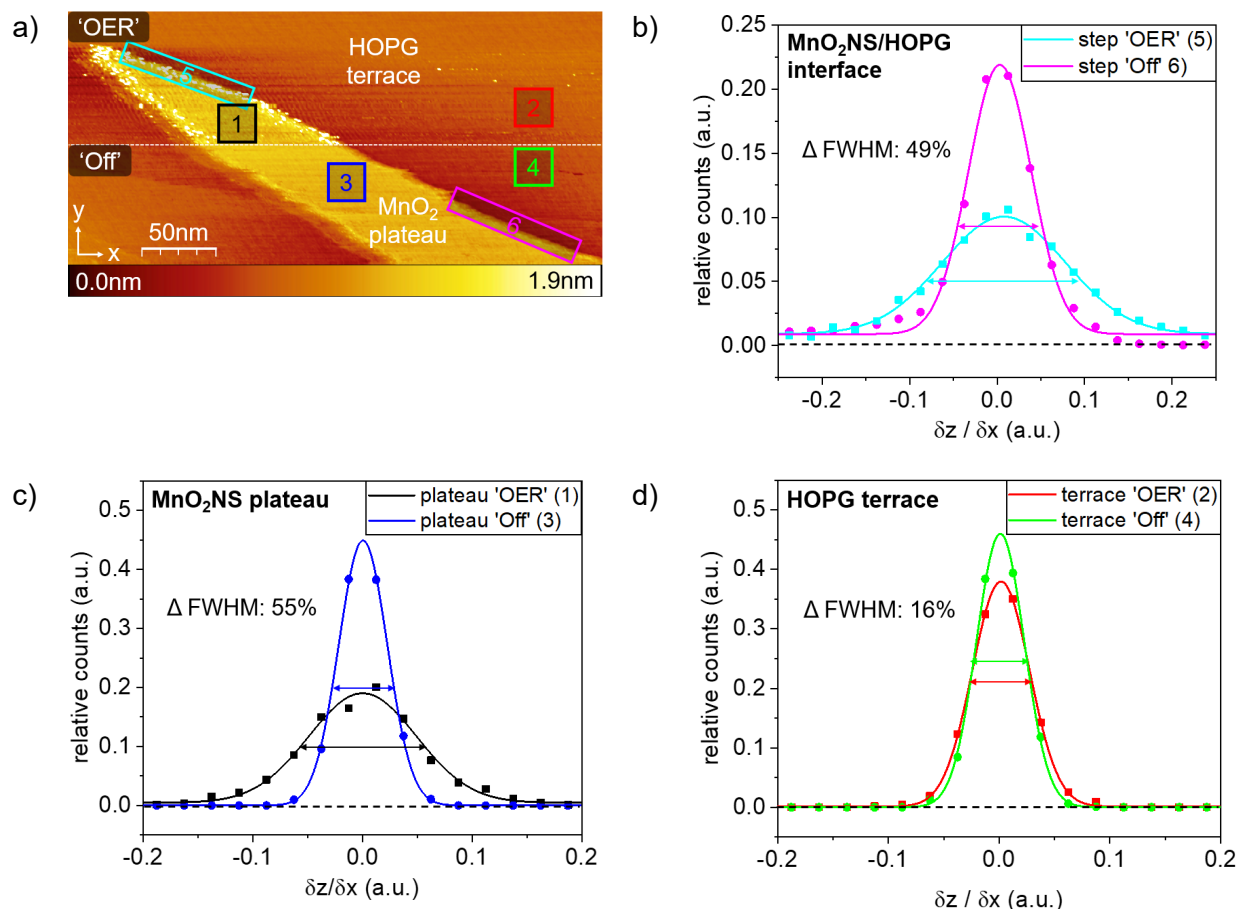


Figure 4.2.9. Roughness analysis comparing the electrochemical activity on characteristic sites on MnO₂NS/HOPG. **a)** Two-dimensional image of a MnO₂NS providing an overview of the analyzed areas. The upper half of the figure shows the surface under 'OER' conditions while the lower one presents it for reaction 'Off'. Roughness analysis of **b)** the MnO₂NS-HOPG- interface, **c)** the MnO₂NS plateau, and **d)** the HOPG support. Data of a) published in reference ^[213], representation of b), c), and d) inspired by reference ^[213].

It is essential to note that the estimate on the step edges is relatively less representative since, for technical reasons, next to the very active step noise, parts of the evaluated area include the less active MnO₂NS plateau and the marginal active HOPG data. Thus, the actual value of the noise on the step edges might be even larger, which agrees with the previous observations. However, this examination mirrors the outstanding activity of MnO₂NS, especially in comparison with

Figure 4.2.9d, which demonstrates the analogous investigation of the HOPG support. Here, the deviation ΔFWHM between 'OER' (red) and reaction 'Off' (green) equals only 16%, demonstrating the relatively poor activity of HOPG compared to MnO₂. On the other hand, this apparently increased value also confirms the presence of electrochemical reactions on the HOPG surface and thus is in line with the findings on the pure HOPG surface discussed in **Subchapters 4.2.1.1** and **Subchapter 4.2.2.1**.

4.2.3 DFT Results and Extended Elucidation of Electrochemical Processes

Due to the limited resolution of experimental approaches and thus constraints to identify the most prominent OER driving active sites, this research project collaborated with the DFT expert André Wark under the lead of Prof. Egill Skúlason at the University of Iceland (Faculty of Chemical Engineering, Mechanical Engineering, and Computer Science). This combination of experimental findings and theoretical explanations is a powerful tool to unveil the electrochemical processes of unexplored electrocatalysts. The DFT results, figures, and interpretations presented in this subchapter are based on the findings of the publication resulting therefrom:

- Schmidt T.O.,⁽⁺⁾ Wark A.,⁽⁺⁾ Haid R.W., Kluge R.M., Suzuki S., Kamiya K., Bandarenka A.S.*, Maruyama J.*, Skúlason E.* *Elucidating the active sites and synergies in water splitting on manganese oxide nanosheets on graphite support*. Advanced Energy Materials **2023**, 13, 2302039.

Further information on the DFT procedure is provided in this publication's experimental section and **Subchapter 2.3.4** in this thesis.

4.2.3.1 Basic Considerations and Conceptual Model Design

As discussed in **Subchapter 2.1.4**, when knowing the potential determining step of different sample sites, one can derive their affinity to serve as a suitable catalyst for the observed reaction. As shown in the published manuscript, for the investigation of MnO₂NS/HOPG, five different models were the focus of the observation ^[213]. First, pristine HOPG was analyzed to get an initial idea of the subsequent interpretation of the findings on the other systems. Here, it turned out that a

single graphene layer was sufficient to simulate the support material since the differences in the energetic landscape between graphene and different graphite models were negligible. In addition, the charge transfer analysis demonstrated that the electrons that migrate to the MnO₂NS originate mainly from the first graphite layer. Analogous to the notation in the publication, this system will be labeled as “graphene” in the following. Furthermore, the investigation of an individual MnO₂ layer as the second system called “pure MnO₂” provided data about the usability of the nanosheet material itself as an OER catalyst. The knowledge of these two systems builds the basis of understanding the synergies detected on the hybrid material MnO₂NS/HOPG. Here, 50 carbon atoms build the graphene layer, which serves as the supporting material underneath the MnO₂NS. In order to model the MnO₂NS plateau, the entire carbon support was covered with MnO₂ on the third investigated system, labeled as “MnO₂NS plateau” and illustrated in **Figure 4.2.10**.

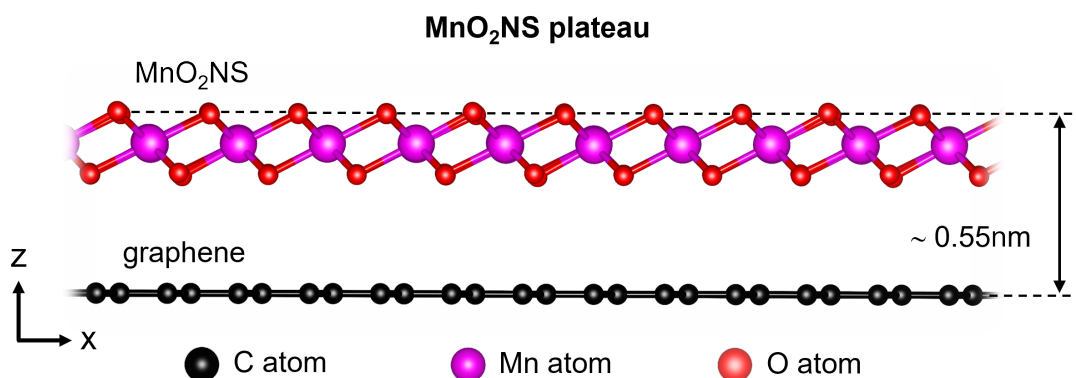


Figure 4.2.10. Cross section of the model system, which represents the MnO₂NS plateau. The distance of 0.55nm between the top of the MnO₂NS (red oxygen and purple Mn atoms) and the first underlying HOPG layer (black) is slightly larger than the experimentally observed height of about 0.7nm. This difference might occur due to the absence of spacers like cations or water within the gap between the films, but it is still to a reasonable scale. Inspired by ^[213].

Moreover, two additional model systems were introduced to investigate the step edges, consisting of the graphene support with small MnO₂NS on top, separated by a vacuum. These two systems, “MnO₂NS-edge_{1ox}” and “MnO₂NS-edge_{2ox}”, differ with regard to the number of oxygen atoms at the endings, represented by the designations 1ox and 2ox, respectively. **Figure 4.2.11** illustrates the first and, as discussed in the following, the more promising system, “MnO₂NS-edge_{1ox}”, from the side and top view. Here, the blue and orange isosurfaces illustrate the positions of charge depletion and accumulation, respectively, which illustrate that the charge is rearranged

predominantly at the edge. The following subchapter provides a detailed discussion of the OER on these five selected systems.

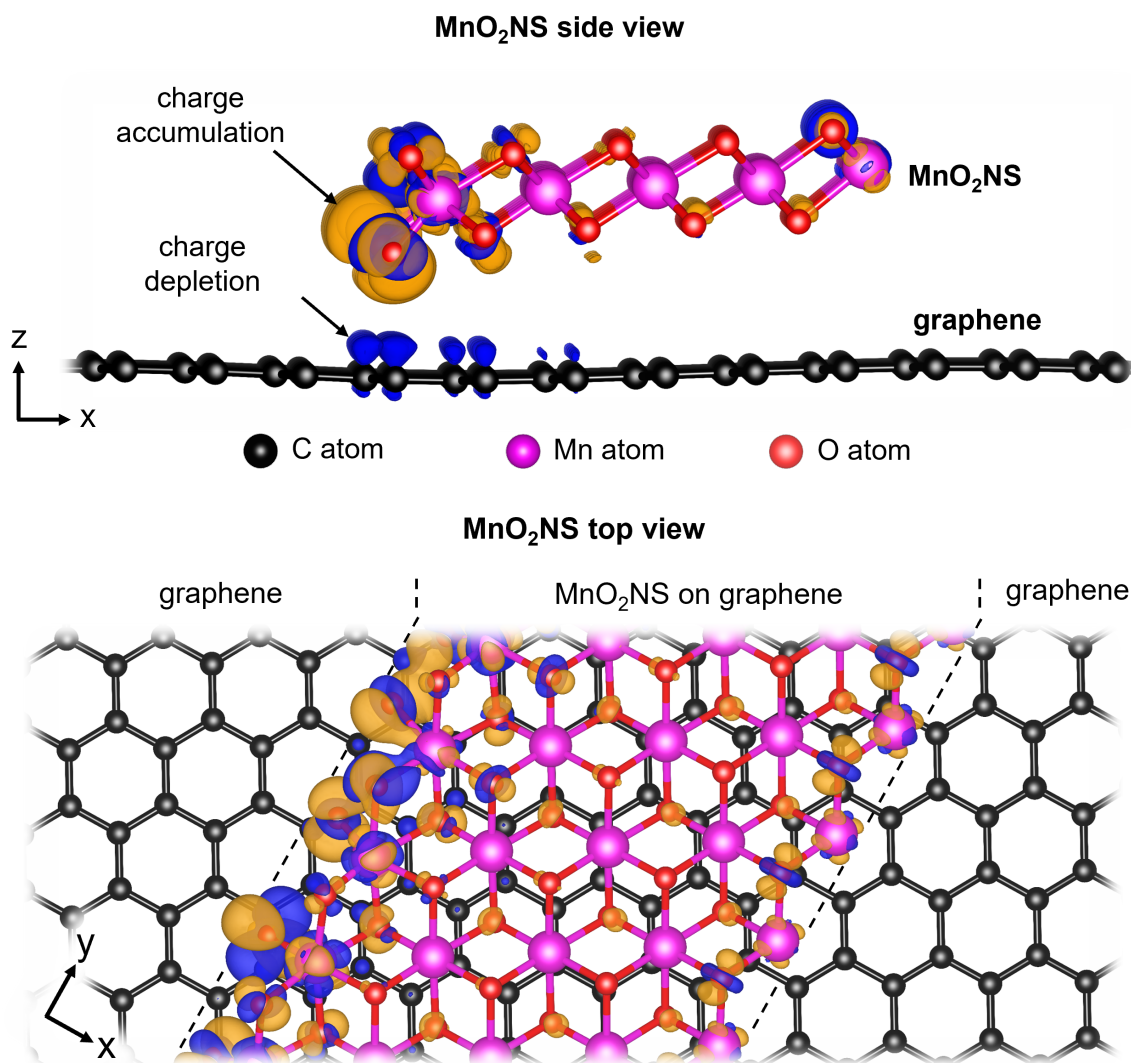


Figure 4.2.11. Extract of the $\text{MnO}_2\text{NS}/\text{HOPG}$ model surface used for the DFT calculations showing a schematic side and top view of $\text{MnO}_2\text{NS-edge}_{10x}$. The orange and blue isosurfaces represent expected charge accumulations and depletions, respectively. Inspired by ^[213].

4.2.3.2 DFT Results and Reinterpretation of EC-STM Measurements

This subchapter presents the DFT results established by André Wark under the lead of Prof. Egill Skúlason at the University of Iceland and published in Schmidt *et al.* ^[213]. It is important to note that electrolyte and kinetic effects were neglected in their calculations to reduce the system's complexity. Thus, possible influences might therefore remain unconsidered in the results.

Furthermore, all DFT calculations investigating the OER process assume $E_0 = 1.23\text{V}$ versus RHE at a temperature of 0K. **Figure 4.2.12** illustrates the thermodynamics of the systems introduced above concerning the OER.

Here, the difference in free energy serves as a measure of the tendency to proceed from one reaction coordinate to the next. As introduced in **Subchapter 2.3.4**, η_{PDS} provides the corresponding measure for an appropriate benchmark. As discussed in **Subchapter 4.2.1.3**, the CV measurements demonstrate that pristine graphene has relatively poor OER activity. Also, the DFT results in **Figure 4.2.12** (green path) suggest this observation: the first electron-proton transfer step shows the highest overpotential of all investigated systems with 1.7eV, thus representing the potential determining step. This high thermodynamic barrier impedes the start of an electrochemical reaction, hence lowering the ability to run the OER on graphene. For pure MnO₂ (blue), the DFT results calculated a similar high η_{PDS} of 1.67V, which predicts a comparable poor performance as OER catalyst as pristine HOPG.

In contrast, the yellow path representing the “MnO₂NS plateau” reveals a much smaller overpotential of 0.97eV for the potential determining step for the first reaction coordinate. Consequently, the presence of graphene underneath the MnO₂NS likely positively affects its OER activity. Considering that the initial charge transfer calculation indicated the migration of electrons from the graphene to the MnO₂NS, as discussed before, this finding seems plausible. When investigating the step edge itself, on MnO₂NS/HOPG, there are three promising candidates as active sites: an oxygen atom, which occupies a position directly on top of the edge Mn atom and has no further binding partners (O=Mn); an oxygen atom bound in-between two Mn atoms, thus building a bridge (Mn-O-Mn); and a carbon atom underneath the MnO₂NS edge. All three sites were investigated by the DFT calculations for “MnO₂NS-edge_{1ox}” and “MnO₂NS-edge_{2ox}”, as elucidated in detail in the published manuscript ^[213]. The results with the lowest detected η_{PDS} for both step edge systems, thus representing the most active site, are shown in **Figure 4.2.12** as the two paths within the negative free energy interval. For both model systems, the decrease in free energy at the first steps indicates that these pathways are thermodynamically favored. For “MnO₂NS-edge_{2ox}”, the lowest η_{PDS} was found on the O=Mn top site with a value of 1.30eV for the last step, charted in black with the ending “top”. Since this overpotential is even higher than the one for the MnO₂NS plateau, it is unlikely that sheet edges of this configuration prevail as the decisive active site on step edges. A more probable origin of the significant step activity was found for “MnO₂NS-edge_{1ox}” on the bridge sites. Out of the three investigated candidates, the Mn-O-Mn moieties represent the functional group with the lowest overpotential of 0.56eV at its

potential determining step, located at the last reaction coordinate (red path with the suffix “bridge”). Next to this exceptionally low η_{PDS} , the balance in free energy of this path's first four intermediate steps is negative or neutral, thus increasing the tendency to favor this way.

Consequently, the DFT results reveal the Mn-O-Mn bridge site of “MnO₂NS-edge_{1ox}” as the most active OER site on the entire MnO₂NS/HOPG, followed by the MnO₂NS plateau and with graphene as the least active one. An additional benefit of these findings is the detailed unraveling of the individual intermediate processes, thus enriching the understanding of MnO₂NS/HOPG as an OER electrocatalyst.

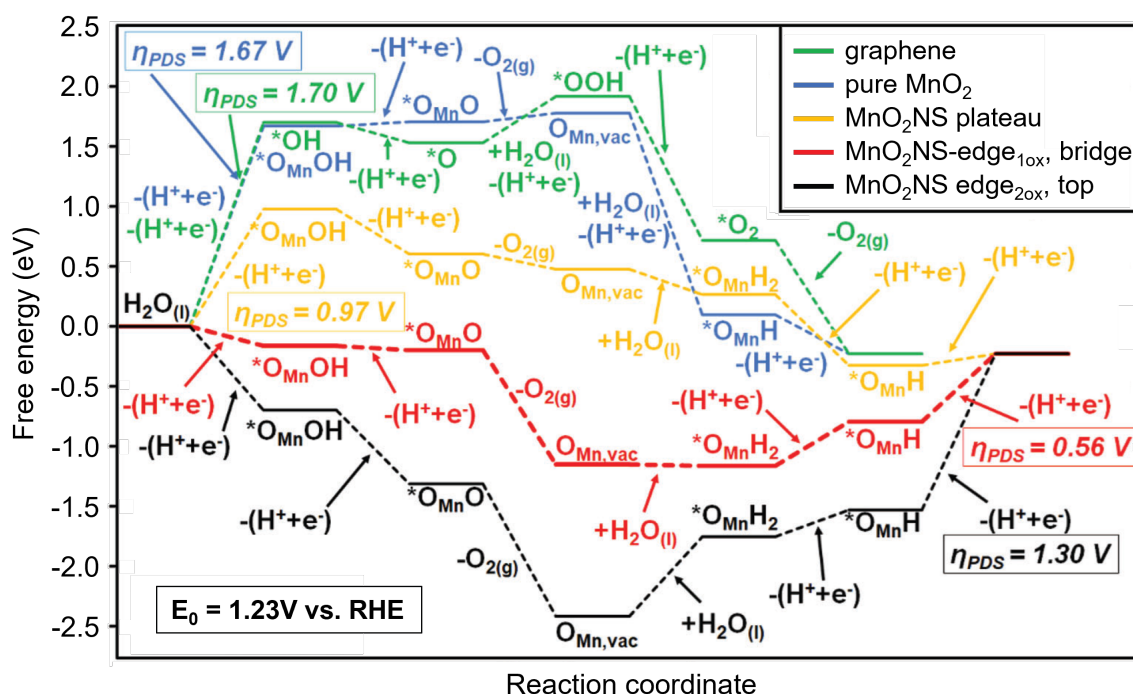


Figure 4.2.12. Overview of the DFT results demonstrating different OER pathways and their intermediate steps. Here, the subscript characters Mn in O_{Mn} designate an oxygen atom originating from MnO₂NS, while O represents an oxygen atom from a water molecule. The prefixed *-symbol indicates the adsorption of the intermediates. Moreover, the algebraic sign in front of the species in-between reaction coordinates visualizes if it enters or exits the system. Reprinted with minor reformatting with permission from ^[213]. Copyright 2023, Wiley-VCH GmbH.

4.2.4 Summary and Prospects

In summary, the comprehensive theoretical and experimental investigation shown in the final publication emphasizes the power of their synergy and provides detailed information about the OER processes on MnO₂NS/HOPG ^[213]. The DFT investigations determined the Mn-O-Mn bridges on the MnO₂NS endings, with one oxygen atom as the outermost atom, being the most active site. This assignment, in combination with the experimentally found outstanding noise behavior on the step edges, leads to the recommendation of future MnO₂-C-based catalysts with high coverage of tiny MnO₂NS. Interestingly, such a Mn-O-Mn moiety was also found as a part of the Mn₄CaO₅ complex in PS II, while its bridged O atom is assumed to play a crucial role in the splitting of water ^[65,284]. In addition, despite the DFT results on pure MnO₂ and HOPG suggesting a similar electrochemical behavior, the experimental and theoretical investigations reveal a significant increase in activity on the MnO₂NS plateau, thus demonstrating the power of the synergy of these two materials. This effect becomes apparent when comparing the noise level of the MnO₂NS plateau with that of the surrounding HOPG surface observed by n-EC-STM. Hence, this investigation on inconspicuous materials combined into an efficient hybrid material promotes the development of innovative novel electrocatalysts based on abundant and comparable cheap elements.

Additionally, this project laid the basis for the follow-up investigation on MnO₂NS/CFcPc/HOPG, which has an even better OER ability. As presented by Maruyama *et al.*, even the doped HOPG with FeN₄ centers (CFcPc/HOPG) results in a significant increase in OER activity ^[285]. Due to the detailed DFT predictions of the specific intermediate steps for each pathway, an extended database about the ongoing OER processes on MnO₂NS is created while receiving validation by the n-EC-STM measurements. Consequently, these findings revealed the synergy effects and the most active sites during OER of a further state-of-the-art Mn-C-based electrocatalyst, filling a gap in the research of MnO_x functional groups. Moreover, it provides detailed information about the surface processes and intermediates, which might be valuable for future electrocatalyst design inspired by nature's Mn₄CaO₅ complex and for understanding the water-splitting process in PS II.

5 Outlook: The Future of Active Sites

Next to the Pd and MnO₂NS/CF₃Pc specific prospects already discussed in **Subchapter 4.1.4** and **Subchapter 4.2.4**, respectively, more general developments that have occurred during the time of this doctorate might impact the future progress in the research of novel electrocatalysts. Starting with the opportunities of the new STM setup launched in this period at our chair, this subchapter discusses the trends in the identification of active sites based on the following publications:

- Haid R.W.,^(*) Kluge R.M.,^(*) Schmidt T.O., Bandarenka A.S.* *Finding efficient catalyst designs: A high-precision method to reveal active sites*. Chem Catalysis **2022**, 2, 657-659.
- Yu H.,^(*) Schott C., Schmidt O.T., Schneider P.M., Song K.-T., Zhang Q., Capogrosso A., Deville L., Gubanova E.,* Bandarenka A.S.* *Investigation of active electrocatalytic centers under reaction conditions using operando microscopies*. Current Opinion in Electrochemistry **2023**, 42, 101386.

Due to the novel opportunity of identifying active sites using EC-STM or AFM inside an Ar atmosphere, the foundation to investigate currently unexplored oxygen-sensitive materials has been created. This setup enables simplified handling of materials like Pd and a distinct investigation of the proton reduction or HER without inducing the ORR. Consequently, this innovation thus paved the way for the already successfully implemented hydride-induced surface reconstruction experiments on Pd and Pt single crystals. In addition, the ability to measure inside an Ar atmosphere makes lithium-based investigations possible. This enhancement has laid the groundwork for new and even more challenging research projects. Thus, it might build the foundation of several future projects to identify active sites.

In addition, during this doctorate, other institutes in Italy and China adopted fundamental concepts of the n-EC-STM technique and explored the nature of active sites. In 2021, Kosmala *et al.* from the University of Padova in Italy presented a modified version of the n-EC-STM technique called current roughness EC-STM (cr-EC-STM) ^[211]. As elucidated in more detail in 2022 by Agnoli *et al.* and previewed by Haid *et al.*, they performed similar noise measurements to the n-EC-STM approach but with an extended evaluation ^[286,287]. To recap, the detected STM signal on active sites contains information about the actual surface morphology, superimposed by the fluctuations

from faradaic processes. Consequently, when capturing a reference measurement for the reaction 'Off', one can extract the noisy ratio and calculate the "roughness" of the current signal. For this purpose, they created a mathematical model that used this reference STM signal as a baseline and introduced a correction value that leads to the definition of a more general "tunneling current roughness value", which allows an activity comparison across different electrocatalysts. Furthermore, they found that the noise intensity stabilizes at a particular sample or surface structure-specific overpotential, which allows the identification of active sites.

Since the cr-EC-STM technique was already presented only four years after the introduction of the n-EC-STM method in 2017, this innovative modification exemplifies the rapid development regarding the observation of faradaic processes using an EC-STM ^[28,211]. At the same time, it raises hopes for further impressive results and an accelerated understanding of electrocatalytic materials. Moreover, in 2023, Liao *et al.* from the Hunan University in China independently presented impressive measurements of active sites on MoO₂NS under strain using the n-EC-STM technique ^[212]. This recent utilization of n-EC-STM on the other side of the world demonstrates the rising popularity of the relatively young and, thus, less employed technique. In other words, an emerging trend towards more EC-STM operators trying to identify active sites in recent years has become noticeable. This tendency is also apparent regarding other *operando* approaches to identify active regions, such as scanning electrochemical microscopy (SECM) and scanning electrochemical cell microscopy (SECCM) ^[288]. SECM measures the diffusion-limited current on a microelectrode that moves close to the sample surface. Analogous to EC-STM, a classical 3-electrode setup induces chemical reactions in the sample's active sites while the tip yields the fourth electrode. When scanning the sample surface, the change in the measured current varies with, e.g., the tip-sample distance, local surface activity, and surface roughness. In this way, it is possible to identify active regions on different electrocatalysts. ^[289–292] In contrast, SECCM has an additional capillary between the sample and the microelectrode, which serves the actual EC-cell, including RE and CE. One significant advantage of this more complicated technique is, besides its higher resolution, the non-destructive imaging ability due to the limited surface area immersed in electrolytes, which leads to a lower possibility of surface alteration during operation. ^[290,293]

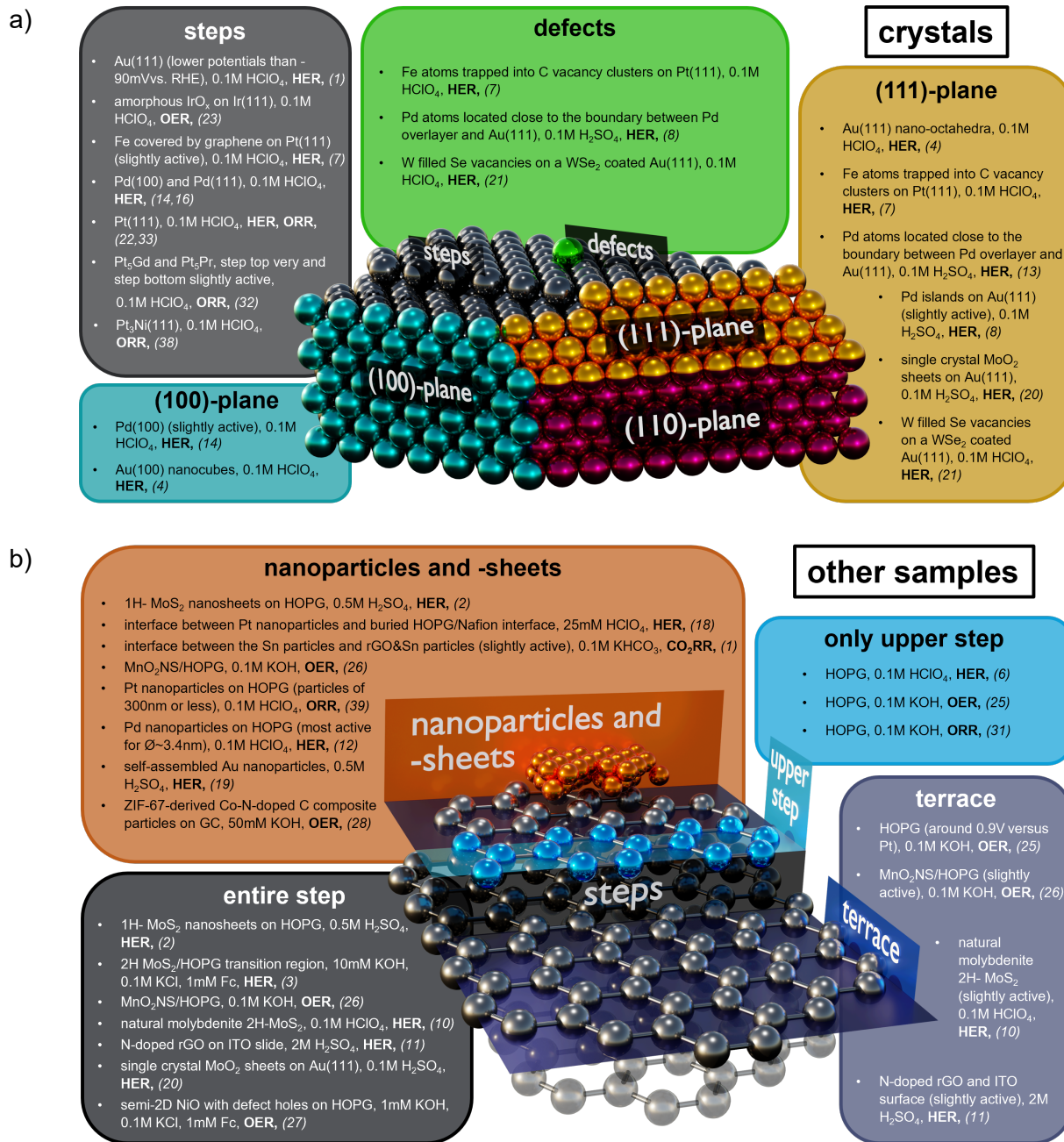


Figure 5.1. Summary of the active sites and regions on a) crystalline materials and b) nanostructures, hybrid materials, and pristine HOPG identified by *n*-ECSTM, *cr*-EC-STM, SECM, and SECCM. The attached numbers on each listing correspond to the numbers in **Table A5.1** in **Appendix E**, which provides more detailed information about the individual active sites, applied electrolytes, and methods. Adapted with permission from reference ^[288]. Copyright 2023 Elsevier B.V, all rights reserved.

The techniques mentioned above for identifying active regions were also the subject of the review article by Yu *et al.*, published in 2023 ^[288]. Based on this work, **Figure 5.1** illustrates an updated version of the presented list, summarizing all identified active sites by n-EC-STM and cr-EC-STM and several active regions by SECM and SECCM so far. While **Figure 5.1a** summarizes the active structures on crystalline samples, sorted by the characteristic surface structures, **Figure 5.1b** provides an overview of nanostructured coatings, hybrid materials, and HOPG. The alphabetically sorted listings have attached numbers, which refer to **Table A5.1** in **Appendix E**, sorted by chemical reactions and linked to the corresponding reference. Despite the initial impression of an already rich active site database, this list represents only a fraction of promising electrocatalysts and nanostructures that might play a crucial role in the global energy transition.

Nevertheless, the value of such detailed lists becomes apparent when following the discussions of Zhao *et al.* about the importance of understanding the electrochemical processes from scratch. They stated that the key goals to advance future electrocatalysis are combining theoretical and experimental approaches, applying operando techniques to highly resolve active sites, and developing sustainable heterogeneous electrocatalytic materials. ^[294] Similarly, in 2022, Vogt and Weckhuysen reached a comparable conclusion in their review article. They designated active sites as the cornerstone in developing novel catalytic materials while emphasizing the increasing importance of photocatalysis and electrocatalysis in the current energy transition. Moreover, they encourage building on natural solutions, such as enzymes, and including biomimetic considerations in the development of modern catalysts. ^[295] Regarding the supposedly rich repertoire of still undiscovered materials and concepts for finding novel energy materials, the immense efforts made by the research community provide an optimistic outlook for discovering innovative, highly efficient catalyst materials made of abundant and sustainable materials.

6 Conclusion

Since developing an elaborated hydrogen economy requires extensive research on innovative state-of-the-art catalyst materials, this work focuses on investigating the electrochemical active sites of different catalysts and, therefore, enhancing the fundamental knowledge of suitable materials for energy applications. Here, the n-EC-STM technique takes the central role due to its powerful ability to identify the surface's active sites on high-resolution scales *in situ*.

The primary research projects presented in this thesis focus on two promising catalysis materials, Pd and MnO₂NS/HOPG, for the HER and OER, respectively, which correspond to the main reactions in electrolysis. Pd is a popular electrocatalytic material, but at the same time, it is still not completely understood in terms of the effects of PdH formation after H-absorption. In contrast, the state-of-the-art hybrid material MnO₂NS/HOPG consists of elements commonly found on earth and features analogies to the Mn-complex of PS II in plants where water oxidation occurs. Consequently, both catalysts yield different advantages and strengths and thus are highly interesting for developing the future hydrogen economy.

The investigation of the HER mechanism on Pd single crystals revealed the requirement of a novel experimental setup, which was realized within the scope of this doctorate and, from now on, enables EC-STM experiments inside a glovebox excluding oxygen. Initial CV measurements in 0.1M HClO₄ demonstrate a high H-absorption ability of Pd(111), Pd(110), and Pd(100) and indicate the vulnerability of their crystalline surfaces to hydrogen and oxygen. When investigating the proton reduction on Pd(111) and Pd(100) by n-EC-STM in 0.1M HClO₄, the step edges represented the most active sites at both crystallographic facets. Moreover, their atomically flat terraces were less electrochemically active. Remarkably, unlike previous investigations, not all step edges show the same activity in this study. While entire step sections on Pd(111) appeared to be both active and inactive, the noise on Pd(100) steps was more sporadic and less frequent. However, the origin of this phenomenon provides plenty of room for speculation, and therefore, it might be a suitable subject for future investigations. Subsequent DFT investigations made by the University of Ireland determined for low amounts of previously absorbed H the crystallographic facet's activity trend of Pd(211) > Pd(111) > Pd(110) > Pd(100). This finding coincides with the results of the CV measurements and the n-EC-STM measurements on freshly annealed Pd. Moreover, due to the step-like characteristic of Pd(211), its high activity corresponds very well to the outstanding noise detected on Pd(111) step edges by n-EC-STM. As a result, the combined experimental and theoretical insights led to a recommendation for designing a nanoparticle

Conclusion

targeting an optimized HER activity by high ratios of Pd(211) and Pd(111) facets. Interestingly, as discovered by STM, after the CV experiments were carried out, the initially atomically flat Pd surfaces developed into a hilly morphology. As stated by DFT calculations, this transformation might originate from the increase in surface strain due to the formation of PdHs within the first layers of the crystal after H-absorption. Furthermore, the n-EC-STM measurements demonstrate an alteration of the active sites from step edges to mainly convex regions on Pd(100)_c and to both convex and concave sites for Pd(111)_c, thus confirming the susceptibility of the Pd surfaces to hydrogen. In brief, the study on distinct Pd crystal facets elucidates new insights into the complex processes under reaction conditions and predicts advantageous HER properties after H-absorption. In addition, this research reveals the active site locations on Pd(111) and Pd(100) single crystals before and after H-absorption.

Furthermore, n-EC-STM was utilized to characterize the electrochemical role of MnO₂NS supported on HOPG during the OER. Interestingly, the combination of MnO₂ and HOPG significantly increases the activity compared to the individual materials and demonstrates the power of this synergy. The measurements, performed in 0.1M KOH, clearly identified the most active sites on the step edges of the MnO₂NS. Moreover, the top of the NS also revealed a lower but still significant noise behavior. Based on the absence of significant activity on the surrounding HOPG terrace, the MnO₂ nanosheets yield the primary source of the impressive OER activity of the investigated system. The accompanying DFT calculations by the University of Iceland individually identified the MnO₂NS edges, more precisely, the Mn-O-Mn bridges on the endings with one outermost oxygen atom, as the most active site. In addition, the DFT results stated that the overpotentials of the potential determining steps of the step edges, nanosheet plateau, and HOPG support were 0.56eV, 0.97eV, and 1.70eV, respectively, for a theoretical potential of 1.23V versus RHE. Consequently, both the n-EC-STM and DFT studies showcase the identical OER activity trend at the MnO₂NS/HOPG system following MnO₂NS edges > MnO₂NS plateau > HOPG support. Moreover, since the computational findings are experimentally verified by n-EC-STM, the accuracy of the theoretically achieved reaction pathway and intermediate steps is also plausible. As a result, this study provides detailed insight into the processes on the catalyst surface during OER and the overpotentials of each intermediated step on all active sites. Understanding the OER on MnO₂ in this depth may also help to further grasp the processes at the Mn-complex in PS II during water splitting. Furthermore, this hybrid material demonstrates that even common materials with relatively poor electrocatalytic properties can increase their activity drastically if combined appropriately and create a basis for the research on novel C and Mn-based highly active catalyst materials, such as MnO₂NS/CFcPc/HOPG.

Conclusion

To conclude, in this work, the active sites on single crystalline Pd(111) as well as Pd(100) and MnO₂NS/HOPG for HER in acidic and OER in alkaline media were unveiled by EC-STM respectively, and elucidated by accompanying DFT calculations. In addition, this thesis once more demonstrates the power of combined theoretical and experimental approaches to investigate electrochemical processes in-depth. The insights gained about the hydrogen interactions on Pd single crystals and the oxygen evolution on MnO₂ enrich the universal knowledge of electrocatalysis with a further piece, thus contributing somewhat to the drive towards energy transition.

Appendix A: Acknowledgments

- First, I would like to express my sincere gratitude to **Prof. Dr. Aliaksandr Bandarenka** for providing me the opportunity to pursue my PhD in the exceptional field of n-EC-STM and for the excellent supervision as well as invaluable support I have received throughout the years of my doctorate. It was a fantastic experience to become part of this exciting research community, and I am very grateful to have had this opportunity.
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- In addition, I would like to thank **Prof. Dr. Jun Maruyama** for providing the MnO₂NS/HOPG samples, the outstanding scientific exchange, empirical contributions, and the wonderful impressions from Japan.

Appendix A: Acknowledgments

- I am genuinely grateful to **Lewin Deville** for the enriching discussions about the fundamental working principle of the n-EC-STM technique and for developing and implementing the Python script for the site-related activity evaluation. Additionally, I want to say sincere thanks for the great assistance in troubleshooting the new multimode device, for proofreading this dissertation, and for the pleasant time.
- Equally, I deeply appreciated the time working on the Pd crystals together with **Andrea Capogrosso** during his Master's thesis, and I am very thankful for his endurance in bringing the new multimode setup inside the glovebox into operation and for proofreading my thesis.
- I wish to extend my heartfelt thanks to **Dr. Richard Haid** and **Dr. Regina Kluge** for the great time, pleasant instruction in the n-EC-STM technique during my time as a Master's student, and unwavering encouragement and inspiring support during my PhD.
- Furthermore, I want to say a big thanks to **Siegfried Schreier** for the great teamwork and support in all purchase and construction projects, especially regarding the installation and commissioning of the new multimode inside the glovebox. In addition, I am thankful to him and **Rainer Götz** for making the SEM records of the STM tips for this thesis.
- I also want to say special thanks to **Peter Schneider**, **Qingdian Liao**, **Christian Schott**, **Raphael Streng**, **Rodrigo Bautista**, **Dr. Katarina Cicvaric**, and **Katrin McCormack** for the great time and proofreading of my thesis.
- In addition, I thank **Leon Haase** for designing and implementing the theoretical overview images of the STM tip and the MnO₂NS/HOPG sample.
- Moreover, I deeply enjoyed the time with **my current and former colleagues** in the department and am very thankful for each moment we spent together. I also thank **Manuela Ritter** for being the backbone of our chair and for her great assistance in all administrative concerns.
- Finally, I want to express my special thanks to **my wife and family** for the incredible support during my doctorate and for always having an open ear for any concerns.

Appendix B: STM and CV Settings

This subsection summarizes all STM and CV settings of each measurement performed in this doctorate. It is important to note that all measurements were performed at room temperature and atmospheric pressure.

Table A4.1. List of the most essential specifications and multimode setting of each STM measurement. All potentials are listed versus a Pt RE electrode if not stated differently. Values published in references ^[118], ^[175], ^[207], ^[213], and ^[267]. Please note that this table continues on the next page.

Figure number	Potential interval (V vs. Pt)	Tip potential (mV vs. Pt)	PG (a.u.)	IG (a.u.)	CS (nA)	Scan size (nm)	Scan rate (Hz)	Electrolyte (0.1M)
4.1.1a	0.0	-50	1.0	0.6	0.5	500	0.5	HClO ₄
4.1.1b	0.88 ^(*)	829 ^(*)	1.0	0.6	2.0	280	0.9	HClO ₄
4.1.1c	0.0	-50	1.0	0.6	0.5	500	0.5	HClO ₄
4.1.1 A1a	0.0	-50	1.0	0.6	0.5	500	0.5	HClO ₄
4.1.1 A1b	0.88 ^(*)	829 ^(*)	1.0	0.6	2.0	280	0.9	HClO ₄
4.1.1 A1c	0.0	-50	1.0	0.6	0.5	500	0.5	HClO ₄
4.1.1 A1d	0.0	50	1.0	0.6	0.5	500	0.5	none
4.1.4a, 4.1.5a, 4.1.5 A1	0.0 to -0.7	-50	1.1	0.7	2.0	200	1.0	HClO ₄
4.1.6a,b	0.0 to -0.7	-50	1.1	0.7	2.0	500	0.5	HClO ₄
4.1.6c,d	0.23 to 0.58 ^(**)	514 ^(**)	1.35	0.73	2.0	500	0.5	HClO ₄
4.1.7a,b,c	0.0 to -0.7	-50	1.1	0.7	2.0	500	0.5	HClO ₄
4.1.7 A1a,b,c	0.0 to -0.7	-50	1.0	0.6	0.5	500	0.5	HClO ₄
4.1.8c, 4.1.8 A1	0.0 to -0.7	-50	1.1	0.7	2.0	500	0.5	HClO ₄

^(*) potential listed versus RHE, measured versus Mercury/Mercurous Sulfide (Hg/Hg₂S, MMS) (0.6M K₂SO₄)

^(**) potential listed versus RHE, measured versus Silver/Silver Chloride (Ag/AgCl, SSC) (3.5M KCl)

Table A4.1 (continued).

Figure number	Potential interval (V vs. Pt)	Tip potential (mV vs. Pt)	PG (a.u.)	IG (a.u.)	CS (nA)	Scan size (nm)	Scan rate (Hz)	Electrolyte (0.1M)
4.1.10a,b	0.0	-50	1.0	0.6	0.5	500	0.5	HClO ₄
4.1.10d,e	0.0 to -0.7	-50	1.1	0.6	2.0	200	1.0	HClO ₄
4.1.10 A1	0.0	-50	1.0	0.6	0.5	500	0.5	HClO ₄
4.1.10 A2a,b	0.0 to -0.8	-50	1.0	0.6	2.0	200	1.0	HClO ₄
4.1.11, 4.1.11 A1, 4.1.11 A2	0.0 to -0.8	-50	1.0	0.6	2.0	200	1.0	HClO ₄
4.1.13a,b	0.0 to -0.7	-50	1.1	0.7	1.0	200	1.0	HClO ₄
4.1.13 A1	0.0 to -0.7	-50	1.1	0.7	1.0	500	0.5	HClO ₄
4.1.13 A2	0.0	-50	0.6	0.5	2.0	200	1.0	HClO ₄
4.1.14, 4.1.14 A1, 4.1.14 A2, 4.1.14 A3	0.0 to -0.7	-50	1.1	0.7	1.0	100	2.7	HClO ₄
4.2.2b ^(***)	-0.6 to 0.9	0	(****)	(****)	1.0	(****)	1.0	KOH
4.2.2c	0.6	-50	1.0	1.4	2.0	500	0.5	KOH
4.2.3a	0.0	0	1.0	0.6	0.5	500	0.6	none
4.2.5a, 4.2.5 A1, 4.2.6a, 4.2.6 A2	0.0 to 0.6	-50	1.7	1.2	1.5	500	0.5	KOH
4.2.6c, 4.2.6 A3, 4.2.6 A4	0.0 to 0.6	-50	2.0	1.4	1.5	500	0.5	KOH
4.2.7a,b, 4.2.7 A1a,c	0.0 to 0.6	-50	1.3	1.0	1.5	200	1.3	KOH
4.2.9a	0.0 to 0.6	-50	1.7	1.2	1.5	500	0.5	KOH

(***) Data taken from reference ^[118].(****) This information cannot be provided as the necessary data is not supplied in reference ^[118].

Table A4.2. List of CV-measurement-related specifications. The gas used for the saturation procedure corresponds to the atmospheric gas employed in the CV experiments. Values published in references ^[118], ^[175], ^[207], ^[213], and ^[267]. Please note that this table continues on the next page.

Figure	Potential interval (V)	Scan rate (mV·s ⁻¹)	Reference electrode	Counter electrode material	Measuring device	Electrolyte (0.1M)	Saturation and atmospheric gas
4.1.2a,b,c	0.2 to 1.2 (vs. RHE)	50	MMS	Pd ^(*)	VSP-300 potentiostat	HClO ₄	Ar
4.1.2d: session 1 session 2 session 3	-0.9 to 0.0 -0.8 to 0.0 -0.8 to 0.0 (vs. Pt)	50	Pt ^(**)	Pd ^(***)	Veeco Nanoscope Universal bipotentiostat	HClO ₄	air
4.1.2 A1: Pd(111) Pd(110) Pd(100)	0.2 to 1.2 (vs. RHE)	50	MMS	Pd ^(*)	VSP-300 potentiostat	HClO ₄	Ar
4.1.3: Pd(111) Pd(110) Pd(100)	-0.18 to 0.52 (vs. RHE)	50	MMS	Pd ^(*)	VSP-300 potentiostat	HClO ₄	H ₂
4.2.2a ^(****)	-0.8 to 1.0 (vs. Pt)	50	Pt ^(**)	C ^(*****)	Veeco Nanoscope Universal bipotentiostat	KOH	air
4.2.4 a	1.25 to 1.74 (vs. RHE)	10	MMO	C ^(*****)	CH Instruments Electrochemical Analyzer 660B (ALS)	KOH	Ar
4.2.4b red	0.03 to 0.6 (vs. Pt)	50	Pt ^(**)	C ^(*****)	Veeco Nanoscope Universal bipotentiostat	KOH	air

(*) wire, Ø: 0.5 mm, 99.95%, MaTeCK, Germany

(**) QRE, wire, Ø: 0.5 mm, 99.99%, MaTeCK, Germany

(***) curled wire, Ø: 0.25 mm, 99.95%, MaTeCK, Germany

(****) Data taken from reference ^[118].

(*****) rod, Ø: 0.5 mm, 99.95%, Goodfellow GmbH, Germany

(*****) cloth, EC-CC1-060T, ElectroChem Inc., USA

Table A4.2 (continued).

Figure	Potential interval (V)	Scan rate (mV·s ⁻¹)	Reference electrode	Counter electrode material	Measuring device	Electrolyte (0.1M)	Saturation and atmospheric gas
4.2.4b black	-0.65 to 0.8 (vs. Pt)	50	Pt ^(**)	C ^(****)	Veeco Nanoscope Universal bipotentiostat	KOH	air
4.2.4 c	0.03 to 0.6 (vs. Pt)	50	Pt ^(**)	C ^(****)	Veeco Nanoscope Universal bipotentiostat	KOH	air

^(**) QRE, wire, Ø: 0.5 mm, 99.99%, MaTeck, Germany

^(****) rod, Ø: 0.5 mm, 99.95%, Goodfellow GmbH, Germany

Appendix C: Additional Information About the Pd Investigations

This subchapter provides additional information and measurements to supplement the findings presented in **Subchapter 4.1**, analyzing the Pd single crystals.

Table A4.3. This table lists all FWHM values and the standard errors determined from the Gauss fits during the noise evaluation on Pd crystals in **Subchapter 4.1**. The “Label” column contains the numbers shown in the respective figures for distinct identification of the analyzed areas. Please note that this table continues on the next page.

Figure	Position	Reaction	Label	FWHM	Error
4.1.5b,c	upper Pd(111) step I	HER	2	0.75050	0.02890
4.1.5c	lower Pd(111) step I	HER	1	0.26358	0.01111
4.1.5b,c	upper Pd(111) step II	HER	4	0.62932	0.01317
4.1.5c	lower Pd(111) step II	HER	3	0.57053	0.01252
4.1.5b,c	upper Pd(111) step III	HER	6	0.47713	0.01574
4.1.5c	lower Pd(111) step III	HER	5	0.37120	0.01004
4.1.5d	lower Pd(111) terrace	HER	7	0.29776	0.00378
4.1.5d	lower Pd(111) terrace	Off	8	0.26062	0.00184
4.1.8a	~3.4nm high Pd(100) step	HER	1	0.32981	0.00985
4.1.8a	~3.4nm high Pd(100) step	Off	2	0.19500	0.00536
4.1.8b	annealed Pd(100) terrace	Off	3	0.10542	0.00087
4.1.8b	annealed Pd(100) terrace	HER	4	0.12302	0.00121
4.1.12a	Pd(111) _c concave region	HER	-	0.37156	0.02228
4.1.12a	Pd(111) _c convex region	HER	-	0.50774	0.01574
4.1.12b	Pd(111) _c concave region	Off	-	0.30954	0.01775

Table A4.3 (continued).

Figure	Position	Reaction	Label	FWHM	Error
4.1.12b	Pd(111) _c convex region	Off	-	0.37773	0.02113
4.1.15a	Pd(100) _c concave region	HER	-	0.37156	0.02228
4.1.15a	Pd(100) _c convex region	HER	-	0.50774	0.01574
4.1.15b	Pd(100) _c concave region	Off	-	0.30954	0.01775
4.1.15b	Pd(100) _c convex region	Off	-	0.37773	0.02113

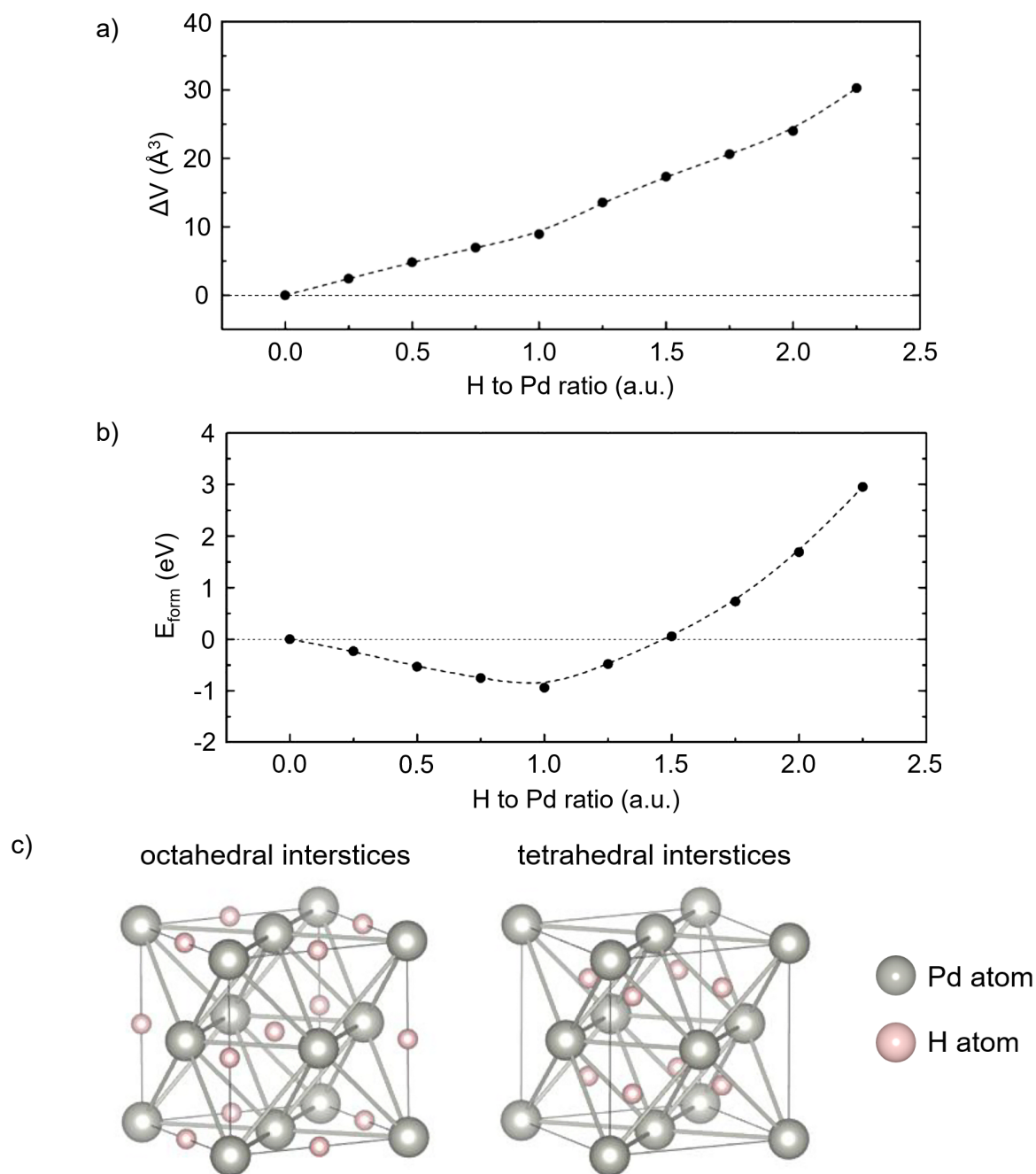


Figure 2.3.9 A1. **a)** Volume and **b)** total formation energy dependency to the ratio of absorbed H per Pd atom. It is important to note that in these calculations, H occupies only octahedral interstices for H to Pd ratios lower than 1.0, but also on tetrahedral interstices for higher ones. **c)** Illustration of by H atoms occupying octahedral and tetrahedral gaps within the Pd crystal. Figures adapted from reference ^[175] and licensed under CC BY 4.0 ^[87].

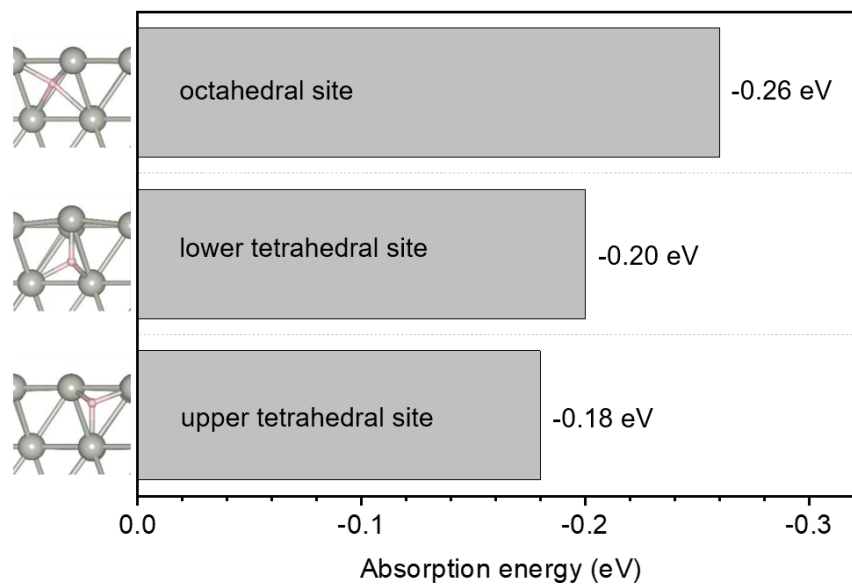


Figure 2.3.9 A2. Absorption energies on Pd(111). The octahedral site has the highest absorption energy and, thus, is expected to be the most favored site for hydrogen adsorption. Adapted from reference ^[175] and licensed under CC BY 4.0 ^[87].

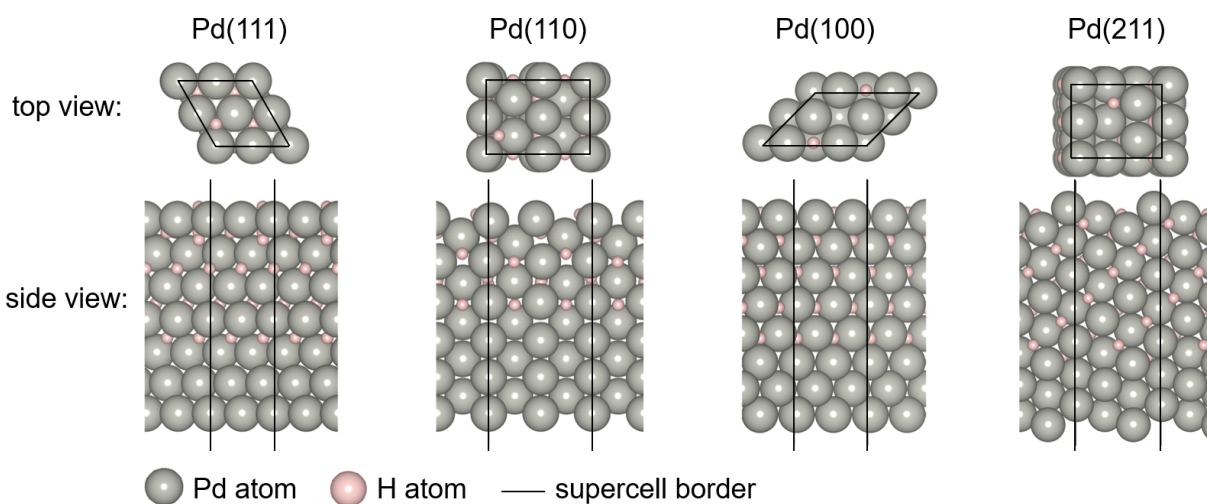


Figure 2.3.9 A3. Schematic view of different Pd surface facets after hydrogen absorption from the top and side perspective. The rose-colored spheres represent the absorbed and intercalated hydrogen atoms on the grey Pd atoms, illustrating the case with the maximum number of 4 PdH sublayers. The black lines highlight the supercells used for the computational investigations. More information about crystal orientations is provided in **Subchapter 2.4.1**. Adapted from reference ^[175] and licensed under CC BY 4.0 ^[87].

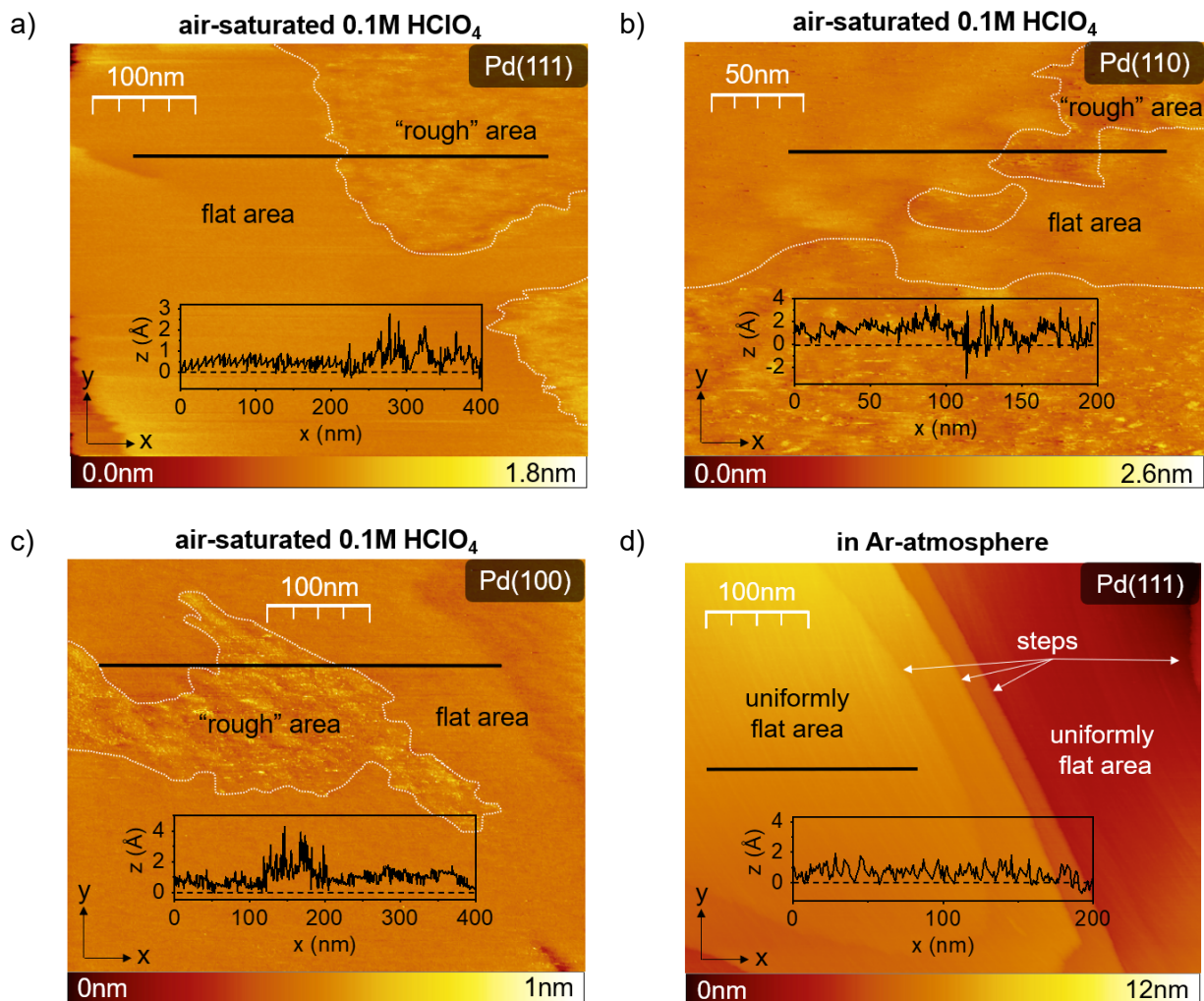


Figure 4.1.1 A1. Comparison of "rough" and flat areas on different single Pd crystals directly after annealing without prior electrochemical experiments. **a)**, **b)**, and **c)** present STM measurements in air-saturated 0.1M HClO₄, which reveal very flat areas and "rough" sections with a height difference up to the diameter of a single Pd atom. This phenomenon was found for all investigated crystallographic planes. Moreover, a comparison measurement on Pd(111) in Ar-saturated 0.1M HClO₄ within an Ar-atmosphere (see **Subchapter 3.1.3**) is presented in **d)**. Since, at his additional measurement, the entire time period between annealing and measuring the crystal was stored in the Ar-atmosphere, the initial hypothesis that these rough areas could be the nucleus of surface corrosion due to oxidation seems to be more unlikely. However, the origin of these rough and flat areas remains unclear at this stage. Data of **a)** and **c)** published in reference ^[175].

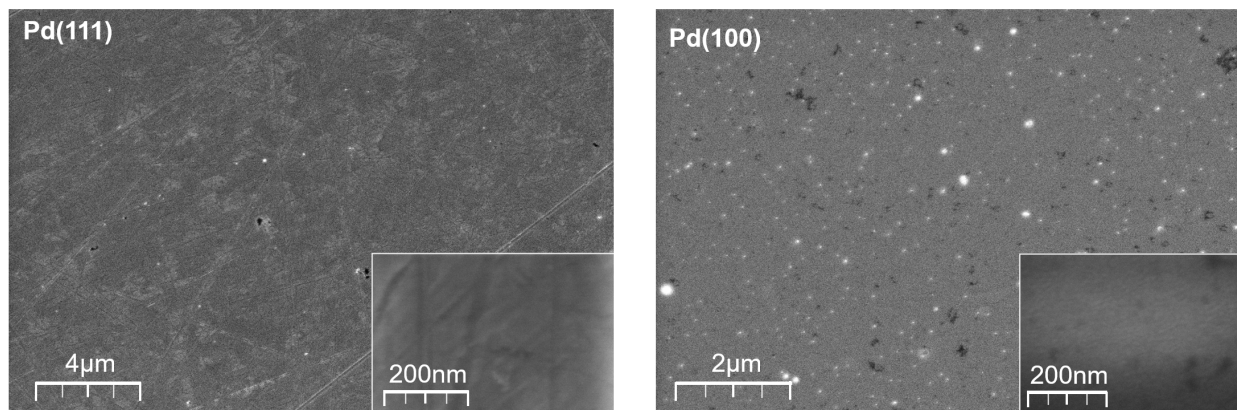


Figure 4.1.1 A2. SEM images of Pd single crystal surfaces after EC measurements for different magnifications. Large, very flat areas mainly shape the morphology of both samples. The polishing procedure probably causes scratches on the Pd(111) crystal, which are visible on the left side. An advantage of small-scale investigations is that the operator is able to choose the observed surface as required. Consequently, the *n*-EC-STM measurements were performed on carefully selected atomically flat areas. Moreover, the bright white dots mainly present on the Pd(100) are likely to be non-conductive particles, which might be powder from insufficient cleaning after the last experiment. Consequently, this image underlines the importance of proper electrochemical cleaning and annealing before each experiment, as described in **Subchapter 3.2.1**.

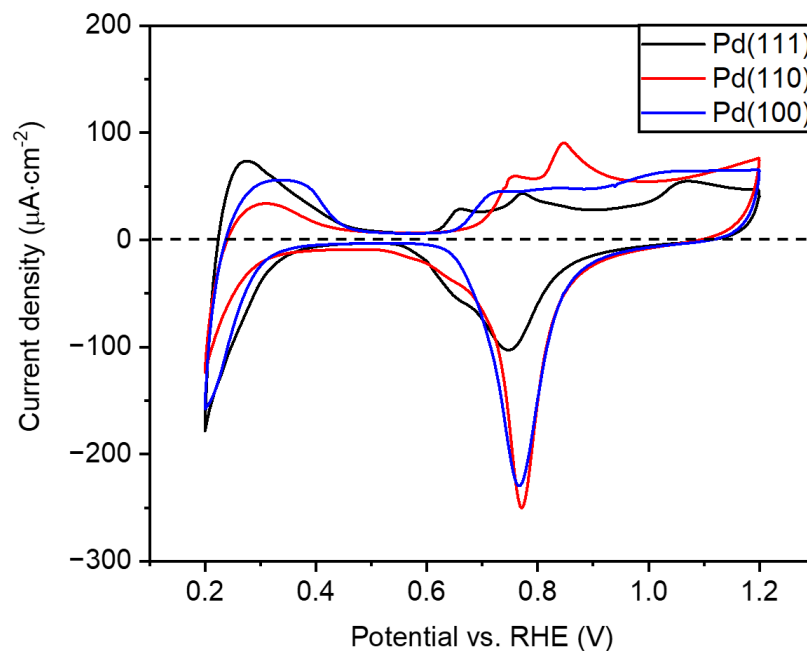


Figure 4.1.2 A1. CV measurements, which represent the potential-current relation for cycles captured after at least 30 laps. In contrast to **Figure 4.1.2**, which shows the first cycles directly after annealing, the characteristic peaks are no longer visible. This circumstance indicates a change in morphology due to cycling. Data published in reference ^[175].

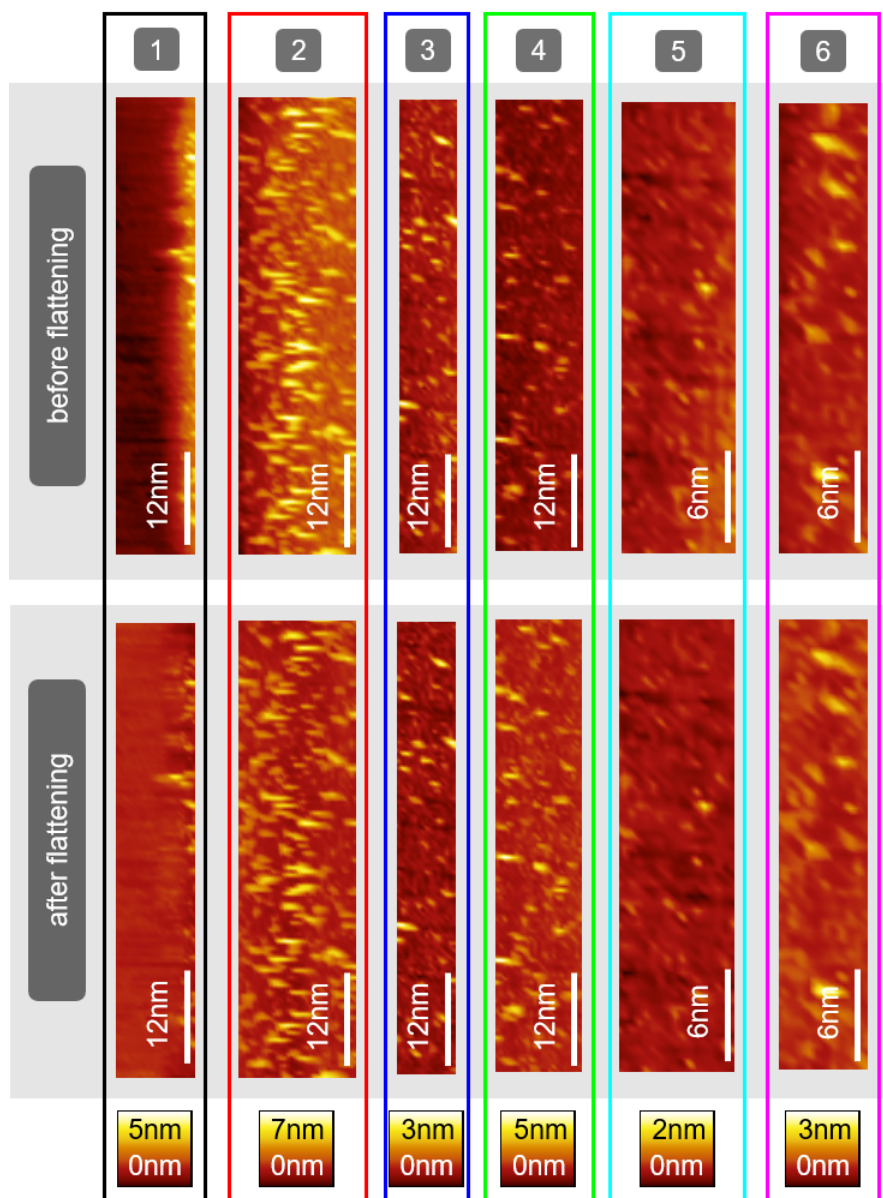


Figure 4.1.5. A1. Extracts from **Figure 4.1.5a** of the areas used for the noise evaluation are shown in **Figure 4.1.5b, c, and d**. In order to reduce the impact of the height difference at the step on the outcome of the evaluation, the areas at the step edges were leveled by using the WSxM tool “Flatten” before the computation started. During this procedure, only the rough height difference gets equalized while the surface roughness, and thus, the noise peaks remain unaltered. For better illustration, the upper row of the image demonstrates the raw sections, while the lower one displays the corresponding areas corresponding to the color code after flattening. More information on the “Flatten” function is provided in **Subchapter 3.4.1** and reference ^[261]. Data published in reference ^[175].

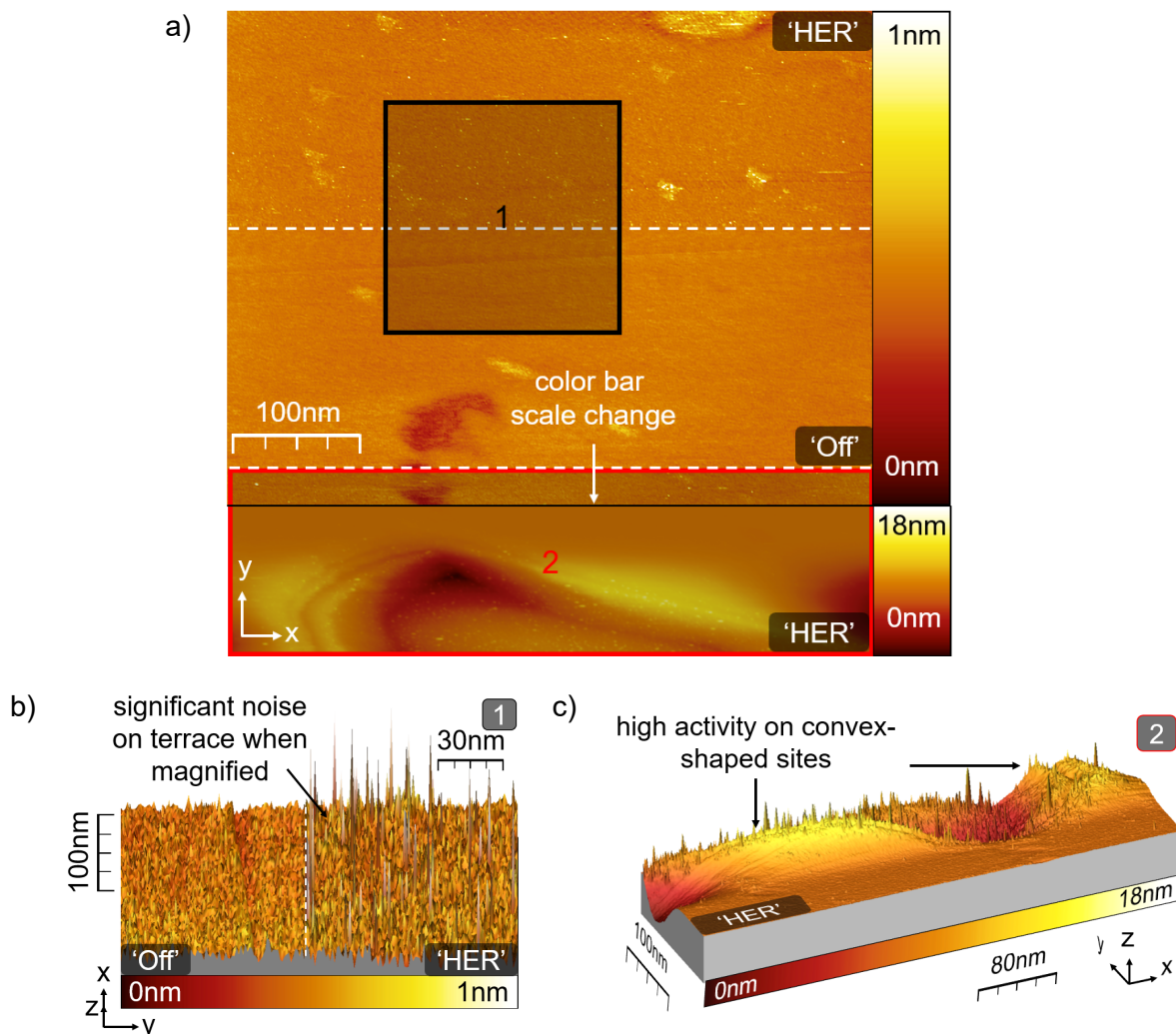


Figure 4.1.7 A1. Additional *n*-EC-STM measurement on freshly annealed Pd(100). **a)** The white dashed lines separate the regions for ‘HER’ and reaction ‘Off’ while the black and red frames highlight the positions of the three-dimensional illustrations in **b)** and **c)**. It is important to note that the upper area, split by a solid black line, is presented with a height interval 18 times smaller than the lower part. This divided presentation of the measurement is required for a detailed observation of the surface structures and the noise in the upper section of the image. With this adjustment, even the small noise in **b)** which is lower than 1nm, and the higher noise in **c)** becomes visible. For comparison, the “flat” terrace in the front of **c)** equals the noisy part on the right side of **b)**. Consequently, these images demonstrate the importance of conscientiously evaluating all areas of a sample, even if the initial impression does not indicate the necessity. Data of all figures published in reference ^[207].

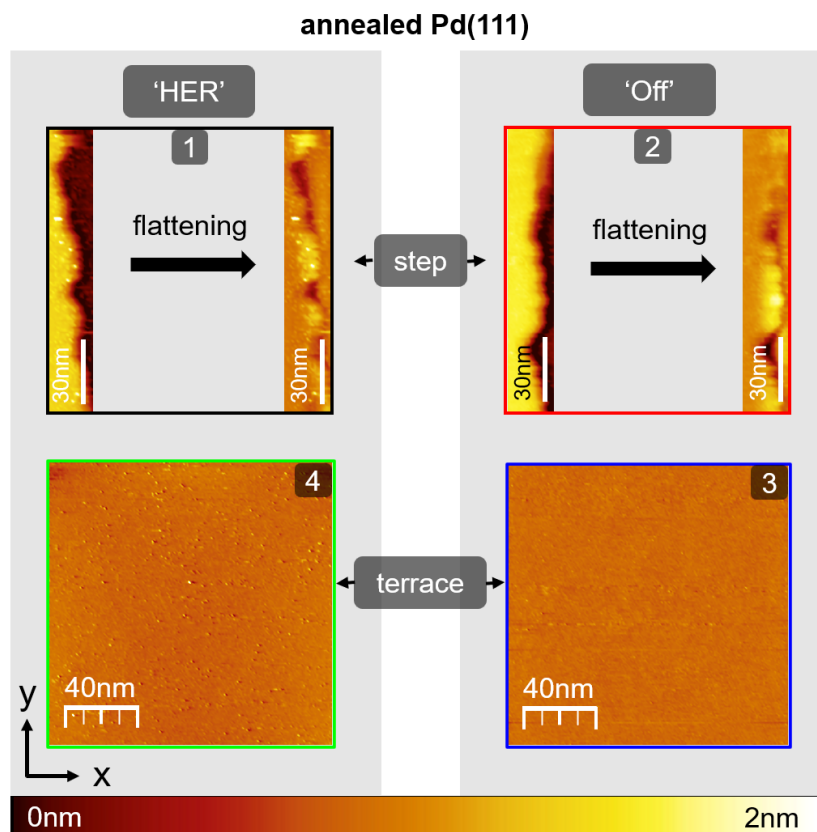


Figure 4.1.8 A1. Extracts of the regions used for the noise analysis in **Figure 4.1.8a and b** for 'HER' (left side) and reaction 'Off' (right side). The areas presenting the step edges are analogous to **Subchapter 3.4.1**, flattened using the WSxM software ^[261].

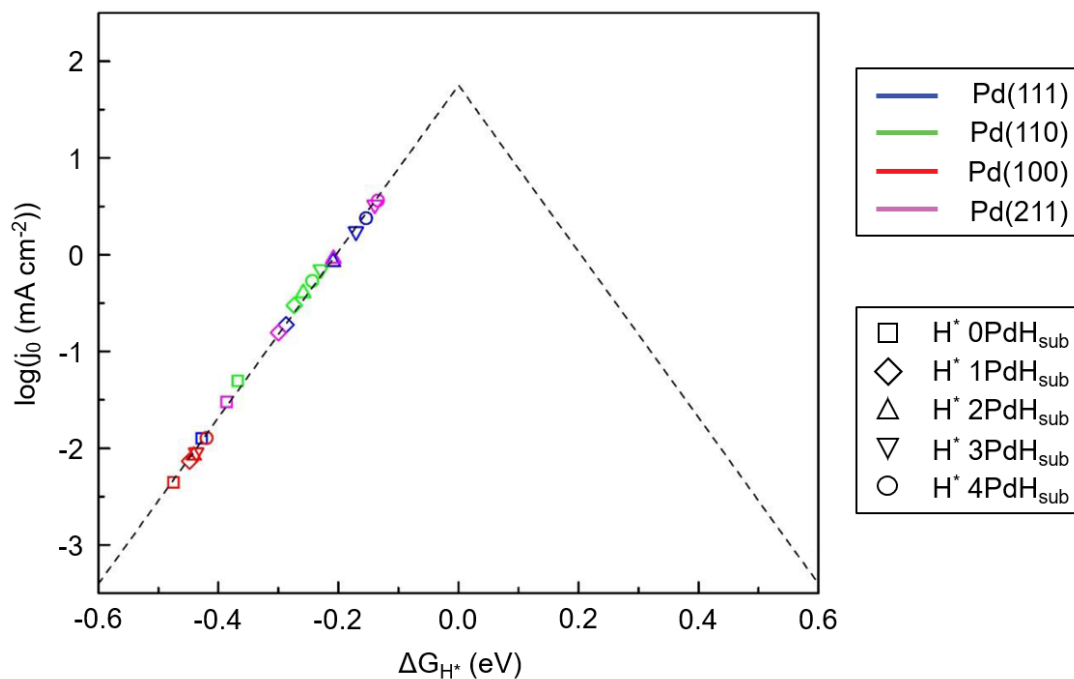


Figure 4.1.9 A1. Volcano plot showing the exchange current densities j_0 calculated at 0V versus SHE in correlation with the Gibbs free energy ΔG_{H^+} for 0 to 4 PdH sublayers in Pd(111) (blue), Pd(110) (green), Pd(100) (red), and Pd(211) (purple) single crystals. As elucidated in **Subchapter 4.1.2.3**, the calculations reveal a linear trend with Pd(211) and Pd(111) showing the highest values for j_0 for the best catalytic properties of the investigated system for higher numbers of PdH sublayers. Adapted from reference ^[175] and licensed under CC BY 4.0 ^[87].

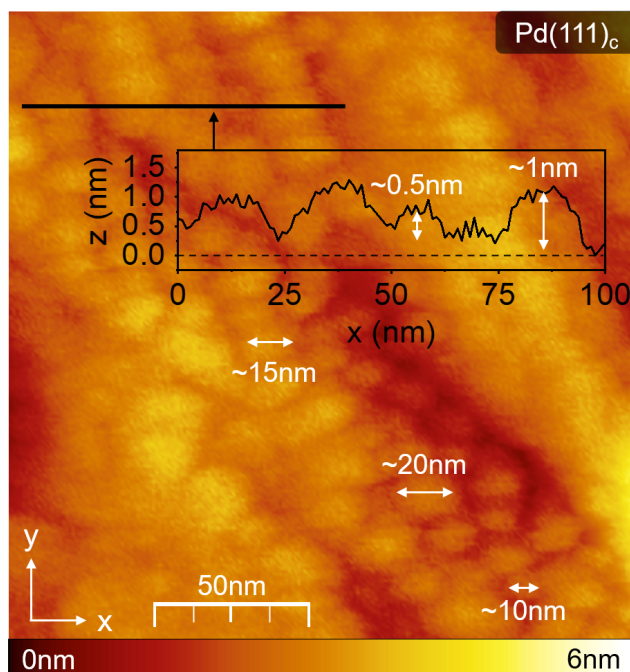


Figure 4.1.10 A1. Magnified view of an EC-STM image on Pd(111)_c for reaction ‘Off’. This image was captured after eight electrochemical cycles between 0.2V and 1.2V versus RHE. The black line marks the position of the presented line scan. Here, two double arrows exemplify possible heights of the hilly surface with a length of ~0.5nm and ~1nm. In addition, three different-sized hills are surveyed, showing an approximate diameter of ~10nm, ~15nm, and ~20nm. This variation in size demonstrates the approximate dimensions of the hills but also indicates the diversity of their shapes and sizes. Data published in reference ^[207].

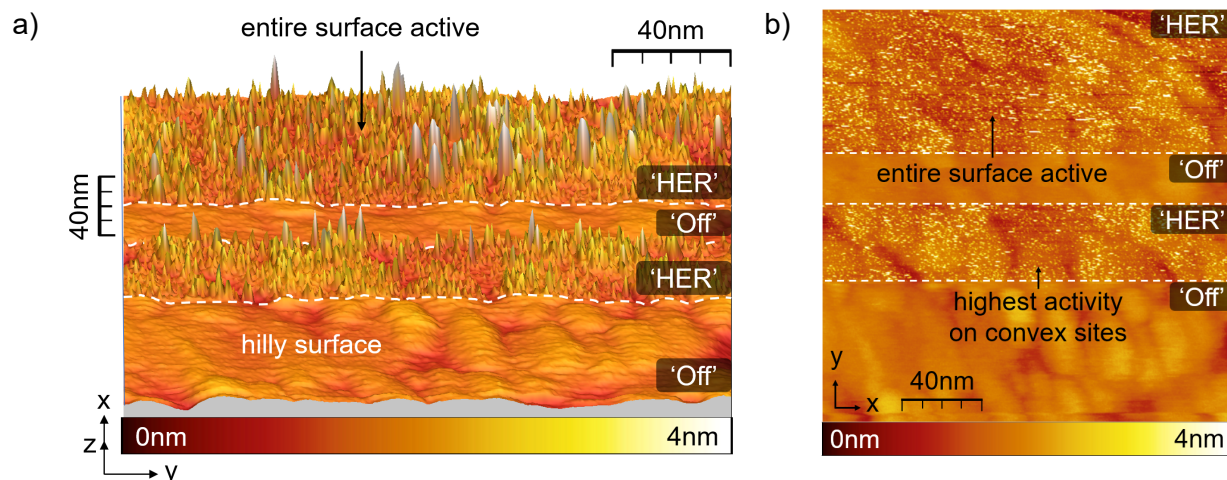


Figure 4.1.10 A2. Additional *n*-EC-STM measurement on Pd(111)_c in air-saturated 0.1M HClO₄ in air atmosphere in **a)** three-dimensional and **b)** two-dimensional perspective. The upper 'HER' part of the image reveals high activity all over the surface, while the section for 'HER' in the middle of the image shows high noise peaks, mainly on convex structures. Furthermore, a hilly morphology is visible all over the surface for reaction 'On'. Data of both figures published in reference ^[175].

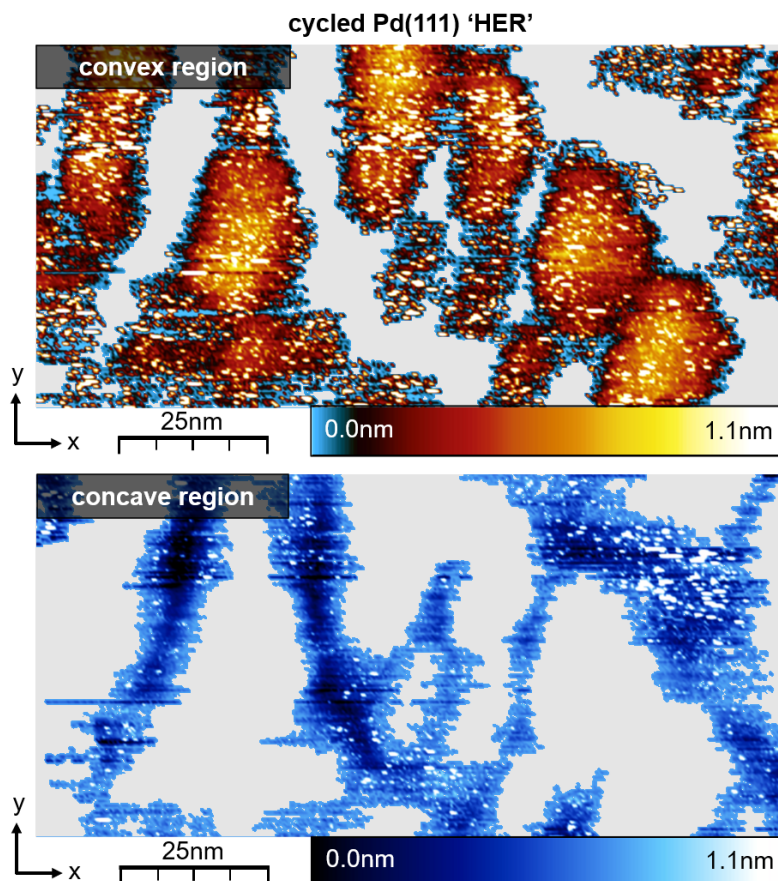


Figure 4.1.11 A1. Extracts of the individual areas for 'HER', which provide the data used for the noise analysis in **Figure 4.1.12**. The upper image showcases the convex structures using an orange-red color bar, while the lower one represents the concave regions in blue shades. On points where a high noise was detected, white dots appeared. Data published in reference ^[175].

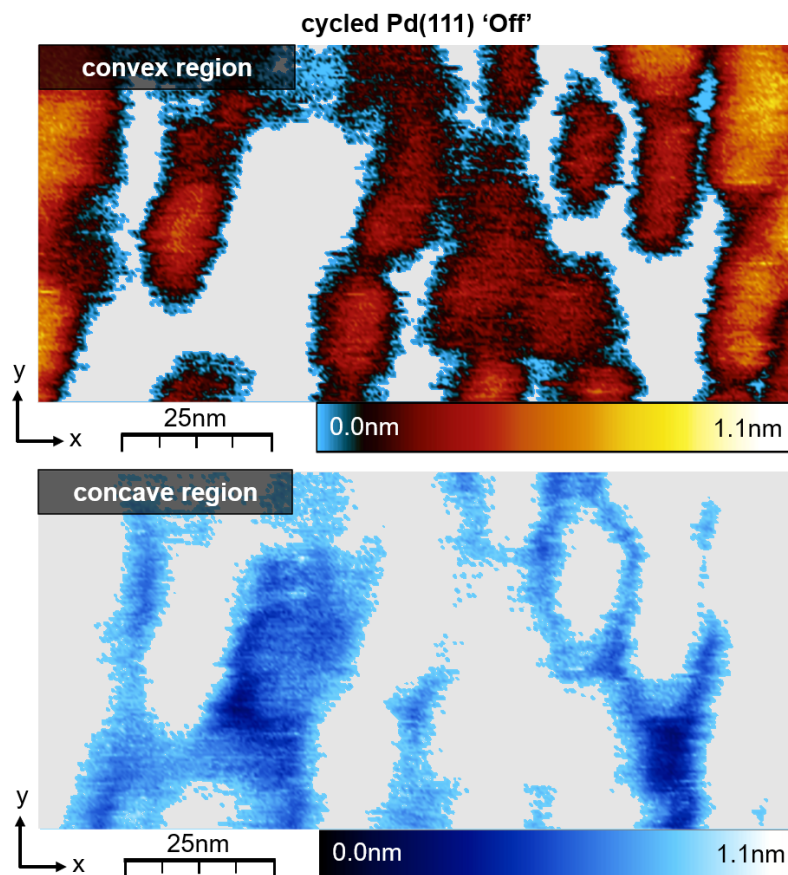


Figure 4.1.11 A2. Extracts of the individual areas for reaction 'Off', which provide the data used for the noise analysis in **Figure 4.1.12**. In contrast to **Figure 4.1.11 A1**, no white dots are visible here due to the absence of noise peaks. Data published in reference ^[175].

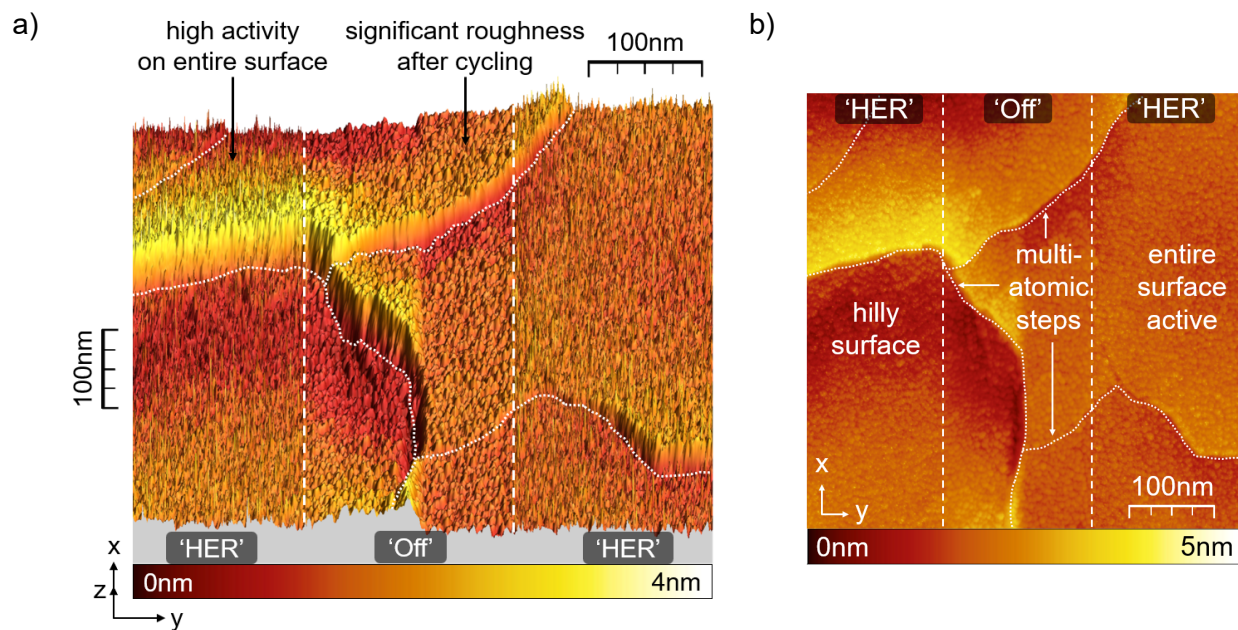


Figure 4.1.13 A1. Additional *n*-EC-STM measurement in air-saturated 0.1M HClO₄. The left and right parts of the image, captured under 'HER' conditions, reveal high noise peaks all over the surface. In contrast, the actual hilly surface without any noise peaks is visible in the middle section. Interestingly, different from the observations on freshly annealed Pd(100), the step edges highlighted by white dotted lines are as active as the surrounding surface and do not exhibit exceptional noise. **a)** and **b)** show the identical measurements in three-dimensional and two-dimensional views. Data of both figures published in reference ^[175].

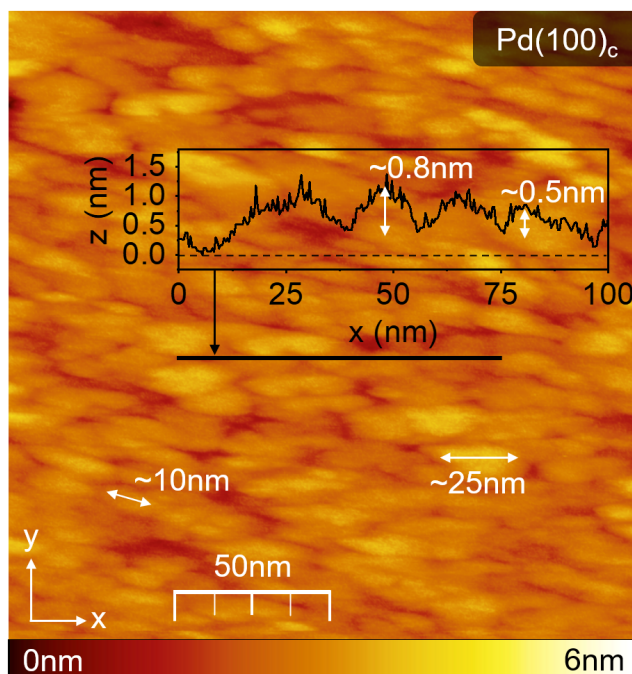


Figure 4.1.13 A2. Magnified view of an EC-STM image on Pd(100)_c for reaction ‘Off’ in air-saturated 0.1M HClO₄. This image was captured after five electrochemical cycles between 0.2V and 1.2V versus RHE. The inserted line scan, extracted at the position indicated by the solid black line, demonstrates the varying altitudes of the individual hills. In addition, the white double arrows represent the spectrum encompassing the diameters of the observed hills. Similar to the findings on Pd(111)_c shown in **Figure 4.1.10 A1**, a large variety of shapes and sizes were also found on Pd(100)_c. Data published in reference ^[207].

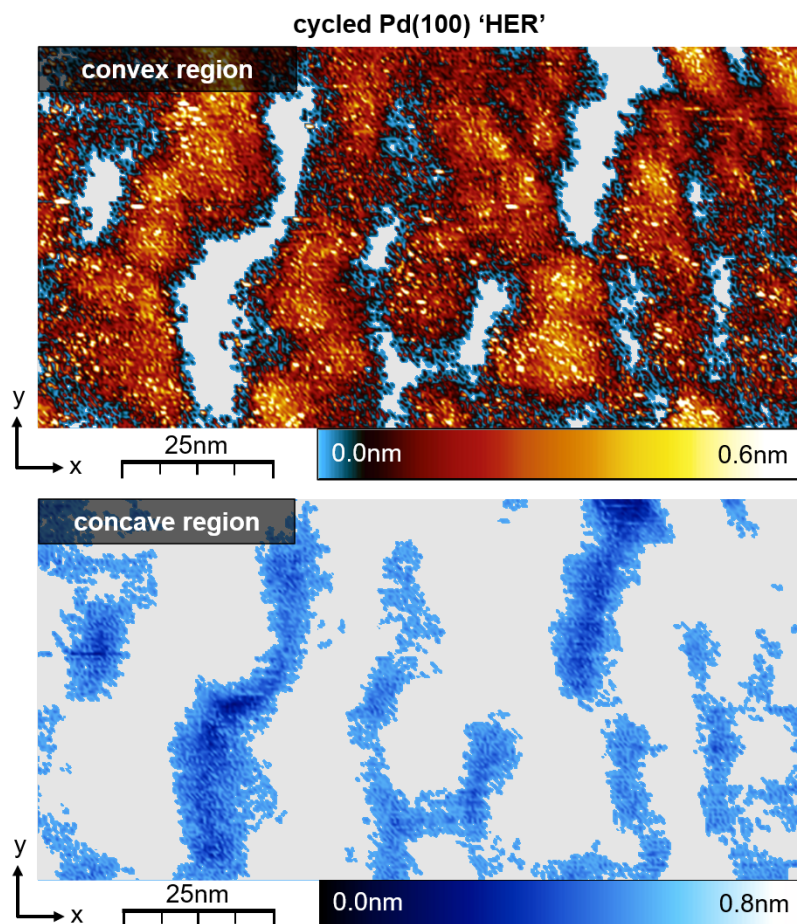


Figure 4.1.14 A1. Extracts of convex-shaped (upper image) and concave-shaped (lower image) regions which are shown in **Figure 4.1.14** for 'HER'. The data extracted from these images was used for the noise evaluation in **Figure 4.1.15**. Data published in reference ^[175].

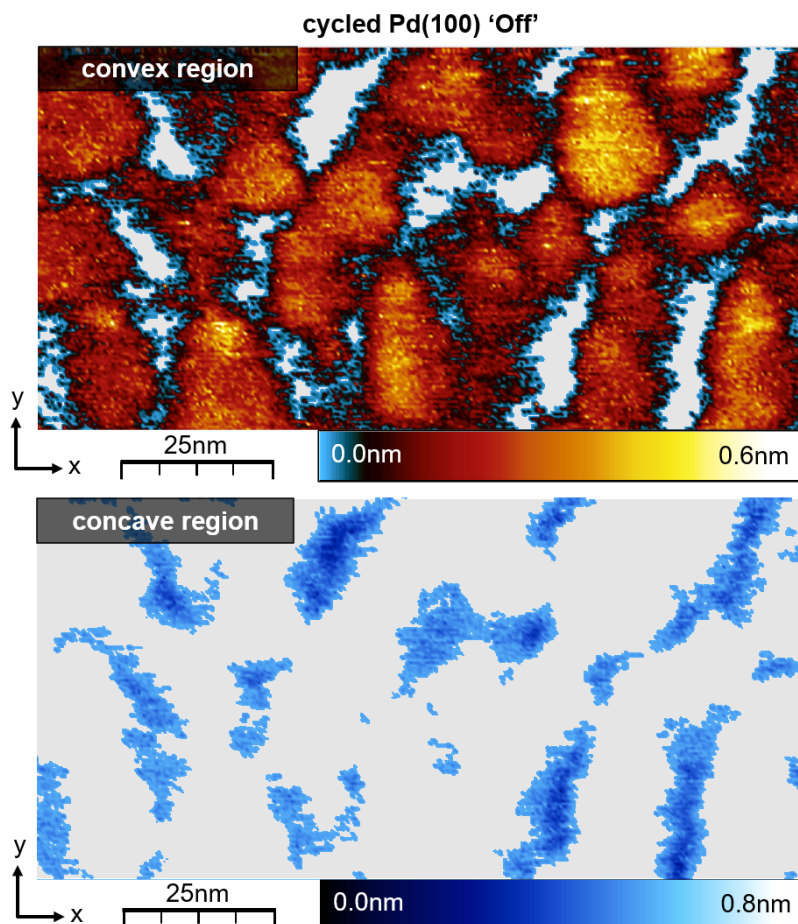


Figure 4.1.14 A2. Extracts of convex-shaped (upper image) and concave-shaped (lower image) regions which are shown in **Figure 4.1.14** for reaction 'Off'. Analogous to **Figure 4.1.14 A1**, the data extracted from these images was used for the noise evaluation in this chapter. Data published in reference ^[175].

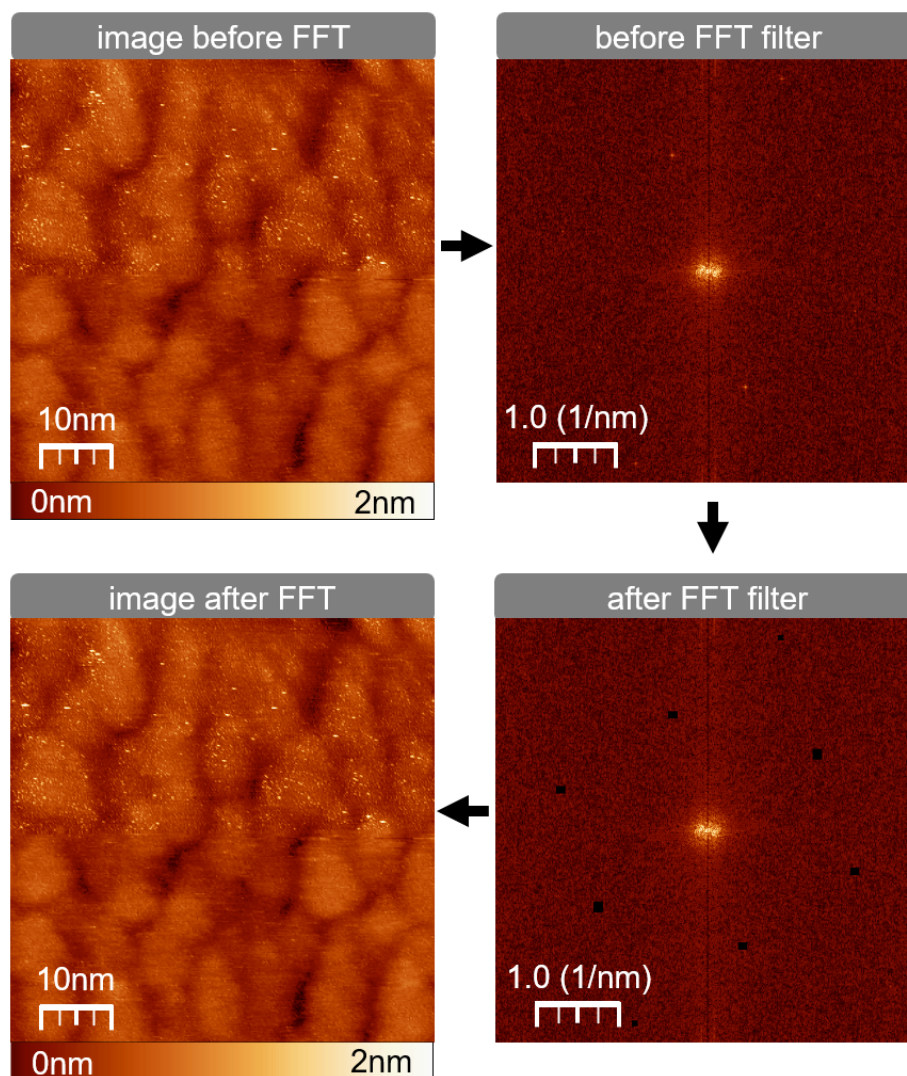


Figure 4.1.14 A3. FFT filtering process of **Figure 4.1.14**, as introduced in **Subchapter 3.4.1**. The step-by-step FFT filtering process starts with the raw image on the top left. Here, some regular stripes, which have an artificial origin, cover the entire image. The top right images represent the Fourier plane, where the bright dots and lines in the outer area contain these stripes' information. In the next step, illustrated on the bottom right side, the artificial noise is cut out at the black highlighted positions. The resulting image on the bottom left side reveals the inverse Fourier transformed image showing fewer artificial structures, allowing better optical visualization of the sheet. Data published in reference ^[175].

Appendix D: Additional Information About the MnO₂NS/HOPG Investigations

This subchapter provides additional information and measurements to supplement the findings presented in **Subchapter 4.2**, discussing the HOPG support and the MnO₂NS/HOPG sample.

Table A4.4. Summary of all FWHM values and their corresponding error extracted from the Gaussian fits used for the roughness analysis on MnO₂NS/HOPG and HOPG in **Subchapter 4.2**. The labels describe the positions in the respective figures for a transparent allocation.

Figure	Position	Reaction	Label	FWHM	Error
4.2.6 b	MnO ₂ NS plateau	OER	b1	0.11564	0.00489
4.2.6 b	HOPG terrace	OER	b2	0.06076	0.00045
4.2.6 b	MnO ₂ NS plateau	Off	b3	0.05221	0.00048
4.2.6 b	HOPG terrace	Off	b4	0.05085	0.00061
4.2.6 d	upper HOPG terrace	OER	d1	0.05313	0.00146
4.2.6 d	lower HOPG terrace	OER	d2	0.05494	0.00115
4.2.6 d	upper HOPG terrace	Off	d3	0.03387	0.00058
4.2.6 d	lower HOPG terrace	Off	d4	0.03472	0.00082
4.2.9 b	MnO ₂ NS step	OER	5	0.16659	0.00504
4.2.9 b	MnO ₂ NS step	Off	6	0.08447	0.00273
4.2.9 c	MnO ₂ NS plateau	OER	1	0.11564	0.00489
4.2.9 c	MnO ₂ NS plateau	Off	3	0.05844	0.00058
4.2.9 d	HOPG terrace	OER	2	0.06076	0.00045
4.2.9 d	HOPG terrace	Off	4	0.05085	0.00061

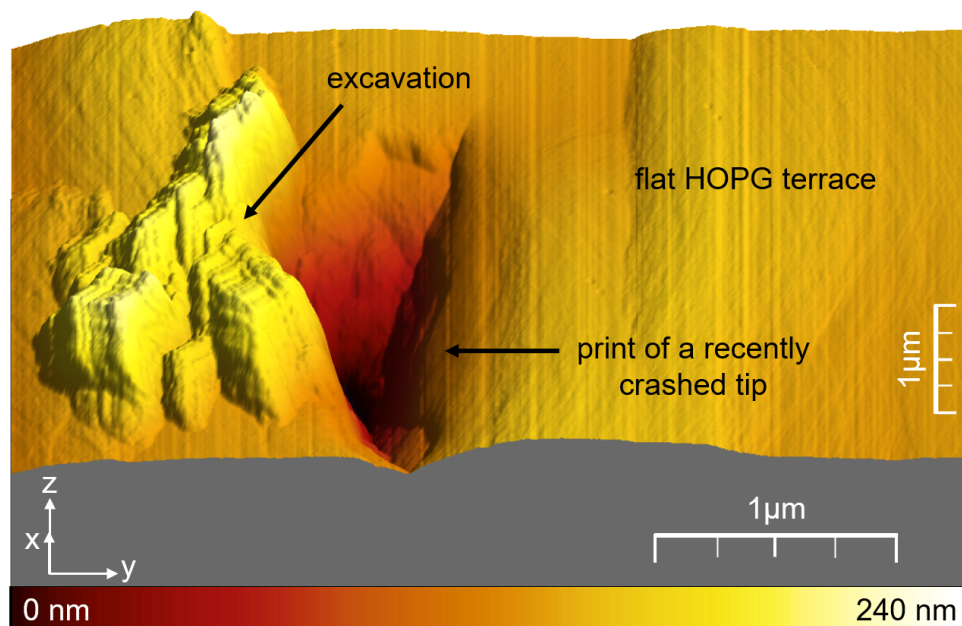


Figure 3.2.4 A1. $4\mu\text{m}$ to $4\mu\text{m}$ image of a tip crash on pure HOPG. A crater of approximately $0.7\mu\text{m}$ to $3.0\mu\text{m}$ with a depth of about 225nm demonstrates the damage that a crashed STM tip could cause on the sample surface. Interestingly, at the excavation, the layered graphene structure is apparent. This unique image provided a print of the STM tip's apex, and it was possible to capture it due to the coincidence that this collision did not destroy the STM tip.

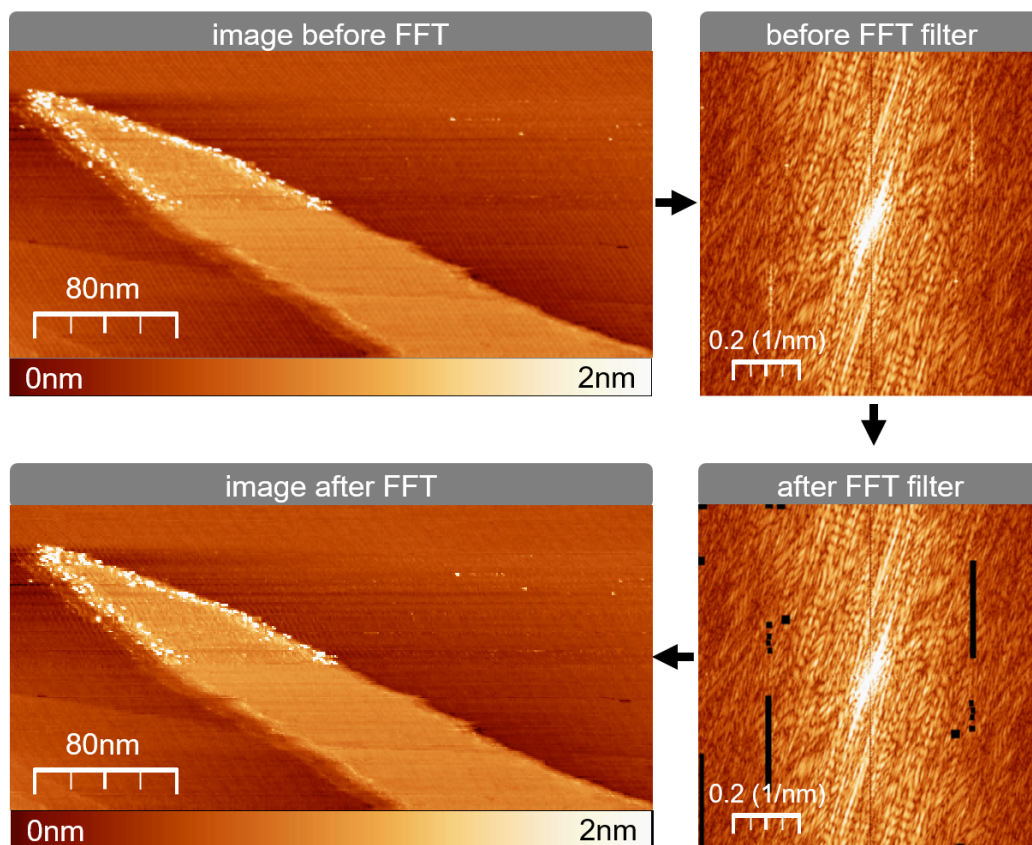


Figure 4.2.5 A1. FFT filtering procedure applied at the *n*-EC-STM measurement in **Figure 4.2.5**. When comparing the images before and after FFT, a significant reduction in the intensity of the vertical stripes is visible. However, as discussed in **Subchapter 3.4.1**, by this method, the electrochemically induced noise is not affected by the filtering. Data published in reference ^[213].

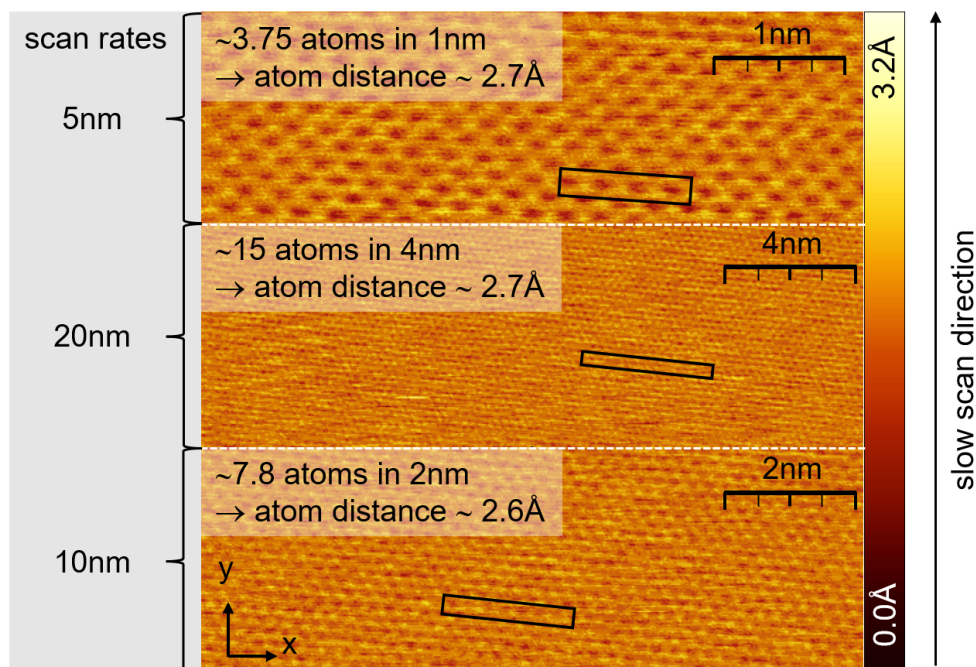


Figure 4.2.5 A2. STM measurement in air captured at different scan sizes on pure HOPG, showing the typical honeycomb pattern. The slow scan direction indicates the observed width in the x-direction of 10nm at the measurement's beginning. The white dashed lines show the positions where the scan size was changed to 20nm and 5nm from down to up, respectively. As expected, when only the scan size value is changed while holding the remaining STM settings, the size of the observed structures changes. This circumstance verifies the observed morphology as an actual atomically resolved surface. Moreover, it is possible to calculate the atom distances when counting the numbers of selected atoms within a local honeycomb arrangement that fit into the respective illustrated scales of 2nm, 4nm, and 1nm from down to up. The determined values between 2.6Å and 2.7Å for the distance between two honeycombs are very close to the theoretical value of 2.5Å, as discussed in **Subchapter 2.4.2** and reference ^[241]. This measurement underlines the ability of the used multimode to reach atomic resolution.

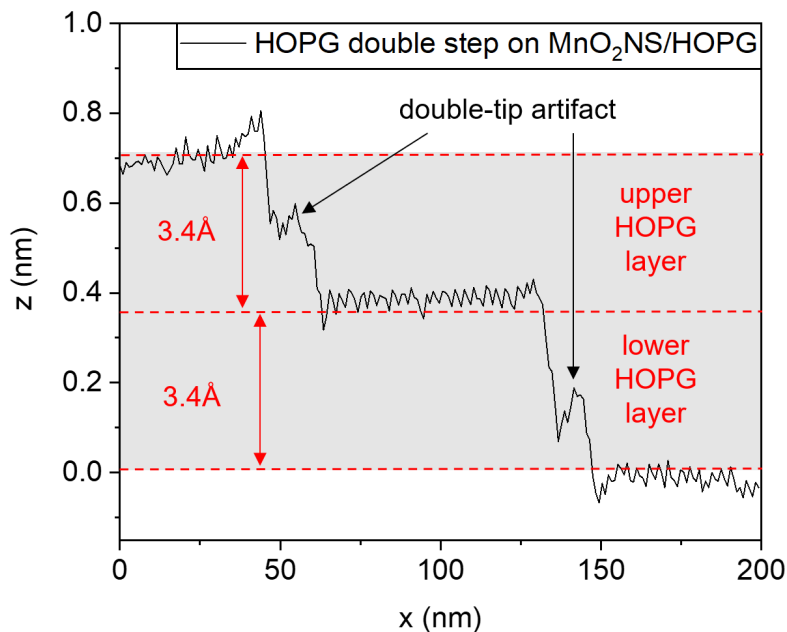


Figure 4.2.6 A1. Line scan highlighted in **Figure 4.2.6 A4b** at position III as a white solid line, representing the height profile of **Figure 4.2.6c**. The two prominent steps, which wrongly seem to consist of two double-layered steps in the two-dimensional image, are actually two single-layered HOPG steps with artifacts. As discussed in **Subchapter 2.3.3**, the initially supposed double step might be an artifact that originates from an STM's double-tip since the detected intermediate steps with a height of about 0.2nm are too small to be an actual atomic structure on the surface. Furthermore, the red two-sided arrows with a height of the theoretical value of 0.34nm indicate HOPG as the sheet material in this case ^[242]. It is important to note that this graph was flattened in the z-direction by subtracting $0.0025\text{nm} \cdot \epsilon$ for each x value, while ϵ is the number of captured points in the x-direction. This adjustment results in a linear rising shift in the z-offset for increasing x-values. Consequently, it counterbalances the shift in the initial data to analyze the actual step height. Compared to the raw data, from left to right, the second x value is shifted in the z-direction by -0.0025nm, the third one by -0.005nm, and the last one by -0.51nm (for 205 x-values). This processing compensates for the artificial stretching of the graph, which originated in an unsuitable selection of the z-offset by the STM device's feedback loop without significantly affecting the actual morphology. Data published in reference ^[213].

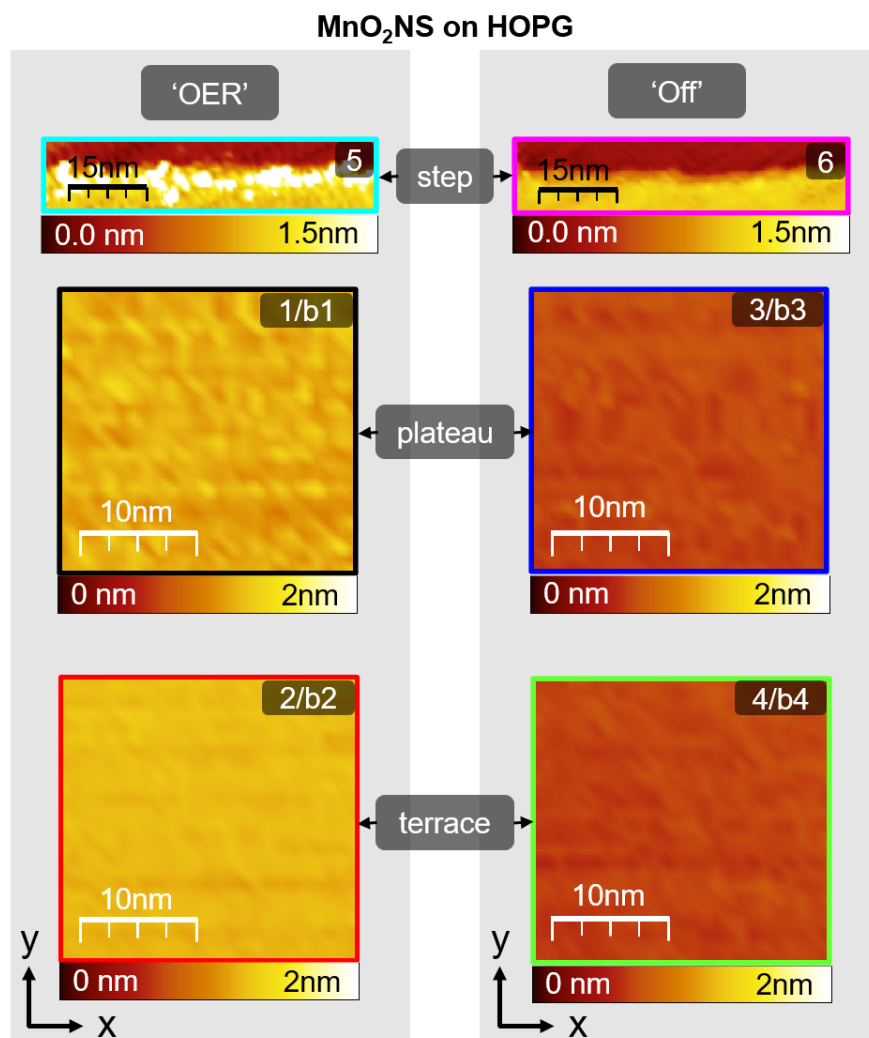


Figure 4.2.6 A2. Summary of the magnified areas, which are highlighted in **Figure 4.2.6a** for the terrace and **Figure 4.2.9a** for the step edges (positions 5 and 6). Even without further analysis, a difference in roughness is visible for 'OER' on the step edges and the plateau under 'OER' conditions. Data published in reference ^[213].

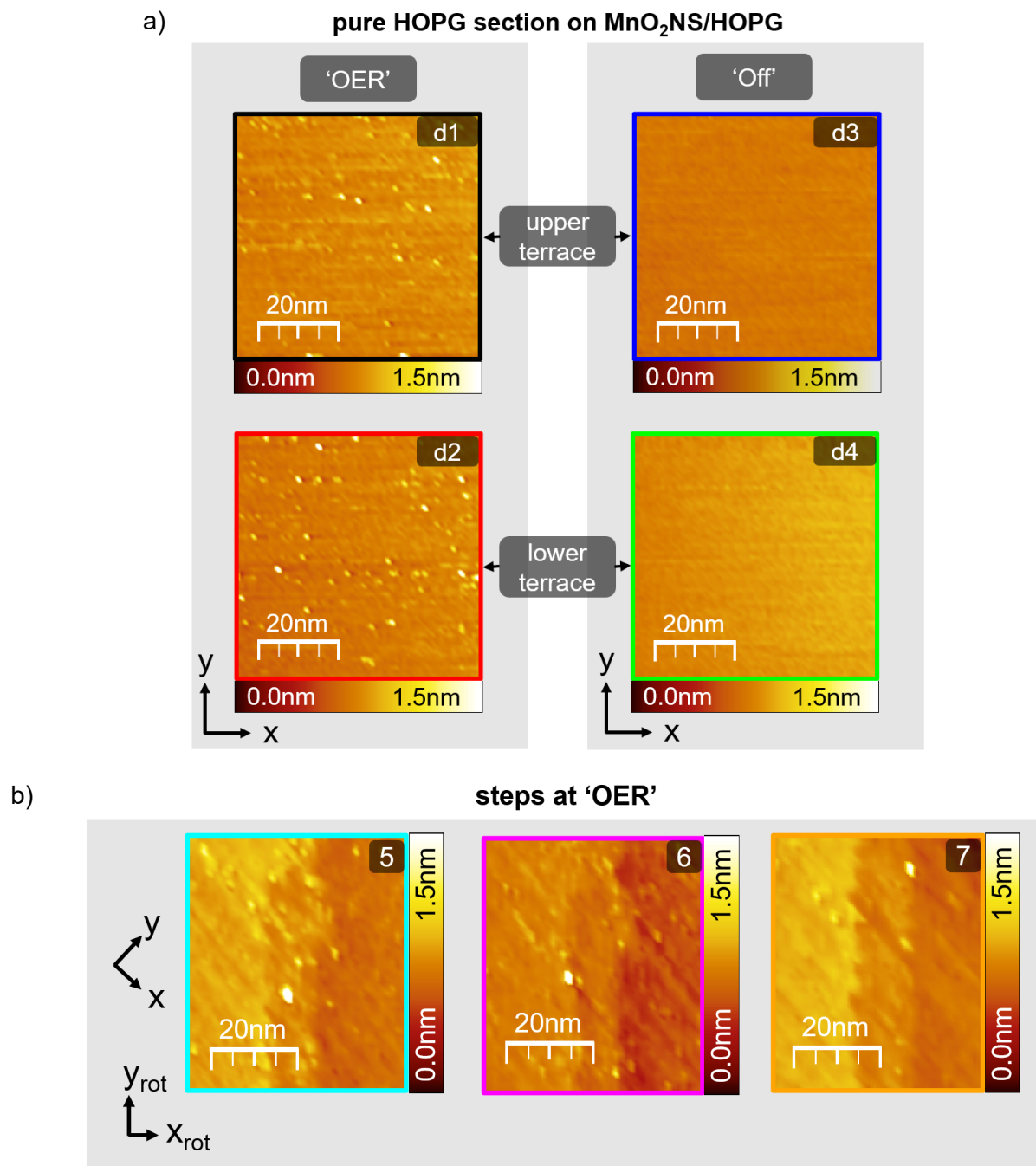


Figure 4.2.6 A3. Magnified areas highlighted in **Figure 4.2.6c** and in **Figure 4.2.6 A4b**. For 'OER', white dots on a) the terrace site and b) step edges screen the increased activity. The directions x_{rot} and y_{rot} present the orientations after the rotation of the x and y axes, respectively. Data of both figures published in reference ^[213].

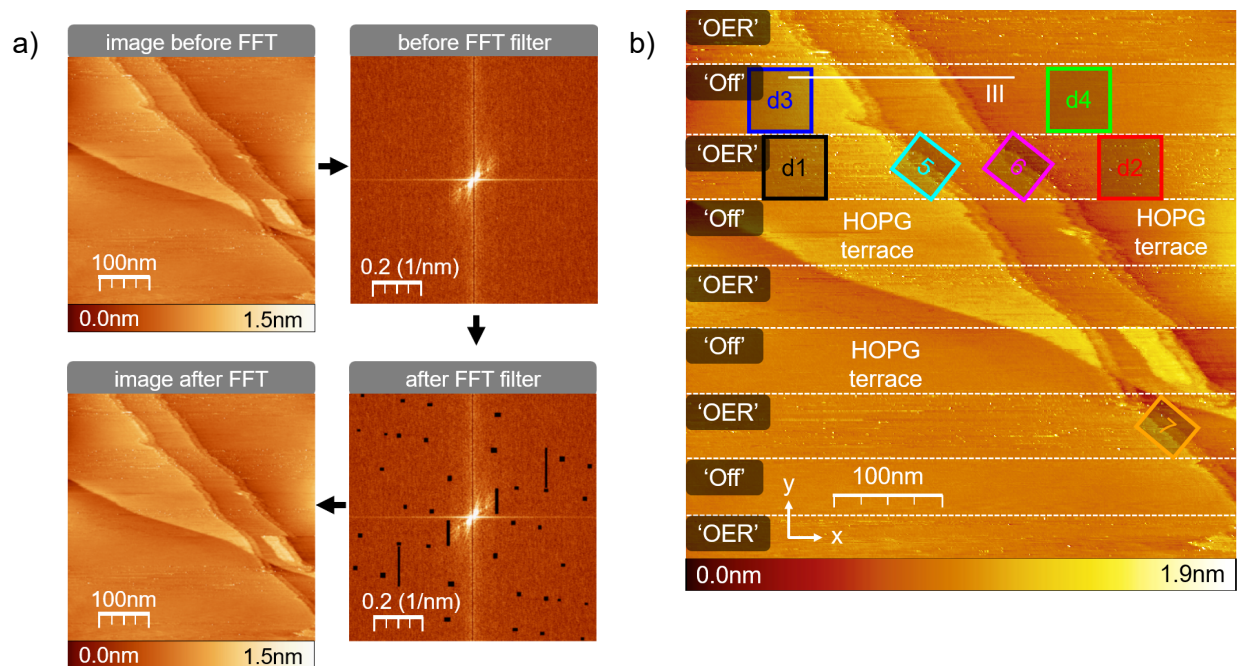


Figure 4.2.6 A4. a) FFT steps illustrating the cut-out areas that once contained the information about the artificial noise. As visible on the bottom left, only artificial structures were removed, while all the morphological and noise-related structures remain. b) Identical image to **Figure 4.2.6c** containing all evaluated areas, including the step noise analysis on step edges in **Figure 4.2.6 A5**. The white solid line represents the linescan shown in **Figure 4.2.6 A1**. Data of both figures published in reference ^[213].

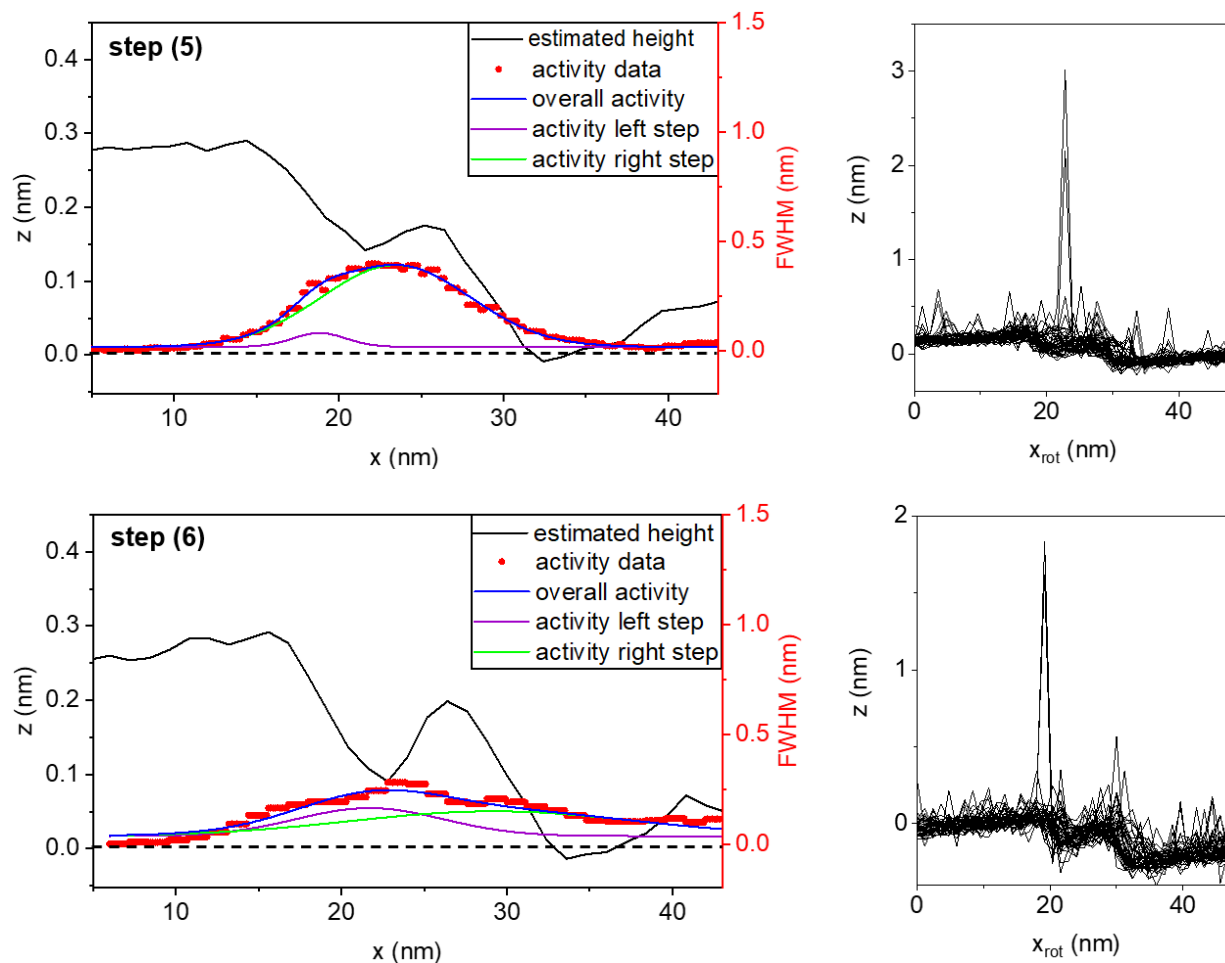


Figure 4.2.6 A5. Site-related activity evaluation of the highlighted step positions (5), (6), and (7) in **Figure 4.2.6 A4b**. As explained more in detail in **Subchapter 3.4.2**, the local activity (red dots) could be simulated by the sum of two Gaussian fits (blue), which correspond to the individual edges (purple and green). In addition, each image shows a single step edge with an artificial intermediate step probably caused by a double apex of the STM tip. Interestingly, the noise on the step edge is captured by both apexes of the tip, which measures the step edge twice. Nevertheless, the graphs of this figure clearly identify an increased activity at the step edge of the HOPG sheet. The images on the right side showcase the raw data of the steps from a cross-section perspective. Data published in reference ^[175].

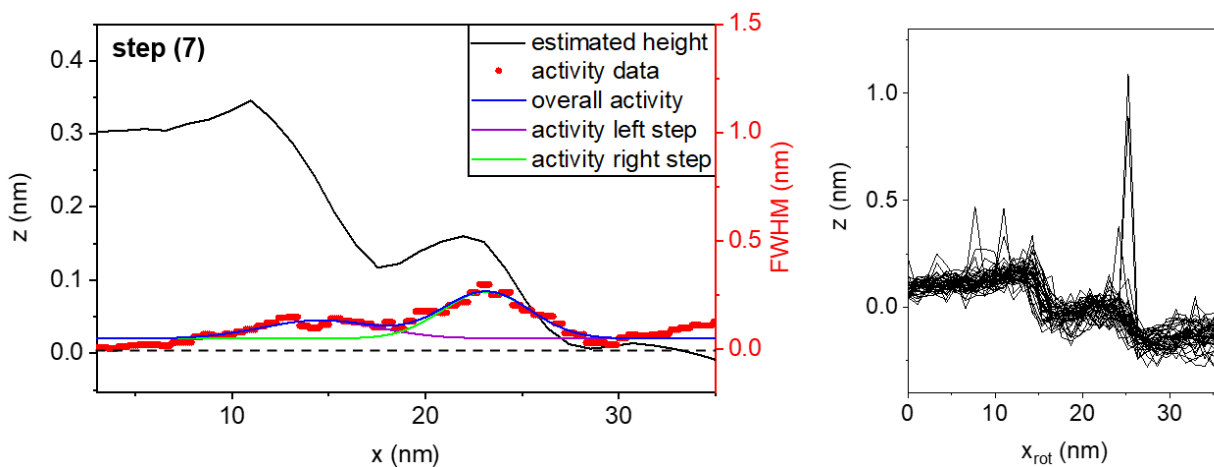


Figure 4.2.6 A6. Analog evaluation as described in **Figure 4.2.6 A5** for position (7) in **Figure 4.2.6 A4b**.

Data published in reference ^[175].

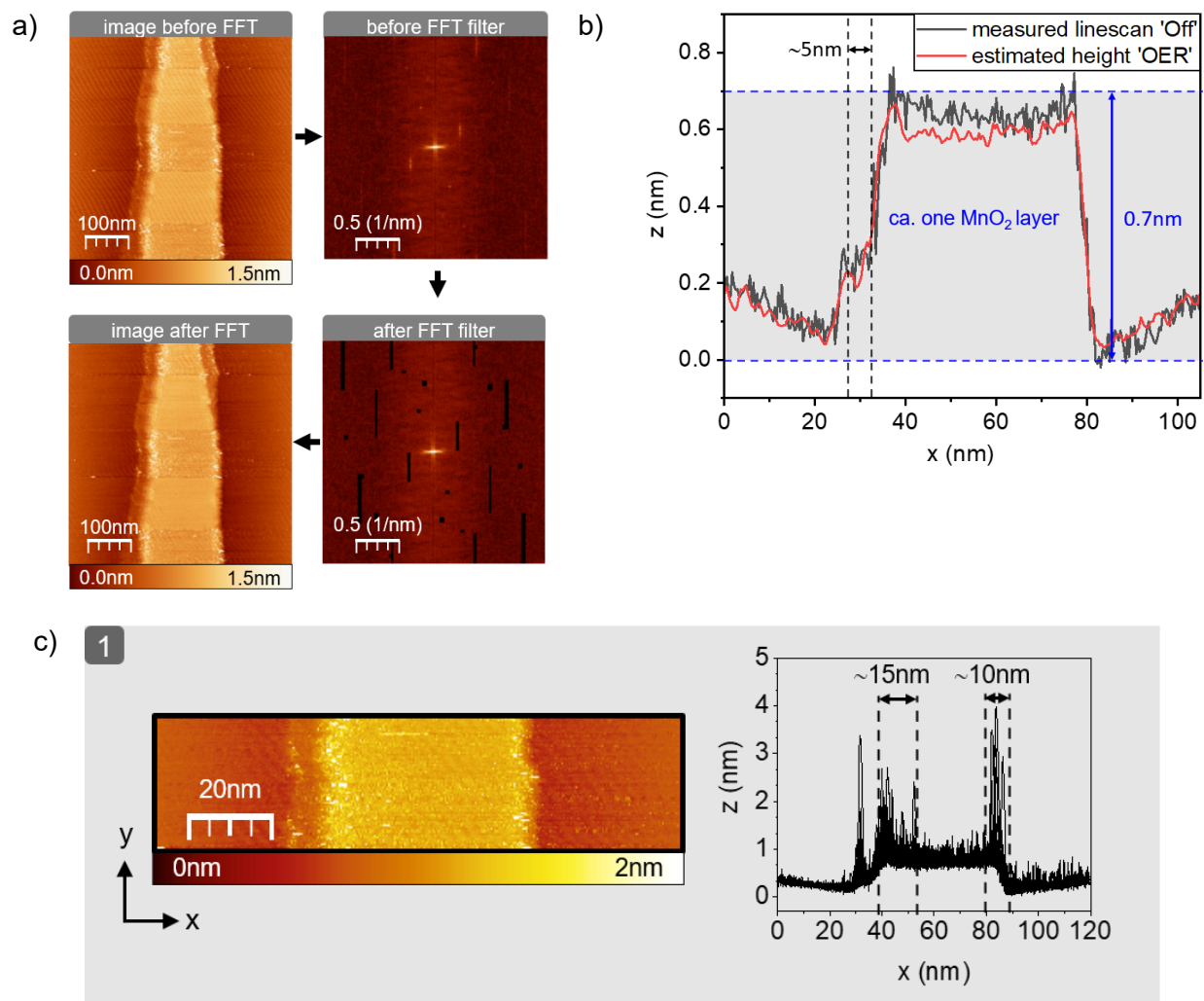


Figure 4.2.7. A1. Additional information to **Figure 4.2.7**. The FFT process in **a)** represents the deleted data and compares the initial and filtered images. **b)** Comparison of an experimentally examined line scan for reaction ‘Off’ (black) and the estimated height for ‘OER’ (cf. **Subchapter 3.4.2**). The positions for the evaluated data are marked in **Figure 4.2.7b** as location I and area 1, respectively. Despite the funnel shape of the sheet, only a slight difference is visible, which verifies the calculated height as a valid estimation. **c)** The two-dimensional top view (left side) and cross-section view (right side) of the evaluated area are used for the site-related activity evaluation in **Figure 4.2.8**. The black arrows in **b)** and **c)** show the rough distances for the expected double step and the extent of the noise relevant to the hypothesis of a double-tip discussed in the main text. Data of all figures published in reference ^[175].

Appendix E: List of Active Sites and Regions

This subchapter presents additional information on the latest discovered active sites and regions discussed in **Chapter 5**.

Table A5.1. Summary of all active sites found so far using *n*-EC-STM and *cr*-EC-STM, as well as selected active regions for SECCM and SECM. The numbers in the first column help to assign the corresponding entry in **Figure 5.1**. Please note that the table extends over several pages. Adapted with permission from reference ^[288]. Copyright 2023 Elsevier B.V, all rights reserved.

#	Reaction	Sample material	Electrolyte	Identified active sites and regions	Applied method	Ref.
1	CO ₂ RR	Sn particles deposited on reduced graphene oxide	0.1M KHCO ₃	interface between the Sn particle and rGO, but also slightly on Sn particles	SECCM	[296]
2	HER	1H-MoS ₂ nanosheets on HOPG	0.5M H ₂ SO ₄	at the edge region of nanosheets	SECCM	[297]
3	HER	2H MoS ₂ /HOPG transition region	10mM KOH, 0.1M KCl, 1mM Fc	edge sites	SECM	[298]
4	HER	Au(100) nanocubes and Au(111) nano-octahedra	0.1M HClO ₄	Au NCs are more active than Au ODs	SECCM	[299]
5	HER	Au(111)	0.1M HClO ₄	edge site (negative than -90mV versus RHE), terrace site (negative than -115 versus RHE)	<i>cr</i> -EC-STM	[287]
6	HER	HOPG	0.1M HClO ₄	upper step edges and defective sites	<i>n</i> -EC-STM	[29]
7	HER	iron films covered with a monolayer graphene on Pt(111)	0.1M HClO ₄	activity order: point defects based on iron atoms trapped into vacancy clusters > iron step edge and iron terrace covered by graphene	<i>cr</i> -EC-STM	[211]

Table A5.1 (continued).

#	Reaction	Sample material	Electrolyte	Identified active sites and regions	Applied method	Ref.
8	HER	mono-atomically high Pd islands on Au(111)	0.1M H ₂ SO ₄	activity order: only a few Pd atoms close to the boundary > Pd island > Au substrate	n-EC-STM	[28]
9	HER	monoatomic-thick Pt island on Au(111)	0.1M HClO ₄	predominantly at the Pt atoms	n-EC-STM	[209]
10	HER	natural molybdenite 2H-MoS ₂	0.1M HClO ₄	activity order: step edges > terraces between two steps > other terraces	SECCM	[300]
11	HER	N-doped graphene oxide at an ITO slide	2M H ₂ SO ₄	activity order: N-rGO edge > N-rGO surface > ITO surface	SECCM	[301]
12	HER	Pd nanoparticles on HOPG	0.1M HClO ₄	highest activity found for Pd NPs with a diameter of ~3.4nm	cr-EC-STM	[287]
13	HER	Pd overlayer on Au(111)	0.1M H ₂ SO ₄	on Pd atoms located close to the boundary	n-EC-STM	[209]
14	HER	Pd(100)	0.1M HClO ₄	mainly on step edges, slightly on terraces	n-EC-STM	[175]
15	HER	Pd(100) after electrochemical cycling	0.1M HClO ₄	mainly on convex areas but also on concave ones	n-EC-STM	[175]
16	HER	Pd(111)	0.1M HClO ₄	mainly on upper step edges, slightly on terraces	n-EC-STM	[175]
17	HER	Pd(111) after cycling	0.1M HClO ₄	all over the surface but mainly on convex areas	n-EC-STM	[175]
18	HER	Pt nanoparticles at the buried HOPG/Nafion interface	25mM HClO ₄	enhanced current at the positions of PtNPs at the interface, variations in current between individual PtNPs, and Nafion thickness	SECCM	[302]
19	HER	self-assembled Au nanoparticles monolayer	0.5M H ₂ SO ₄	higher activity of Au NPs than that of the Au substrate electrode	SECCM	[303]

Table A5.1 (continued).

#	Reaction	Sample material	Electrolyte	Identified active sites and regions	Applied method	Ref.
20	HER	single crystal MoO ₂ sheets on Au(111)	0.1M H ₂ SO ₄	terrace, edge site, and interface regions between two MoO ₂ sheets under compressive strain	n-EC-STM	[212]
21	HER	W filled Se vacancies on a WSe ₂ coated Au(111)	0.1M HClO ₄	on point defects	cr-EC-STM	[287]
22	HER	Pt(111)	0.1M HClO ₄	mainly on step-like defects but also on terraces	n-EC-STM	[28]
23	OER	amorphous IrO _x on Ir(111)	0.1M HClO ₄	step and terrace sites are comparably active	n-EC-STM	[204]
24	OER	Hematite (α -Fe ₂ O ₃) nanorods	10mM NaOH	higher activity at the body portion compared to the tip portion	SECCM	[304]
25	OER	HOPG	0.1M KOH	upper step edge, and terraces for high potentials around 0.9V _{Pt}	n-EC-STM	[118]
26	OER	MnO ₂ NS/HOPG	0.1M KOH	Upper step edges of the MnO ₂ NS and slightly on the nanosheet terrace	n-EC-STM	[213]
27	OER	semi-2D NiO with defect holes on HOPG	1mM KOH, 0.1M KCl, 1mM Fc	edge sites	SECM	[305]
28	OER	ZIF-67-derived Co-N-doped C composite particles on GC	50mM KOH	an increased activity for a higher number of nanocomposite units	SECCM	[306]
29	OER	β -Co(OH) ₂ particles	0.1M KOH	particle edge facets	SECCM	[307]
30	ORR	complex solid solution: Ag ₁ Ir ₁₇ Pd ₅₆ Pt ₁₅ Ru ₁₁	0.1M HClO ₄	~29,000 sites contribute to the measured electrocatalytic current with a ~50nm probe size	SECCM	[308]
31	ORR	HOPG	0.1M KOH	upper step edge	n-EC-STM	[118]

Table A5.1 (continued).

#	Reaction	Sample material	Electrolyte	Identified active sites and regions	Applied method	Ref.
32	ORR	polycrystalline Pt ₅ Gd and Pt ₅ Pr	0.1M HClO ₄	mainly upper steps and terraces	n-EC-STM	[206]
33	ORR	Pt(111)	0.1M HClO ₄	mainly on step-like defects but also on terraces	n-EC-STM	[28]
34	ORR	Pt(111)	0.1M LiOH	Pt(111) terraces	n-EC-STM	[208]
35	ORR	Pt(111)	0.1M KOH	Pt(111) terraces	n-EC-STM	[208]
36	ORR	Pt(111)	0.1M CsOH	Pt(111) terraces	n-EC-STM	[208]
37	ORR	Pt(111) with step defects	0.1M HClO ₄	step defects (concave sites at the steps) exhibit higher activity than terraces	n-EC-STM	[208]
38	ORR	Pt ₃ Ni(111)	0.1M HClO ₄	terrace and step sites contribute similar to the overall activity	n-EC-STM	[205]
39	ORR	Pt-nanoparticles on HOPG	0.1M HClO ₄	particles of 300nm or less	AFM-SECM	[309]

Appendix F: List of Abbreviations and Symbols

The following list summarizes all crucial abbreviations and symbols frequently used in this thesis. It is arranged alphabetically according to the short forms and extends over several pages.

Short form	Long form
'HER'	potential where the proton reduction takes place
'OER'	potential where the oxygen evolution takes place
'Off'	potential where no reaction takes place
'On'	potential where a reaction takes place
AMOC	Atlantic Meridional Overturning Circulation
CE	counter electrode
CFePc/HOPG	HOPG with FeN ₄ centers
cr-EC-STM	current roughness EC-STM
CS	current setpoint
CV	cyclic voltammetry
DFT	density functional theory
DMFC	direct methanol fuel cell
E_0	equilibrium potential or Nernst potential
EC-cell	electrochemical cell
EC-STM	electrochemical scanning tunneling microscopy
EDL	electrical double-layer
E_{form}	formation energy
E_F^{s}	Fermi level of the sample
E_F^{t}	Fermi level of the STM tip
E_{OC}	open-circuit potential

$E_{\text{vac}}^{\text{s}}$	vacuum levels of the sample
$E_{\text{vac}}^{\text{t}}$	vacuum levels of the STM tip
EXAFS	X-ray absorption fine structure
fcc	face-centered cubic
FFT	fast Fourier transformation
FWHM	full width at half maximum
GCN	generalized coordination number
H_2SO_5	Peroxymonosulfuric acid
HClO_4	perchloric acid
HER	hydrogen evolution reaction
HOPG	highly oriented pyrolytic graphite
HOR	hydrogen oxidation reaction
H_{UPD}	hydrogen underpotential deposition
IG	integral gain
IHP	inner Helmholtz plane
IPCC	Intergovernmental Panel on Climate Change
j_0	exchange current density
KOH	potassium hydroxide
LOHC	liquid organic hydrogen carrier
LSV	linear sweep voltammetry
MMS	Mercury/Mercurous Sulfide
Mn_4CaO_5	Manganese(IV) Calcium Oxide
MnO_2NS	Manganese dioxide nanosheets
$\text{MnO}_2\text{NS/CFePc/HOPG}$	Manganese dioxide on HOPG with FeN_4 centers
$\text{MnO}_2\text{NS/HOPG}$	MnO_2NS on HOPG support

MnO ₂ NS-edge _{1ox}	MnO ₂ NS with one oxygen ending (1ox) on graphene support
MnO ₂ NS-edge _{2ox}	MnO ₂ NS with two oxygen endings (2ox) on graphene support
MnO _x	Manganese oxides
n-EC-STM	noise electrochemical scanning tunneling microscopy
OER	oxygen evolution reaction
OHP	Helmholtz plane
ORR	oxygen reduction reaction
Pd(hkl) _c	Cycled Pd(hkl) crystal
PdH	Pd hydrides
PDS	potential determining step
PEM	proton exchange membrane
PEMFC	PEM fuel cell
PG	proportional gain
PS II	Photosystem II
QRE	quasi-RE
RDS	rate-determining step
RE	reference electrode
RHE	reversible hydrogen electrode
R-MnO ₂	Ramsdellite polymorph
RSF	pseudo-radial structure function
SECCM	scanning electrochemical cell microscopy
SECM	scanning electrochemical microscopy
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
SNM	scanning noise microscopy

SOFC	solid oxide fuel cell
SSC	Silver/Silver Chloride
S_{Tafel}	Tafel slope
STM	scanning tunneling microscope
TOF	turnover frequency
UNEP	United Nations Environment Program
UPD	underpotential deposition
WE	working electrode
WMO	world meteorological organization
XANES	X-ray absorption near-edge structure
$\alpha\text{-MnO}_2$	hollandite polymorph
$\beta\text{-MnO}_2$	pyrolusite polymorph
$\gamma\text{-MnO}_2$	nsutite polymorph
ΔFWHM	percentage deviation between two FWHMs
ΔG_{react}	free energy relative to the reactant at E_0
$\delta\text{-MnO}_2$	birnessite polymorph
η_{PDS}	overpotential of the PDS
$\lambda\text{-MnO}_2$	spinel polymorph
Φ_e	electrode potential
Φ_s	solvent potential

Appendix G: Collection of First Autor Publications

This subchapter summarizes all first-author manuscripts published during this doctorate as first or first-shared author. The following list contains the required permissions for each publication reprinted in this subchapter according to the order presented. The additive ⁽⁺⁾ indicates the first authors, while * refers to the corresponding authors of the publication.

- Schmidt T.O.,⁽⁺⁾ Ngoipala A.,⁽⁺⁾ Arevalo R.L., Watzele S.A., Lipin R., Kluge R.M., Hou S., Haid R.W., Senyshyn A., Gubanova E.L.,* Bandarenka A.S.,* Vandichel M.* *Elucidation of structure-activity relations in proton electroreduction at Pd surfaces. Theoretical and experimental study.* Small **2022**, 18, 2202410.

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- Schmidt T.O.,⁽⁺⁾ Wark A.,⁽⁺⁾ Haid R.W., Kluge R.M., Suzuki S., Kamiya K., Bandarenka A.S.*, Maruyama J.*, Skúlason E.* *Elucidating the active sites and synergies in water splitting on manganese oxide nanosheets on graphite support.* Advanced Energy Materials **2023**, 13, 2302039.

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- Gubanova E.,⁽⁺⁾* Schmidt T.O.,⁽⁺⁾ Watzele S., Alexandrov V.,* Bandarenka A.S.* *Structure-dependent electrical double layer capacitances of the basal plane Pd(hkl) electrodes in HClO₄.* J. Phys. Chem. C **2022**, 126, 11414-11420.

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- Schmidt T.O.,⁽⁺⁾ Haid R.W., Gubanova E.L., Kluge R.M.,* Bandarenka A.S.,* *Electrochemical scanning tunneling microscopy as a tool for the detection of active electrocatalytic sites.* Topics in Catalysis **2023**, 66, 1270-1279.

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RESEARCH ARTICLE



Elucidation of Structure–Activity Relations in Proton Electroreduction at Pd Surfaces: Theoretical and Experimental Study

Thorsten O. Schmidt, Apinya Ngoipala, Ryan L. Arevalo, Sebastian A. Watzele, Raju Lipin, Regina M. Kluge, Shujin Hou, Richard W. Haid, Anatoliy Senyshyn, Elena L. Gubanova,* Aliaksandr S. Bandarenka,* and Matthias Vandichel*

The structure–activity relationship is a cornerstone topic in catalysis, which lays the foundation for the design and functionalization of catalytic materials. Of particular interest is the catalysis of the hydrogen evolution reaction (HER) by palladium (Pd), which is envisioned to play a major role in realizing a hydrogen-based economy. Interestingly, experimentalists observed excess heat generation in such systems, which became known as the debated “cold fusion” phenomenon. Despite the considerable attention on this report, more fundamental knowledge, such as the impact of the formation of bulk Pd hydrides on the nature of active sites and the HER activity, remains largely unexplored. In this work, classical electrochemical experiments performed on model Pd(hkl) surfaces, “noise” electrochemical scanning tunneling microscopy (n-EC-STM), and density functional theory are combined to elucidate the nature of active sites for the HER. Results reveal an activity trend following Pd(111) > Pd(110) > Pd(100) and that the formation of subsurface hydride layers causes morphological changes and strain, which affect the HER activity and the nature of active sites. These findings provide significant insights into the role of subsurface hydride formation on the structure–activity relations toward the design of efficient Pd-based nanocatalysts for the HER.

1. Introduction

In the ongoing global process of decarbonization toward a sustainable future,^[1,2] hydrogen has been extensively regarded as a sustainable, next-generation energy carrier due to its high energy density. Additionally, it is a carbon-free fuel, which can in principle be generated by water electrolysis all over the world.^[3–5] To realize such a hydrogen-based economy,^[6–8] it is imperative to gain a fundamental understanding of the interaction of hydrogen with (metal) catalysts. Evaluating these electrode materials’ stability, activity, and selectivity is a key step to improving the hydrogen reaction kinetics. In particular, the structure–activity relation of interfacial electrode/electrolyte interactions are crucial for various technological applications that include hydrogen

storage,^[9,10] hydrogen sensing,^[11,12] hydrogenation/dehydrogenation,^[13,14] hydrogen purification/separation,^[15,16] and electrocatalysis.^[17–19]

Due to this expanding range of applications, especially hydrogen-metal systems have increasingly come to the forefront of the research community; more precisely, the interaction of hydrogen with metal catalysts such as platinum (Pt), palladium (Pd), or nickel has been extensively studied using a variety of experimental and computational techniques.^[20–22] Among these metal catalysts, Pd has received a significant research interest for the study of metal-hydrogen interaction, as it can readily absorb large volumetric quantities of hydrogen at accessible temperatures and pressures, possesses a high hydrogen diffusion coefficient, and promotes a facile dissociation of hydrogen molecules at the surface.^[23–26] Pd-based systems have previously been studied through both experimental techniques such as low-energy electron diffraction (LEED),^[27–29] electron energy loss spectroscopy (EELS),^[30,31] thermal desorption spectroscopy (TDS),^[32] X-ray diffraction (XRD),^[33] X-ray photoelectron spectroscopy (XPS),^[34] and theoretical approaches such as semiempirical approaches like embedded-cluster methods^[35] or effective-medium models^[36] and ab initio methods based on density functional theory (DFT).^[37,38] These reports, among

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others, have identified the preferred adsorption/absorption sites, -geometries, and -energies, surface diffusion, and electronic structures of H chemisorption on Pd(111), Pd(100), and Pd(110) surfaces. More interestingly, experimentalists observed an anomalous generation of excess heat in the Pd-catalyzed electrochemical hydrogen evolution reaction (HER), which later became known as the highly debated “cold fusion”.^[39–41] Despite the tremendous research interest that emerged from such reports, still, many questions concerning the structure–activity relation for hydrogen reactions on Pd surfaces remain unresolved. In particular, there is a lack of a comprehensive understanding of the dynamic behavior and surface mobility of Pd, the effect of subsurface hydride formation and lattice/surface strain on the HER activity, as well as the stability of the surface under HER conditions.

In this work, experimental and theoretical tools were used to assess the complexity and dynamics of such Pd-hydrogen systems, focusing on the low-indexed basal planes Pd(111), Pd(110), and Pd(100) as well as on the stepped Pd(211) surface. For this purpose, findings of XRD, electrochemical impedance spectroscopy (EIS), “classical” electrochemical activity and electrochemical scanning tunneling microscopy (EC-STM) measurements as well as DFT-based calculations were combined, leading to a bigger picture of hydrogen-induced changes in the lattice strain, diffusion behavior, electrochemical activity, and the morphology of the Pd surface. Correspondingly, we present the 3-state free energy diagrams for HER activities on the Pd basal planes with different numbers of Pd hydride sublayers as well as the effect of the surface coverage on the areal strain. The resulting transformation of the surface morphology and the consequent influence on the active sites are experimentally shown in detail for Pd(111) and Pd(100) by using “noise” EC-STM (n-EC-STM).^[42,43] For this purpose, the nature of active sites of both Pd single crystals is elucidated before and after hydrogen absorption. To the best of our knowledge, this work reports for the first time the HER activity trends for different Pd(hkl) model systems obtained from systematic measurements and calculations that take into account the effect of subsurface hydride formation in structure–activity relations. These findings contribute to a better understanding of the complex and dynamic processes at the Pd surface and sublayers in correlation with hydrogen adsorption.

2. Results and Discussion

In the following, several theoretical and experimental tools are applied to investigate the nature of hydrogen adsorption on the single crystalline Pd planes (111), (110), (100), and (211).

2.1. Hydrogen Absorption Behavior, Surface Mobility of Pd, Reaction Mechanism, and Kinetics

To compare the relative stabilities of the Pd(111), Pd(100), Pd(110), and Pd(211) surfaces, their surface energies were calculated. The computational details are provided in Section S1 (Supporting Information). The obtained surface energies are

0.132, 0.150, 0.145, and 0.147 eV Å^{−2} for pristine Pd(111), Pd(110), Pd(100), and Pd(211) surfaces, respectively, and indicate that the Pd(111) surface is the most stable, followed by the Pd(100) surface. Furthermore, the stepped Pd(211) surface is more stable than the Pd(110) surface. This is reasonable as the Pd(211) surface is composed of Pd(111) terrace sites and a step that has a Pd(100) character, while the Pd(110) surface has a more open structure. Note that the order of these three low-index surface energies, [Pd(111) < Pd(100) < Pd(110)], is in good agreement with the results from previous theoretical studies on the surface energies of the fcc-metals.^[44,45] Our finding indicates that the Pd(111) surface is expected to be the most dominant surface in a Pd nanostructure.

Next, the electrochemical behavior of the annealed Pd(hkl) model surfaces was investigated using a cyclic voltammetry method. Cyclic voltammograms (CV) were recorded and compared for the Pd(111), Pd(110), and Pd(100) surfaces in a potential range between 0.2 and 1.2 V versus a reversible hydrogen electrode (V_{RHE}) in Ar-saturated 0.1 M HClO₄. A continuous change of the CV shapes was observed over time until the system stabilized after more than 30 cycles (Figure S2, Supporting Information). Previous literature^[23–26,46] suggests that hydrogen adsorption and absorption play a pivotal role. The interplay of these processes is assumed to explain the dynamic behavior (morphological changes) of the Pd surfaces, which occurred under electrochemical reaction conditions. Therefore, only the first cycles of the typical CVs (Figure 1a–c) are considered to be representative for the freshly annealed surfaces of Pd single crystals. Since the recorded CVs are in good agreement with the literature data,^[47,48] the successful preparation of well-defined single crystalline surfaces was confirmed. It should be noted that further measurements were performed with the as-prepared (freshly annealed) surface, while the number of cycles was reduced to the minimum to avoid surface reconstruction.

For further evaluation of the adsorption and subsequent absorption process, the hydrogen under-potential deposition (H_{UPD}) region was closely examined. For this, the anodic and cathodic peaks were integrated and compared as shown in Figure 1a–c. On the freshly annealed Pd(111), the cathodic scan yielded an integrated charge (Q_c) of $\approx 290 \mu\text{C cm}^{-2}$ (Figure 1a). For comparison, one monolayer (ML) of adsorbed hydrogen on Pt(111) corresponds to a charge of $\approx 240 \mu\text{C cm}^{-2}$.^[49,50] Due to the observed charge, higher than the theoretically expected value for 1 ML of hydrogen, indicates that a possible absorption of adsorbed protons might have occurred. In contrast, the integrated anodic scan (Q_a) on Pd(111) returned only a charge of $\approx 225 \mu\text{C cm}^{-2}$. This implies that only $\approx 78\%$ ($Q_a/Q_c = 0.78$) of the protons got oxidized during the anodic scan, and therefore $\approx 22\%$ was absorbed into the bulk. The highest hydrogen absorption was detected for Pd(110), as visible in Figure 1b. Here, only $\approx 69\%$ of the produced hydrogen got oxidized during the anodic scan, meaning that $\approx 31\%$ was absorbed into the bulk. The total value of the integrated cathodic scan of this crystal was $\approx 145 \mu\text{C cm}^{-2}$, so half of the one for Pd(111). A possible explanation for this could be a lower number of available active sites. For the freshly annealed Pd(100) only $\approx 12\%$ of the produced hydrogen was absorbed into the bulk in the first cycle (Figure 1c). This results in an adsorption/desorption ratio of $Q_a/Q_c = 0.88$. In summary, this electrochemical behavior of the

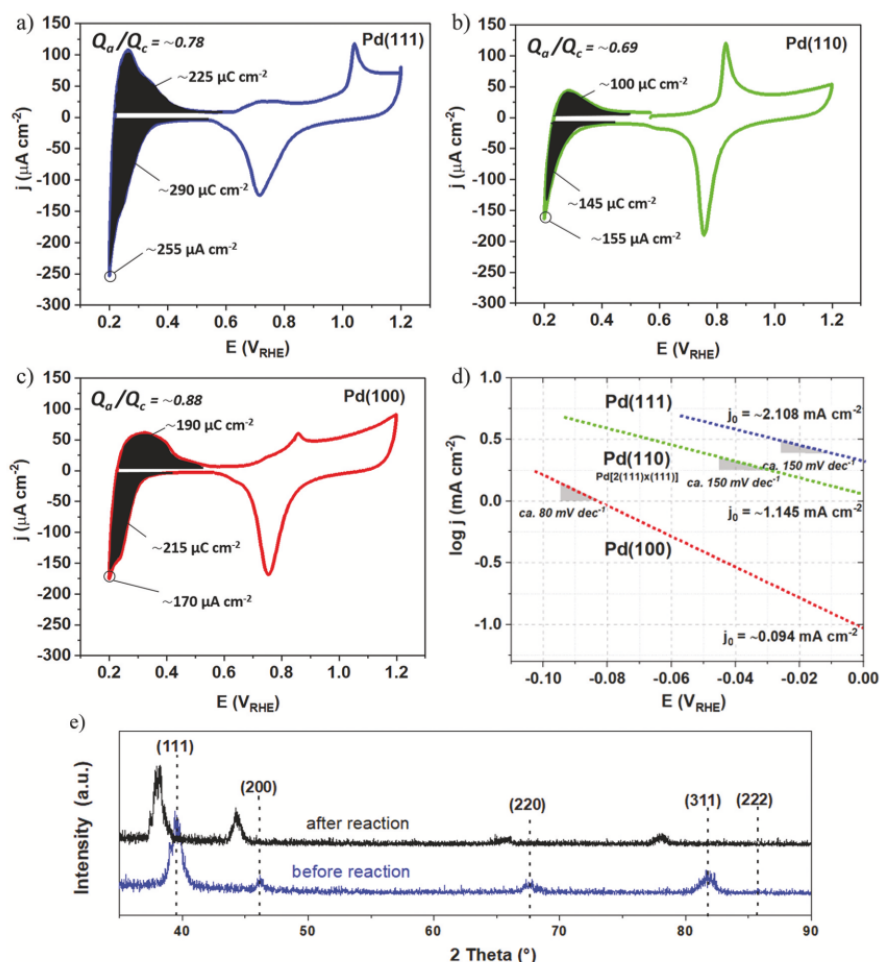


Figure 1. The first scans of the CVs of the annealed a) Pd(111), b) Pd(110), and c) Pd(100) single crystals in Ar-saturated 0.1 M HClO₄ recorded at a scan rate of 50 mV s⁻¹. d) Tafel plots of the HER activity on the Pd(111), (110), and (100) single crystals, recorded in H₂-saturated 0.1 M HClO₄ with a scan rate of 50 mV s⁻¹. e) Grazing-incidence XRD patterns of single-crystalline Pd(111) before and after HER (6 cycles) indicate peak shifts from the pristine Pd electrode to PdH_{0.72}.

Pd surface can indicate that even after a single electrochemical cycle, a certain amount of hydrogen absorbs into the Pd bulk.

The Tafel plots in Figure 1d present the activity trend of the Pd(111), (110), and (100) surfaces for the HER, using an experimentally estimated exchange current density (j_0), as discussed below. Tafel plots as well as Tafel slopes are typically used to identify the rate-determining step of the HER. In particular, Tafel slope values of 30, 40, and 120 mV dec⁻¹ are typically associated with Tafel, Heyrovsky, and Volmer as possible rate-determining steps (RDS), respectively.^[51] However, in reality, the Tafel slopes frequently change over the potential and do not always adopt one of the theoretical values, which

makes it difficult to determine the RDS. Remarkably, for both Pd(111) and Pd(110) the estimated Tafel slope values were equal to 150 mV dec⁻¹, while for Pd(100), it was found to be ≈80 mV dec⁻¹. This finding indicates that the energetic and geometrical properties of the most active sites on Pd(111) and Pd(110) could be similar, while they are different from those of Pd(100). The exchange current densities of the Pd electrodes were calculated by extrapolating the Tafel plots. The values of ≈2.108, ≈1.145, and ≈0.094 mA cm⁻² for Pd(111), Pd(110), and Pd(100), respectively, were estimated. Additionally, we calculated the exchange current densities by DFT and rendered a volcano plot, as shown in Figure S3 (Supporting Information). The

experimentally observed trend was confirmed by these theoretically obtained results, which will be presented in the following.

The influence of the absorbed hydrogen on the lattice parameter was investigated by XRD measurements for the most active Pd single crystal, i.e., Pd(111). For this purpose, XRD patterns were recorded for the pristine sample and for the sample after six cycles of HER (Figure 1e). The results indicated a lattice parameter of 3.89 Å before the HER and about 4.07 Å after the HER, corresponding to an H:Pd ratio of about 0.72 (extrapolated on the basis of data from ref. [52]). This corresponds to a relative lattice expansion of ≈4.6%, suggesting an increased surface strain. Investigations of the surface strain and its effects on the morphology and local electrochemical activity are discussed in Section 2.3.

Further, EIS was applied to investigate the reaction mechanism and kinetics at the Pd single crystal surfaces. For this purpose, spectra were recorded at $-30\text{ mV}_{\text{RHE}}$ allowing to probe the electrified interface during the HER, without significant noise that could be caused by stochastic surface blockage by $\text{H}_2(\text{g})$ at higher overpotentials. Figure 2a–c shows the EIS spectra of Pd(111), Pd(110), and Pd(100), respectively. The Nyquist plots of the three investigated surfaces have a similar shape, consisting of an almost perfect semicircle in the high-frequency regime and a transition to an ≈ 45° regime at lower frequencies. The latter indicates some diffusion limitations of the reaction kinetics.

In a previous work,^[53] we showed a model to analyze the dominating reaction mechanism on Pt surfaces. With this, a distinction can be made between the Volmer–Heyrovsky mechanism and the Volmer–Tafel mechanism. Briefly, the Faradaic part of the equivalent electrical circuit (EEC) consists of one

branch reflecting the reaction kinetics of the Volmer–Heyrovsky and another reflecting the kinetics of the Volmer–Tafel mechanism. The former consists of a charge transfer resistance, in series with an adsorption capacitance and adsorption resistance in parallel, while the Volmer–Tafel branch consists of only a charge transfer resistance and a Warburg diffusion element.^[53] Applying the same EEC to the impedance spectra of the Pd surfaces shown in Figure 2a–c, it was possible to fit them appropriately. However, the charge transfer resistance of the Volmer–Heyrovsky branch is extremely high, and the adsorption capacity is rather undefined values. The relatively high charge transfer resistance indicates that the reaction kinetics of this branch is comparatively slow. Further, the large uncertainties of the adsorption capacitance imply that this parameter contributes only little to the overall fitting. This, and the fact that an excellent fit of the impedance is achieved with only the Volmer–Tafel branch, show that the Volmer–Heyrovsky mechanism plays a subordinate role at most. Therefore, the equivalent circuit shown in Figure 2d was used for further analysis. Applying this EEC, the root-mean-square deviation of the fitting is less than 1%. Further, individual parameters show low uncertainties, which asserts the accuracy of the model for describing the impedance response of the electrochemical system. The applicability of this EEC indicates the Volmer–Tafel and/or the direct absorption of protons as the dominating mechanism for the Pd surfaces at low overpotentials. Note that the EEC for both processes is indistinguishable. In any case, most of the generated hydrogen was directly absorbed as no formation of hydrogen bubbles was detected.

To further analyze the electrified interface, we focus on the parameters of the Faradaic branch: the charge transfer

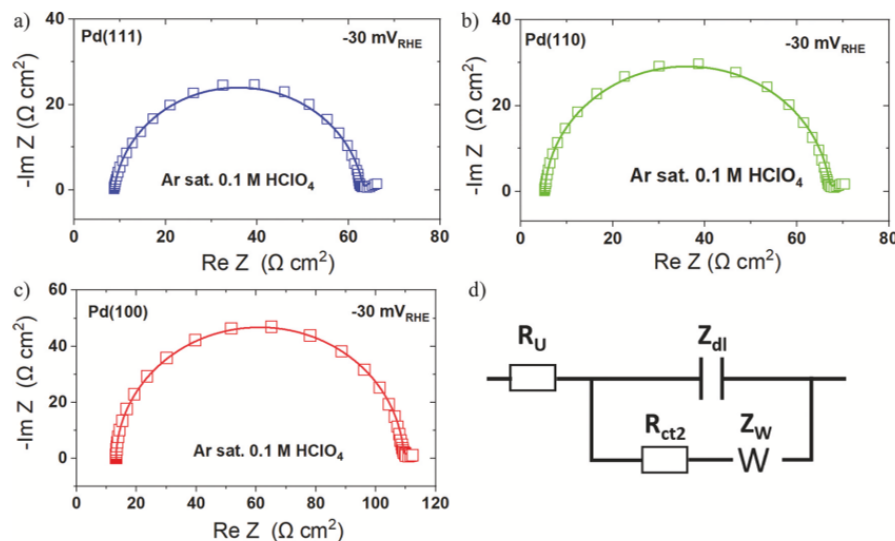


Figure 2. Impedance data of different Pd single crystal surfaces recorded in Ar-saturated 0.1 M HClO_4 electrolyte, represented as Nyquist plots. a–c) shows spectra of the Pd(111), Pd(110), and Pd(100), respectively. Open symbols represent measured data points, and the line corresponds to fitting using the EEC shown in (d). The EEC consists of a constant phase element to fit the response of the electrochemical double layer and a charge transfer resistance in series with a Warburg element, accounting for reaction kinetics and mass transfer.

resistance R_{ct} and the Warburg coefficient A_w .^[54] The ratio of both parameters was determined as $\frac{A_w}{R_{ct}} = 0.02412 \text{ s}^{-0.5}$, $\approx 0.02695 \text{ s}^{-0.5}$, $\approx 0.02392 \text{ s}^{-0.5}$ for Pd(111), Pd(110), and Pd(100), respectively. As shown in Section S4 in the Supporting Information, this allowed to roughly estimate the H coverage of Pd(111), Pd(110), and Pd(100) as ≈ 0 , 0.3–0.4, and ≈ 0.95 , respectively. This indicated that Pd(111) and Pd(110) have a rather low surface coverage while the surface of Pd(100) was almost entirely covered.

2.2. In Situ Active Site Investigation of as-Prepared Pd Surfaces

After verifying a well-defined surface structure, n-EC-STM was employed to elucidate the nature of active sites of the freshly annealed Pd. Note that “freshly annealed” means annealed according to Section 4, without any previous CV measurements before the experiment. Standard STM measurements of these freshly annealed single crystals are illustrated in Figure S4 of the Supporting Information. On both crystals, completely flat areas and sections with a roughness of approximately the height of one Pd atom were found (cf. Figure S4, Supporting Information). These measurements further confirm the surface quality. More details on the working principle and applications of the n-EC-STM technique can be found in Section 4 as well as in previous literature.^[42,43,55–59] In short, the level of noise in the STM signal under reaction conditions serves to identify the active sites experimentally. As the reaction causes perturbations of the tunneling barrier, noise spikes will superimpose active areas in the images. In contrast, nonactive areas will be rather noise-free. Since the catalytically best and the worst performing crystals were Pd(111) and Pd(100) (Figure 1d), respectively, we employed the method to these surfaces, starting with the freshly prepared samples.

To choose adequate potentials for HER “On” and “Off,” potential sweeps were carried out in the STM set-up against a Pt quasi-reference electrode (RE) (Figure S5, Supporting Information). For HER “On,” the potential was chosen between -0.7 and -0.8 V versus Pt (V_{Pt}) in order to maintain a low reaction rate and thus minimize possible morphological changes. For HER “Off” the potential was set to 0.0 V_{Pt} , as here the current is practically zero. Figure 3a shows a typical noise measurement on Pd(111) in 0.1 M HClO_4 . Four steps of different heights are visible, separating two atomically flat terraces (compare Figure S6, Supporting Information). Multiple line scans (height profile in fast scan direction) were extracted near the border of the potential change from “On” (black) to “Off” (red) and were stacked on top of each other for comparison. The different noise levels imply that the highest activity on the Pd(111) surface can be found on step edges, while the terraces are less active. As expected, for reaction “Off,” the STM signal is noise-free, ensuring that the evaluated noise indeed stems from reaction processes instead of, e.g., shot noise or thermal noise. In addition, it is important to note that the captured step edges exhibited different noise levels, as demonstrated by the histograms in Figure 3b. More information on the noise analysis can be found in Section 4; and in Section S7 of the Supporting Information.

A similarly high step separating two terraces is visible in Figure 3c on freshly annealed Pd(100). An additional image showing a larger scale of this image can be found in Figure S7 (Supporting Information). Near the upper part of the step edge, some distinct noise spikes appeared for HER “On,” and all the noise disappears for HER “Off.” The right lower graph shows the difference between an active site at the step (black) and an adjacent nonactive site (red), both for reaction “On.” The noise features were only observed at a few positions along the edge, which indicates a low density of active sites and, therefore, a low impact of the steps on the overall surface activity. Additionally, the noise was detected homogeneously across the terraces, which indicates activity all over the sample. The behavior of the terraces was further analyzed in the histograms in Figure 3d, showing a broader curve for the HER “On” data compared to HER “Off.” It is important to note that a direct comparison of the terraces on Pd(111) and Pd(100) in Figure 3d is not possible due to specific individual experimental conditions, e.g., the shape and noise sensitivity of the STM-tip vary between individual measurements. However, a clear trend in the noise behavior of each measurement is observable. Unfortunately, STM is not able to detect the orientation of the step sites under these conditions. Note that only the low-index planes of Pd were investigated experimentally. The inclusion of Pd(211) in the theoretical considerations merely served as a model system for the step sites on the Pd surfaces that were observed especially in the n-EC-STM measurements. Nevertheless, we can assume that the differences in local activity for different step sites may originate from differences in local coordination or orientation.

2.3. The Strain Effect on the HER Activity

Since we observed hydrogen absorption during the experiments, together with an alteration of the surface lattice parameter from XRD measurements, the Pd hydride formation was further investigated using DFT calculations. It has been found from neutron diffraction studies that the hydrogen atoms in Pd hydride randomly occupy the octahedral interstices in the Pd-metal lattice.^[60,61] This result is also supported by DFT studies.^[62] For this reason, the formation of a Pd hydride (PdH_x) was investigated by initially populating the octahedral sites of an fcc bulk Pd crystal, followed by the tetrahedral sites. That is, the hydrogen atoms occupy the octahedral interstices only for $x \leq 1$. The calculated formation energies shown in Figure S8 (Supporting Information) indicate that the most stable Pd:H ratio is 1:1, in agreement with other DFT studies.^[62,63] Interestingly, all PdH_x crystals with $x < 1.50$ are energetically feasible (i.e., formation energy is negative). This suggests that the hydrogen atoms in a PdH_x can stably occupy both the octahedral and tetrahedral interstices. After all the octahedral interstices are occupied ($x = 1$), the additional hydrogen atoms can stably reside in the tetrahedral interstices for up to a Pd:H ratio lower than 1.50. Moreover, the calculated lattice constant of $3.891 \text{ \AA}$ for pure Pd is in good agreement with the experimental result, where the lattice constant of the pristine Pd(111) surface determined by XRD (Figure 1e) was $3.890 \text{ \AA}$. Under electrochemical conditions, the DFT-calculated Pourbaix diagram for bulk PdH_x (Figure S9, Supporting Information)

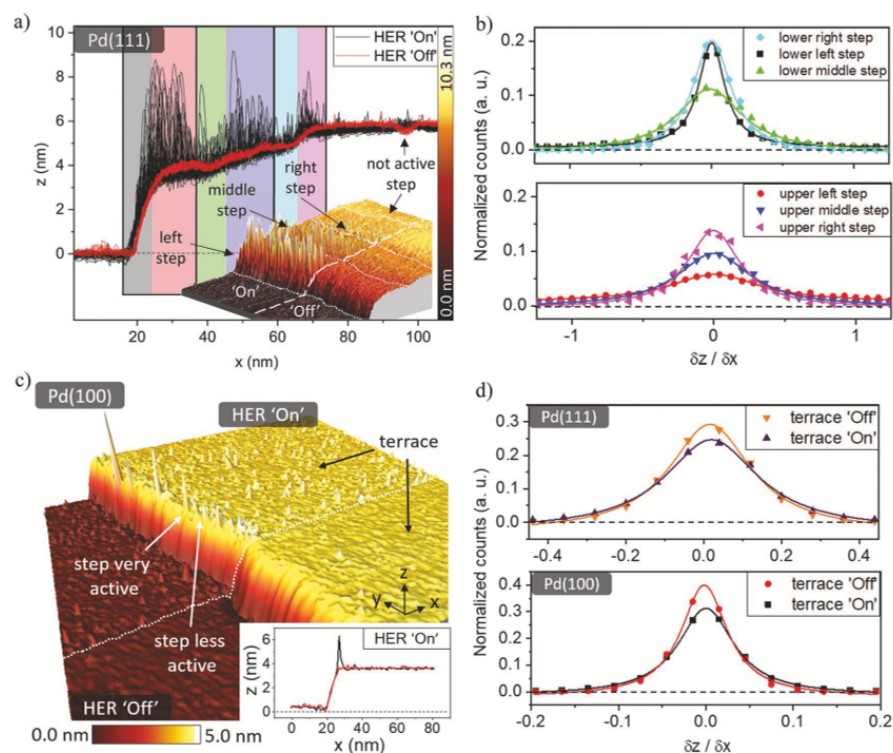


Figure 3. n-EC-STM measurements of freshly annealed Pd(111) and Pd(100) in 0.1 M HClO₄ for the HER turned “On” at -0.7 V_{PE} and “Off” at 0.0 V_{PE}. a) 3D n-EC-STM image of Pd(111) and corresponding line scans, which were extracted close to the potential change from HER “On” (black) to HER “Off” (red). According to noise spikes, we observed active step sites and inactive terraces. b) Histograms of the signal derivatives at the vicinity of the three step edges, color code according to the background of the line scans in (a). A high noise level yields a broad and low-intensity histogram (see details in text). c) Multiatomic step on an otherwise atomically smooth Pd(100) surface. Here, under HER “On” conditions, the terraces exhibited electrocatalytic activity. The highest activity was found scattered along the upper step edge. In the inset, the adjacent line scans for HER “On” illustrate the difference in the noise level if high noise (black) or no noise (red) appears at the step. d) Histograms of the lower terrace of Pd(111) in (a) and the upper terrace of Pd(100) in (c), showing increased activity for HER “On.”

shows that in the region around the equilibrium potential and pH for the HER, the most stable Pd:H ratio is 1:1. This agrees with the earlier noted result that such a Pd:H ratio is the most thermodynamically stable (Figure S8, Supporting Information). For a particular pH, shifting the electrode potential into more negative values increases the amount of hydrogen in bulk. The details for the calculation of the Pourbaix diagram are provided in Section S9 (Supporting Information).

Additionally, it is interesting to evaluate the effect of the formation of PdH sublayers on the stability of the Pd model surfaces. To this end, the surface energies of Pd(111), Pd(110), Pd(100), and Pd(211) surfaces containing different numbers of PdH sublayers were examined. First, we investigated the most stable absorption configuration of the H in the subsurface, where the Pd(111) surface was taken as a representative system as it is the close-packed structure, which is the most stable among the other more open surfaces. In this regard, the absorption energies of three possible H absorption sites, namely,

octahedral site, upper tetrahedral site, and lower tetrahedral site were calculated for the Pd(111) surface, as shown in Figure S10 (Supporting Information). Here, it can be seen that H is most strongly absorbed in the octahedral site, followed by lower and upper tetrahedral sites. Therefore, all surfaces containing zero to four PdH sublayers with H atoms at the octahedral sites were considered to calculate the surface energies. As demonstrated in Figure S1 (Supporting Information), the surface energies for Pd(111), Pd(110), Pd(100), and Pd(211) surfaces decrease as the number of PdH subsurface layer increases. This result indicates that the surfaces containing hydrogen subsurfaces are more stable than the corresponding clean surfaces. Therefore, it is crucial to examine the HER activity of the surfaces with different numbers of PdH sublayers in the model systems. To this end, we investigated the hydrogen atom adsorption (H*; where “*” denotes a surface-bound species) on the Pd(111), Pd(110), Pd(100), and Pd(211) surfaces containing different numbers of PdH subsurface layers in the near-surface region, with a

1:1 Pd:H ratio and with H atoms at the octahedral sites. The most stable H adsorption configuration for all four Pd surfaces was explored by comparing the adsorption energies of H* at the high symmetry sites of these surfaces (see Figure S11, Supporting Information). As reported in Tables S1–S4 (Supporting Information), H* is most stable at the fcc hollow site, pseudohexfold site, fourfold hollow site, and fcc hollow site for the Pd(111), Pd(110), Pd(100), and Pd(211) surfaces, respectively. All of these identified stable adsorption sites for H* agree with previous theoretical studies.^[64,65] Accordingly, the adsorption energies of H* on different Pd surfaces with different numbers of PdH sublayers were calculated in the most favorable adsorption sites. Before investigating the HER activity on all surfaces with hydrogen subsurfaces, we remark on the diffusion mechanism of the adsorbed H atom on the surface and in the subsurfaces (up to the fourth subsurface layer) to understand the behavior of the H atom after adsorbing on the surface. Here, the Pd(111) surface was taken as a representative system for H diffusion, where the diffusion path of the H atom passes through the fcc hollow site on the surface, then through the first, second, third, and fourth octahedral (O) sites in the subsurfaces (see Figure S12a, Supporting Information). We carried out climbing image nudged elastic band (CI-NEB) calculations to determine the minimum energy path and the corresponding diffusion barrier. The energy profile of the considered diffusion path of the H atom is illustrated in Figure S12b (Supporting Information). According to this diagram, the H atom has to overcome a barrier of 0.53 eV to move from the fcc hollow site on the surface to the first subsurface O site. This result is consistent with the previous theoretical study where the diffusion barrier obtained by the DFT potential energy surface was found to be 0.57 eV.^[66] For the subsequent steps, the H atom diffuses from the first subsurface O site (1st sub O) to 2nd sub O, from 2nd sub O to 3rd sub O, and from 3rd sub O to 4th sub O, with barriers of 0.38, 0.31, and 0.21 eV, respectively. The H diffusion barrier of 0.21 eV from 3rd sub O to 4th sub O, i.e., passing through the bulk region is in good agreement with the experimental value of 0.23 eV for the H diffusion barrier in the Pd bulk.^[67]

We now turn to evaluate the HER activity on the Pd(111), Pd(110), Pd(100), and Pd(211) surfaces with zero to four PdH sublayers. In terms of hydrogen electrocatalysis, the Gibbs free energy change of hydrogen atom adsorption, ΔG_{H^*} is a widely accepted descriptor for the HER activities of various catalysts,^[68] where a value of ΔG_{H^*} that is close to zero (thermoneutral) indicates a good catalyst for the HER. To obtain ΔG_{H^*} , we considered the hydrogen adsorption step (Volmer reduction) on surfaces with and without PdH subsurface layers, evaluated at $U_{SHE} = 0$, $T = 300$ K and $P = 1$ atm. The details for the calculation of ΔG_{H^*} are provided in Section S9 (Supporting Information). Here, a low H* coverage was used to reflect the HER activity that corresponds to our experimental observation discussed earlier (Section 2.1). The H* coverage is defined as the number of the adsorbed H atoms divided by the number of exposed atoms of the corresponding clean surface in units of ML (monolayer). Therefore, the ΔG_{H^*} at a low H* coverage of 1/4, 1/8, 1/4, and 1/6 ML for Pd(111), Pd(110), Pd(100), and Pd(211), respectively, was calculated and the 3-state free energy diagrams for the HER on the four surfaces with different numbers of PdH sublayers are illustrated in Figure 4.

For reference, the free energy diagrams for the high H* coverage cases (1 ML for all surfaces studied) are presented in Figure S13 (Supporting Information). We first discuss the HER activity on clean surfaces without PdH sublayer (0 PdH_{sub}). The ΔG_{H^*} on pristine Pd(111), Pd(110), Pd(100), and Pd(211) surfaces are −0.427, −0.367, −0.474, and −0.386 eV. When H atoms are absorbed in the subsurface layers, the absolute values of ΔG_{H^*} on the corresponding Pd(111), Pd(110), Pd(100), and Pd(211) surfaces tend to decrease, indicating an improvement for the HER performance. The values of ΔG_{H^*} on the Pd(211) and Pd(111) surfaces that contain three to four PdH subsurface layers are much closer to zero; thus, these surfaces would display better HER activities, compared with those of all clean surfaces. The lower HER activities on all pristine surfaces arise from the strong adsorption energy of H* on the surface of Pd, which leads to weaker hydrogen desorption and active site poisoning. Note that all considered Pd(100) surfaces show large magnitudes of ΔG_{H^*} , which would explain the inferior HER performance observed in the electrochemical measurements. For all surfaces with the highest number of PdH sublayers (4PdH_{sub}), the trend of increasing HER activity, i.e., the decreasing magnitude of ΔG_{H^*} [Pd(100); −0.419 eV → Pd(110); −0.244 eV → Pd(111); −0.154 eV → Pd(211); −0.134 eV], is in excellent agreement with our experimental results that found the Pd(111) surface to exhibit the best HER performance, followed by the Pd(110) and Pd(100) surfaces (see Figure 1d).

It is interesting to note that the existence of different numbers of PdH subsurface layers significantly changes the HER activity for all surfaces. To obtain insights into the effect of an increasing number of PdH sublayers on the enhanced electrochemical HER activity, the geometric properties, i.e., lattice parameters of all considered surfaces, were investigated upon the formation of PdH subsurfaces. Since the volume of the bulk PdH increases as the Pd:H ratio increases (Figure S8, Supporting Information), the PdH subsurface layers that are formed on top of pure Pd are compressed, resulting in compressive strain. In Figure 5, the ΔG_{H^*} and compressive areal strain for all studied surfaces at low H* coverage were plotted as a function of the number of PdH subsurface layers. The results for the high H* coverage cases are also provided in Figure S14 (Supporting Information). As noted earlier, a surface that has the value of ΔG_{H^*} that is close to zero can be regarded to exhibit excellent HER activity. From Figure 5a, it can be assumed that when the first PdH subsurface is formed in the Pd(111) surface, ΔG_{H^*} changes from −0.427 eV (bare surface) to −0.287 eV. This means that the presence of subsurface hydrogen significantly decreases the magnitude of the H* binding energy, which results in a higher HER activity compared to without PdH subsurface. This finding is consistent with a previous theoretical study that found the Pd subsurface H to destabilize the adsorbed H, which led to an increased reaction rate for ethyl hydrogenation.^[69] A compressive areal strain of 1.44% occurs when the first and second subsurface layers are completely occupied by adsorbed H atoms. As a result, the corresponding surface is more active for HER with a ΔG_{H^*} of −0.209 eV. Upon the formation of three PdH sublayers, ΔG_{H^*} is found to be −0.171 eV, where the surface is subjected to 3.16% areal compression. Finally, when the fourth PdH subsurface is reached, the Pd(111) surface is

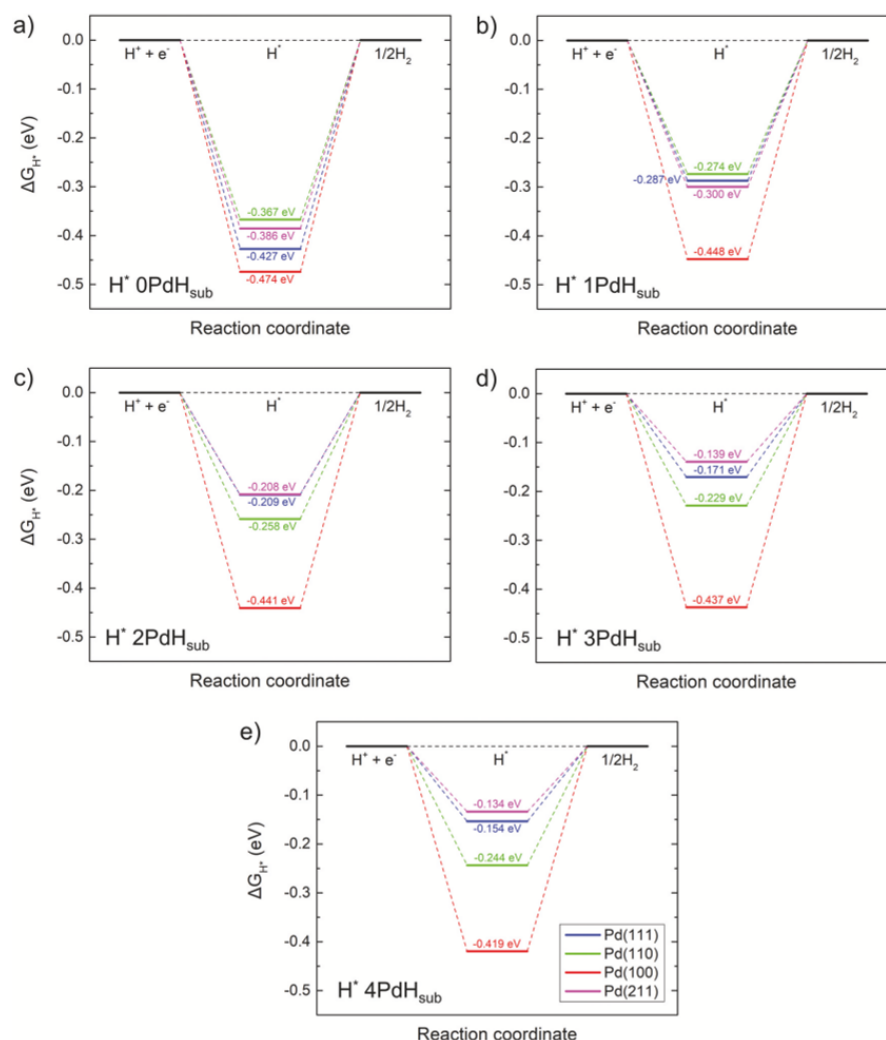


Figure 4. Free energy diagram for HER at low H^* coverage on the Pd(111), Pd(110), Pd(100), and Pd(211) surfaces with zero to four PdH sublayers.

compressed with 4.18% areal strain, and the ΔG_{H^*} gets closer to zero (-0.154 eV). These results indicate that the increase in compressive strain by the formation of PdH subsurfaces leads to weaker adsorption energy of H^* on the surface and thus a higher HER activity. For the Pd(110) surface, the compressive areal strain is 0.77% upon hydrogen absorption in the first sublayer (Figure 5b). Such strain causes the change in the value of ΔG_{H^*} from -0.367 eV on the bare surface to -0.274 eV. The Pd(110) surfaces with two and three PdH sublayers have compressive areal strains of 1.08% and 2.00%, and ΔG_{H^*} values of -0.258 and -0.229 eV, respectively. Remarkably, in the presence of four PdH sublayers on the Pd(110) surface, the absolute

value of ΔG_{H^*} slightly increases (-0.244 eV) although a large compressive areal strain (2.87%) is observed. For the Pd(100) surface (Figure 5c), the ΔG_{H^*} values are -0.448 and -0.441 eV for the surface with one and two PdH sublayers, respectively (c.f., $\Delta G_{H^*} = -0.474$ eV for the pristine surface). Note that there is no strain observed until three subsurface H layers are reached. The surface with three PdH sublayers has a compressive areal strain of 0.70% and shows a ΔG_{H^*} of -0.437 eV. When four PdH sublayers are formed, a compressive areal strain of 1.85%, and a ΔG_{H^*} of -0.419 eV are found. These results indicate that the ΔG_{H^*} on Pd(100) surfaces are relatively insensitive to the number of PdH sublayers and strain. For the Pd(211)

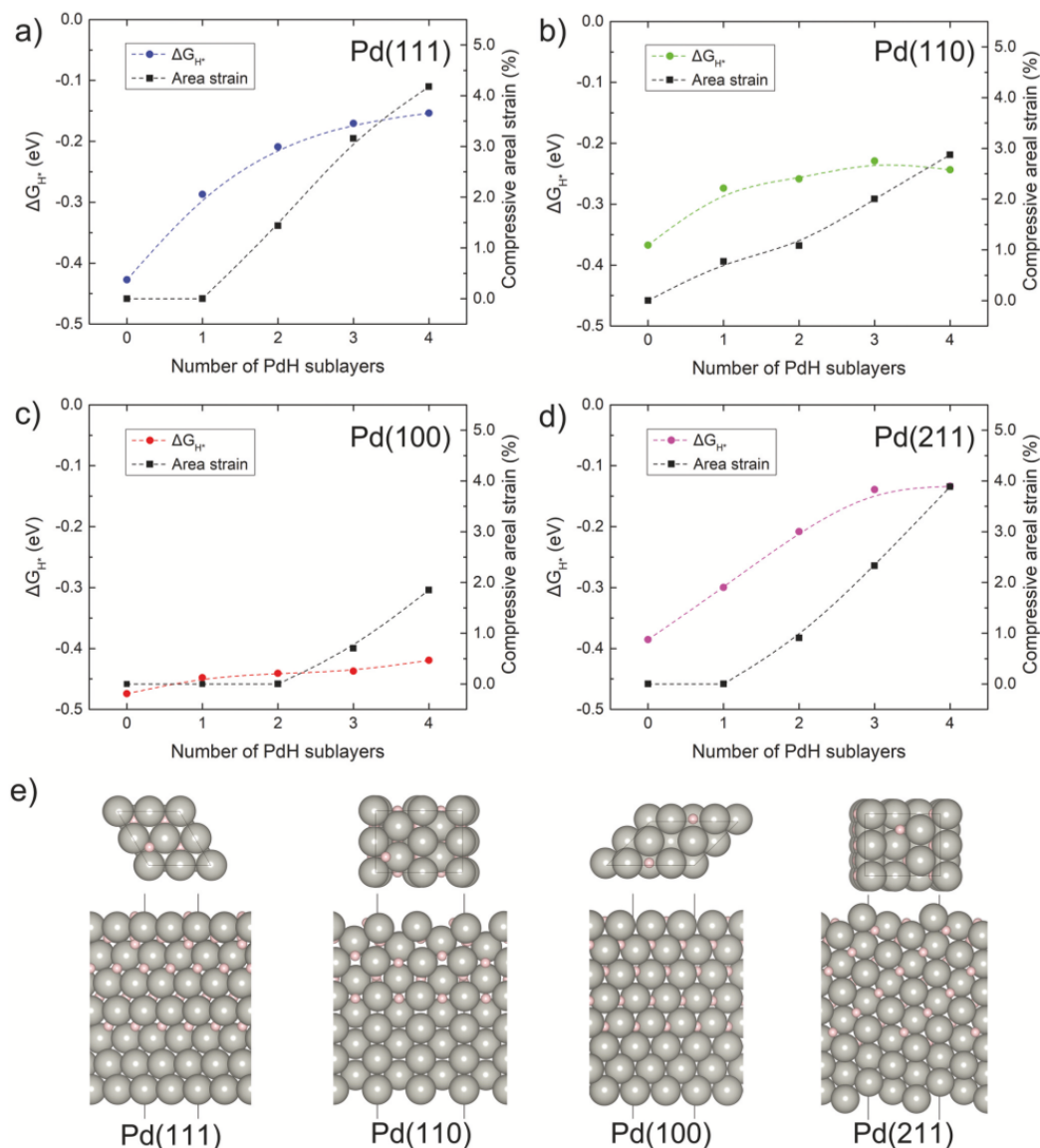


Figure 5. Hydrogen adsorption free-energy change (ΔG_{H^*}) at low H^* coverage and compressive areal strain as a function of the number of PdH sublayers for a) Pd(111), b) Pd(110), c) Pd(100), and d) Pd(211) surfaces. The compressive areal strain, ϵ_A , is defined as $\epsilon_A(\%) = \frac{A_{uc} - A_c}{A_c} \times 100$, where A_{uc} and A_c are the areas of the unconstrained and constrained PdH/Pd interface systems, respectively. e) The structural configurations of H^* on the surface with four PdH sublayers (i.e., largest strain considered) for all studied surfaces.

surface, as the PdH sublayers and strain increase, the trend of the decrease in the magnitude of ΔG_{H^*} is very similar to that of the Pd(111) surface. As displayed in Figure 5d, while there is no strain occurring when the first PdH sublayer is formed, ΔG_{H^*}

changes from -0.386 eV (bare surface) to -0.300 eV. For the surface with two, three, and four PdH sublayers which possess a compressive areal strain of 0.91%, 2.33%, and 3.89%, respectively, their ΔG_{H^*} values approach zero (-0.208 , -0.139 , and

−0.134 eV, respectively). Comparing all surfaces with four PdH sublayers (i.e., largest strain considered), a trend of increasing compressive areal strain was observed [Pd(100); 1.85% → Pd(110); 2.87% → Pd(211); 3.89% → Pd(111); 4.18%], whereas a decreasing trend of the magnitude of ΔG_{H^*} was found [Pd(100); −0.419 eV → Pd(110); −0.244 eV → Pd(111); 0.154 eV → Pd(211); −0.134 eV]. Essentially, a larger compressive strain on the surface results in a lower magnitude of ΔG_{H^*} , implying a more efficient HER performance. However, the Pd(211) surface yields a lower magnitude of ΔG_{H^*} although it has a smaller compressive strain compared with the Pd(111) surface. Therefore, besides the strain, the surface orientation still influences the hydrogen adsorption ability.

Besides the effect of strain induced by an increasing number of PdH sublayers on the improved HER activity, we further investigated the sole strain effect (without PdH sublayers) on the H adsorption for all Pd surfaces. To this end, the ΔG_{H^*} for Pd(111), Pd(110), Pd(100), and Pd(211) surfaces at low H^* coverage, were calculated as a function of the compressive areal strain. In order to be consistent with the strain occurring by the formation of PdH sublayers, we applied the compressive areal strain of up to 4% to all pure Pd systems. As depicted in Figure S15 (Supporting Information), the magnitudes of the ΔG_{H^*} for all pure surfaces decrease as the compressive areal strain increases indicating the enhanced HER activity, as similarly found in the case of the surfaces containing PdH sublayers. However, for this system, there is a smaller change in the ΔG_{H^*} compared to the case with PdH sublayers (Figure 5). Comparing ΔG_{H^*} of the pristine surfaces to the ones with the largest applied compressive areal strain (4%), the ΔG_{H^*} changes from −0.427 to −0.375 eV, −0.367 to −0.350 eV, −0.474 to −0.469 eV, and −0.386 to −0.332 eV for Pd(111), Pd(110), Pd(100), and Pd(211), respectively. Remarkably, the Pd(100) surface is still relatively insensitive to the compressive strain.

From an electronic point of view, the decrease in the magnitude of adsorption energy of H^* with increasing compressive strain can be understood by the increased overlap of the Pd d-orbitals, which results in increased bandwidth. To preserve the degree of electron filling, the position of the d-band of Pd shifts to a lower energy relative to the Fermi level. Upon H absorption, this downshifting of the position of the d-band results in the increased population of the H-s–Pd-d antibonding orbital, which weakens the adsorption of H^* on the surface. That is, the position of the d-band of the surface that contains a higher number of PdH sublayers and a larger compressive strain, is far from the Fermi level (more negative value), indicating a weaker binding of H^* on the surface (ΔG_{H^*} gets closer to zero).

Already from the CV and XRD measurement (Section 2.1), the observation arose that the Pd surfaces are prone to change upon electrochemical cycling, which is likely connected to the absorption of hydrogen and subsequent strain effects, as discussed earlier. Therefore, we investigated the nature of active sites due to these changes by using n-EC-STM measurements after electrochemical cycling on Pd(111) and Pd(100). For both orientations, we observed a change in the morphology and, therefore, a change in the noise-behavior, as illustrated in Figure 6. Compared to the freshly annealed, atomically flat surface (Figure S4, Supporting Information), a “hilly” surface with

islands of ≈10–20 nm with a height of ≈0.3–1.5 nm appeared (Figure S16, Supporting Information). This is very likely caused by the release of strain, as it is also assured by the DFT data that the absorption of hydrogen leads to strain effects. As a possible result, the newly shaped surface is concave and convex curved. Another interesting observation is that apart from the morphology, also the nature of the active sites changed.

Figure 6a shows a $125 \times 125 \text{ nm}^2$ area of cycled Pd(111), labeled as Pd(111)_c, with the potential set to −0.8 V_{Pt} for the upper half of the image (HER “On”) and in the lower half to 0.0 V_{Pt} (HER “Off”) in 0.1 M $HClO_4$. The color scheme highlights the difference between concavely (blue) and convexly curved (orange) areas. The exact separation of these different curved areas is illustrated in Figure S17a of the Supporting Information. Here, the noise, visible as white dots, was found predominantly in convex, but also in several concave curved areas for HER “On.” While the concave curved areas have a similar activity all over, some concave curved areas show a relatively low and others a very high activity. A 3D view and a similar measurement can be seen in Figure S18b,d of the Supporting Information, showing the same trend. As visible in the histograms in Figure 6b, on average, concave curved areas show a similar behavior to convex curved areas. Compared to the flat relatively inactive terrace regions for the annealed crystal found in Figure 3a the electrocatalytic behavior at the cycled surface seems to be fundamentally different.

A significant change in the noise behavior was also observed for the cycled Pd(100), labeled Pd(100)_c, in Figure 6c. The concave curved areas show a very low activity compared to the convex curved areas. Similar 2D and 3D images of Pd(100) and the separation of the curved areas can be found in Figures S19 and S17b (Supporting Information), respectively. Here, for HER “On” the potential was set to −0.7 V_{Pt} and for HER “Off” to 0.0 V_{Pt} . This trend is verified in the plot in Figure 6d, which was calculated analogously to b), illustrating the difference between concave and convex curved areas. A much larger increase in the noise level was observed in the convex curved areas compared to the concave curved areas when the reaction was turned “On.” In comparison to the noise behavior of the freshly annealed Pd(100) in Figure 3c, showing some activity all over the surface, here, the noise was predominantly found in convex curved regions. This is also visible in the line scan showing a 28 nm broad area which equals ≈100 Pd-atoms, with distinct noise spikes in the convex curved areas. An interesting conclusion is that steps seem to transform from being the most active on the freshly annealed surface (Figure 3a,c) to convex sites after electrochemical cycling (compare the step in Figure S19d (Supporting Information) in case of Pd(100)_c). The reason for this is most likely the changed hydrogen adsorption properties due to strain effects, as indicated by the DFT calculations. We can summarize that the absorption of hydrogen and the subsequent creation of strain changes the surface morphology and the nature of the active sites.

2.4. Design Principle of Pd Nanoparticles for Optimized HER Performance

From the previous discussions, it is clear that the strain induced by hydrogen absorption, as well as the average surface

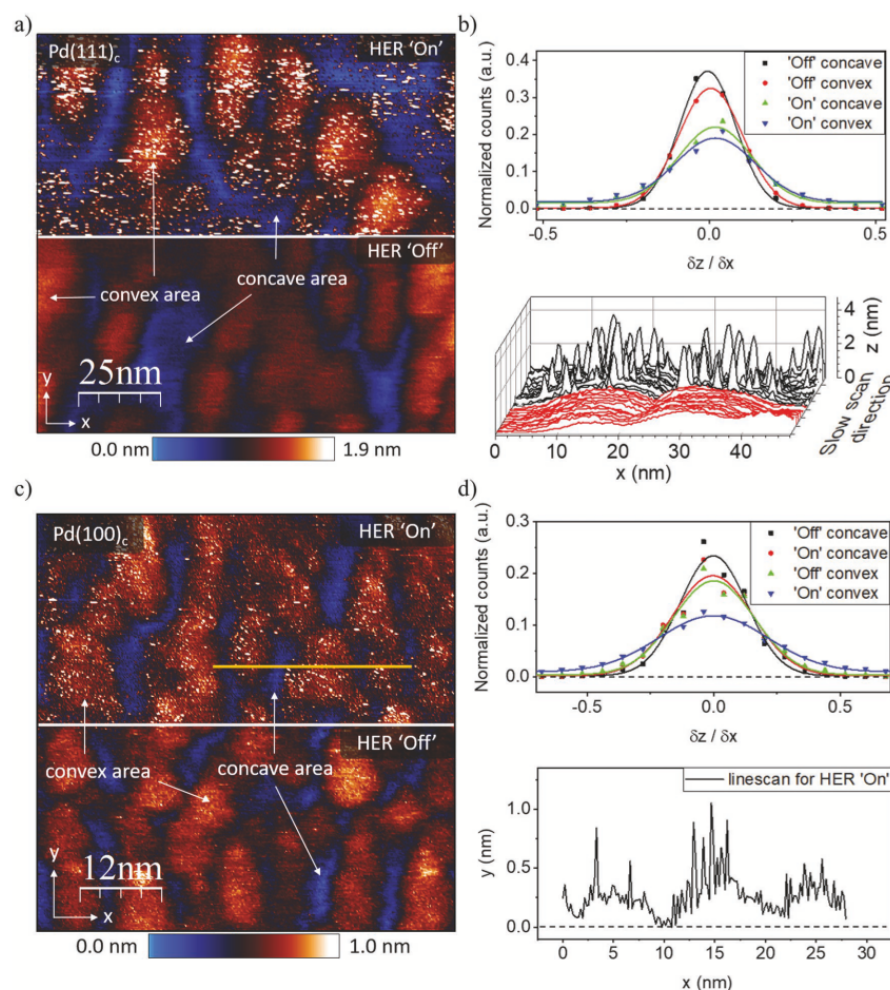


Figure 6. n-EC-STM measurement of Pd(111)_c and Pd(100)_c after cyclic voltammetry in 0.1 M HClO₄ for HER turned "On" (−0.8 and −0.7 V_{PE}, respectively) and "Off" (0.0 V_{PE}). The blue-colored areas show the concave curved areas, while the convex ones are illustrated in orange color (separation of the areas is shown in Figure S17 of the Supporting Information). a) The convex areas of Pd(111) show high activity for reaction "On." Very active and mostly inactive sites were found in the concave curved areas. b) Normalized counts versus the derivative of the slopes of the concave and convex sites of a) showing the highest activities for convex areas followed closely by concave regions. The waterfall plot provides an additional perspective of a border between HER "On" (black) and HER "Off" (red) and the noise behavior at this interface (compare Figure S18a in the Supporting Information for the exact position). c) Analogous measurements for Pd(100) while in contrast to Pd(111) the concave curved areas are less active. d) The noise level of concave sites increases only slightly for reaction "On." In contrast, the convex area shows a high activity when the reaction is turned "On." The line scan shows the orange highlighted line in c) for HER "On," which has a length of 28 nm and therefore illustrates ≈100 Pd atoms. c) and d) are fitted by the Gaussian function.

coverage, plays a crucial role in the activity of Pd surfaces. Nevertheless, the Pd(111) and especially the Pd(211) surfaces can be classified as particularly active with respect to the HER. To boost its activity, for nanostructured catalysts, this means that these surfaces are to be maximized when normalized to the catalyst mass. This, in turn, implies for nanoparticles that due

to their higher volume to surface ratios, only the smallest particles should be considered. On the other hand, one should not forget the critical role of the PdH subsurface layers. As shown in this study, one can optimize the binding energies by more than 200 meV due to induced strain. Therefore, a size of several nanometers is desirable, allowing to integrate sufficient

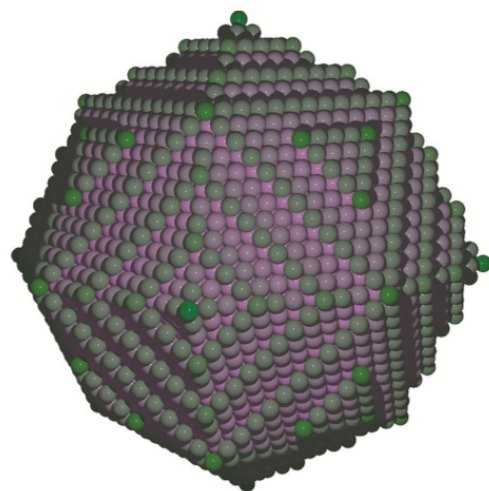


Figure 7. Schematic of a Pd nanoparticle with optimized surface morphology. The particle consisting of 8127 Pd atoms has an average diameter of 6.85 nm. It shows a high ratio of Pd(211) and Pd(111) surfaces which have shown to be highly active.

absorbed hydrogens in the subsurface layers. Considering these requirements and surface stability, we applied the Wulff construction to generate arbitrarily nanoparticles with predominantly Pd(211) and Pd(111) as exposed surfaces. One of the most promising candidates is displayed in **Figure 7**. This particle consisting of 8127 atoms has a diameter along the longest and shortest axis of 7.0 and 6.7 nm, respectively. It consists mainly of Pd(211) surfaces which are particularly active and Pd(111) surfaces. For better representation, the atoms are colored according to their coordination. Results for single crystal surfaces indicate that the active sites should be highly coordinated threefold (fcc hollow) at the step edges and on the Pd(111) planes.

3. Conclusion

The aim of this study was the characterization of the HER activity on model Pd surfaces, directing a particular focus on the effects of hydrogen absorption on the nature of the active sites. Pd(111) was identified to be the most stable basal plane by DFT calculations, followed by Pd(100) and Pd(110) surfaces. The experimental measurements showed the following HER activity trend: Pd(111) > Pd(110) > Pd(100). Using cyclic voltammetry and the XRD technique, we demonstrated that hydrogen absorption into the bulk changes the electrochemical behavior and increases the lattice parameter. EC-STM images provided further confirmation of the morphological transformation. The nature of HER active sites is likely affected by the generation of strain due to hydrogen absorption. This was supported by DFT calculations, which indicated that the population of Pd subsurface layers with H results in a compressive strain that lowers the magnitude of the H adsorption free energy on the low-index (111), (100), and (110) surfaces, thereby increasing the

HER activities on these surfaces. In the presence of strain, the DFT-calculated HER activities in the model surfaces were in the decreasing order of (211) > (111) > (110) > (100), in agreement with the experimental results. Further, using the impedance analysis, we estimated the surface coverage of Pd(111), Pd(110), and Pd(100) as ≈ 0 , ≈ 0.3 – 0.4 , and ≈ 0.95 , respectively, and elucidated that the Heyrovsky mechanism is suppressed on all investigated Pd surfaces in acidic media. From the EC-STM measurements, we determined the most active sites on freshly annealed Pd(111) near step edges. More specifically, the upper edge seemed to be more active than the bottom of the step. In contrast, terraces remained less active. Interestingly, not all steps were equally active, which is explained by their different coordination. Similarly, freshly annealed Pd(100) showed the highest activity on step edges, although in this case, significant activity was found on the terrace as well. The absorption of hydrogen into the bulk during cyclic voltammetry results in a change of the surface morphology and distribution of the active sites at both crystalline planes. A hilly structure was observed, exhibiting significantly increased activity on convexly curved areas. For Pd(100), the concave areas were less active than the convex areas. In contrast, for the Pd(111), concave and convex curved areas possess a very similar activity. The alteration of crystal surface morphology is presumably induced by the absorption of hydrogen into the bulk during potential cycling. This induces strain which, in turn, changes the nature of active sites. Finally, a possible nanoparticle design was introduced, consisting of mostly Pd(211) and Pd(111) surfaces, as they show the best HER activity of all investigated planes in this study. In summary, this work combined theoretical and experimental approaches to elucidate the surface-activity relation for the HER on Pd model surfaces. The obtained results are indispensable for the general understanding of metal hydride systems and formulation of design principles for the optimal Pd-based nanostructured catalysts.

4. Experimental Section

In the following, the most relevant methods and techniques which were used for the calculations and measurements presented in this work will be discussed in detail. Tables including the most relevant settings used for the experiments are attached in Section S17 of the Supporting Information.

Sample and Electrolyte Preparation: For the experiments, Pd(111) ($\varnothing$ 6 mm, 99.999%, MaTeck, Germany) and Pd(111), Pd(110), Pd(100) single crystals ($\varnothing$ 5 mm, 99.999%, MaTeck, Jülich, Germany) disc electrodes were used. Each surface was prepared by the manufacturer with a roughness of less than 0.01 μm and an orientation accuracy better than 0.1°. Before each experiment, a well-orientated surface was assured by annealing in either a tubular furnace or an inductive heater setup. The Heraeus Instruments RO 7/50 furnace enables high-temperature annealing in an inert atmosphere to prevent oxidation of the Pd surface. The Pd crystal was placed in a small ceramic boat into the middle of a quartz tube fed by a continuous flow of Ar (Argon 5.0, Westfalen, Germany). After ≈ 1 h of heating, a temperature of 950 °C was reached and held for around three more hours. The cooling period to room temperature took ≈ 18 h. For further transportation and preparation, the single crystal's surface was covered with a drop of electrolyte inside the furnace to protect the freshly annealed surface from air. Alternatively, the usage of a high-frequency induction heater (20–80 kHz, 15 kW–EQ-SP-15A, MTI, USA) with a maximum output power of 15 kW was

introduced. The Pd crystals were placed into a special compartment which enabled a pure Ar atmosphere. The crystal was annealed three times with a first heating period of 90 s and each following 60 s and a relaxation time of 5 min in between. Again, to avoid exposure to air, the surface was protected with a drop of the electrolyte after the annealing process. The 0.1 M HClO₄ electrolytes were prepared by diluting 70% perchloric acid (Suprapur, Merck, Germany) using ultrapure water (Evoqua Milli-Q (18.2 MΩ cm)).

Cyclic Voltammetry and Activity Measurements: Before the electrochemical measurements, all glassware and experimental cells were cleaned with a 3:1 mixture of sulfuric acid (96% H₂SO₄ Suprapur, Merck, Germany) and hydrogen peroxide (30% H₂O₂, Suprapur, Merck, Germany), and subsequently washed by boiled ultrapure water for several times. All experiments were controlled by a VSP-300 potentiostat (Bio-Logic, France). The working electrode (WE) was immersed into the electrolyte at a starting potential of 0.57 V_{RHE} in order to minimize possible electrochemical surface processes beforehand. A mercury–mercury sulfate (MMS) and a curled polycrystalline Pd-wire (Ø = 0.25 mm, 99.95%, MaTeck, Jülich, Germany) were used as a reference and counter electrode (CE), respectively. The quality of the annealed single crystalline surface was confirmed by CVs in Ar-saturated 0.1 M HClO₄ in the potential range between 0.2 and 1.2 V_{RHE} at a scan rate of 50 mV s⁻¹. Polarization curves for evaluating the HER activity were recorded in a hanging meniscus configuration in H₂-saturated electrolyte. The potential range was set between -0.18 and 0.52 V_{RHE} at a scan rate of 50 mV s⁻¹. However, the HER activity evaluation was performed in the potential interval from -0.18 to 0.22 V_{RHE}. In this configuration, the risk of mass transfer limitations is limited since the HER over Pd in comparison to other catalysts is considerably slower. Further, hydrogen is essentially absorbed into the bulk. Thus, no gas bubbles were present at the electrode, which allows taking benefit of the full mass transfer rate from the electrolyte to the surface. More information about the experimental settings for each measurement is shown in Table S5 in the Supporting Information.

Electrochemical Impedance Measurements: Impedance spectra were acquired in 10 mV steps between 0.00 and -0.05 V_{RHE}. For this, a perturbation amplitude of 10 mV was applied, and spectra were recorded in a frequency range between 30 kHz and 0.1 Hz. The 0.1 M HClO₄ electrolyte was saturated with argon before and during the measurements. To compensate for measurement artifacts caused by the impedance of the RE in the high-frequency regime, a shunt capacitor was connected between the RE and an additional Pt wire. This wire was immersed in the electrolyte in the proximity of the tip of the Luggin-capillary. The quality of the recorded spectra was verified by a Krammer–Kronig check. The impedance data were analyzed using the homemade software EIS Data Analysis 1.3.^[70,71]

Grazing-Incidence X-Ray Diffraction Measurements: Grazing-incidence X-ray diffraction (GIXRD) patterns of the Pd(111) single crystal in the pristine state and after six cycles of HER (potential range between -0.18 and 0.22 V_{RHE}) were collected on an X'Pert PRO PANalytical instrument with a Ni-filtered Cu Kα radiation (λ = 1.5406 Å). The procedure used for GIXRD measurements consisted of a 2θ range of 35°–90° and a slow-scanning step of 2° min⁻¹. The settings used for each GIXRD measurement can be found in Table S6 in the Supporting Information.

EC-STM Measurements: The EC-STM measurements were performed by a Nanoscope III SPM Multimode from Veeco Instruments with a Veeco Nanoscope Universal bipotentiostat connected to a Nanoscope IIID controller. The STM-tips were mechanically ripped from a platinum/iridium (Pt80/Ir20, Ø = 0.25, 99.9+%, Goodfellow GmbH) wire with a side cutter. To minimize the impact of reactions at the tip-electrolyte interface on the tunneling signal, the tip was insulated by Apiezon wax.^[72] The sample was clamped between a Teflon ring and a steel plate fixed with screws acting as a miniature electrochemical cell. For all measurements a Pt wire (Ø 0.5 mm, 99.99%, MaTeck, Germany) as a quasi-RE and a curled Pd wire (Ø 0.25 mm, 99.95%, MaTeck, Germany) as a CE were used. Detailed information about the values set for each STM measurement can be found in Table S7 in the Supporting Information.

Noise-EC-STM Technique: The innovative idea of the noise-electrochemical scanning tunneling microscopy (n-EC-STM) technique is to identify active sites by analyzing the noise in the STM signal under reaction conditions as first published by Pfisterer et al.^[42] An ongoing electrochemical reaction will persistently change the electrolyte composition and structure in the tunneling barrier between the scanning tip and the WE. The movement of ions in the tunneling barrier, as well as the structure of the electrolyte has been shown to influence the tunneling barrier and thus the STM signal.^[73–80] Therefore, if the tip is placed over an active area, the detected tunneling current varies with time and a noisy signal is detected. Most likely, this is a direct consequence of the ad- or absorption of molecules on the surface. In contrast, in areas with low electrochemical activity, the detected noise level is significantly lower. Thus, the noise level of the STM signal serves as a tool to detect the active sites. All STM measurements were performed in air atmosphere at room temperature and evaluated using WSxM 5.0 Develop 9.4.^[81]

Noise Analysis: For this evaluation, the STM signal (here, height *z*) is derived in the fast scan direction *x* according to the “numpy.gradient()” function of the python's library NumPy. Here the different derivatives of the slopes between neighboring data points of each line scan were plotted versus its normalized quantity and were fitted afterward. Detailed information of the working principle can be found at the NumPy website^[82] and in refs. [83,84, and 85]. Subsequently, histograms are compiled from the signal derivatives. In this work, bin sizes of 0.08 were used, except for Figure 3d, which was rendered using a bin size of 0.03 for Pd(100). At high noise levels, the derivative values (slopes in line scans) possess a broad FWHM and low-intensity distribution. Therefore, the width and height of an adequate fit of the histograms serve as a quantification of the noise level.^[57]

DFT Calculations: First-principles calculations based on spin-polarized DFT approach were performed using the Vienna Ab Initio Simulation Package (VASP 5.4).^[86,87] The projector augmented-wave (PAW) method^[88,89] was employed to describe the electron-ionic core interactions where Pd 4d¹⁰ and H 1s¹ were treated as valence electrons. Their wavefunctions were expanded with the plane-wave basis using a cutoff energy of 500 eV. The exchange-correlation functional was approximated using the generalized gradient approximation (GGA) in the form of Perdew, Burke, and Ernzerhof (PBE).^[90] To account for the van der Waals interactions, the lattice constants of a bulk face-centered cubic (fcc) Pd were calculated by various dispersion correction methods, as summarized in Table S8 (Supporting Information). It can be found that the obtained lattice constant (3.891 Å) using the DFT-D3(BJ) approach proposed by Grimme et al.^[91] is closest to the experimental value (3.890 Å), which was determined using XRD in this work (Figure 1e) and other experimental studies.^[92,93] Therefore, the DFT-D3(BJ) approach was used for all subsequent calculations. All structures were optimized using the conjugate gradient method.^[94] The Methfessel–Paxton smearing technique^[95] (σ = 0.05 eV) was used during the geometry optimization.

Different Pd surfaces were modeled by cleaving the optimized structure of a bulk fcc Pd unit cell (containing 4 atoms) in the low-index Pd(111), Pd(110), and Pd(100) facets for the flat surfaces, as well as the Pd(211) facet for the stepped surface. The Pd(111) and Pd(211) surfaces were obtained using a 1 × 1 unit cell, while Pd(100) and Pd(110) surfaces were constructed using a 2 × 1 supercell, containing four Pd atoms per layer for Pd(111), Pd(110), and Pd(100) surfaces and six Pd atoms per layer for Pd(211) surface. In order to investigate the H adsorption on Pd surfaces with different numbers of PdH sublayers (up to 4 sublayers), the appropriate slab thickness was determined. Here, the thickness of the Pd(111) surface was used as a criterion for the other three surfaces. Therefore, these slabs were built with the thickness of seven (13.48 Å), eleven (13.76 Å), eight (13.62 Å), and seven (14.30 Å) atomic layers for (111), (110), (100), and (211) surfaces, respectively. A vacuum space of 20 Å along the *z* direction was added to avoid interaction between the periodic images. Figure S20 (Supporting Information) illustrates the top and side views of these surfaces. During the structural relaxation of the slabs, the two bottom layers (2.25, 1.95, and 2.38 Å) for Pd(111), Pd(100), and Pd(211) surfaces, respectively, and the three bottom layers

(2.75 Å) for Pd(110) surface, were completely fixed to mimic its bulk structure. The sampling of the Brillouin zone using the Monkhorst-Pack scheme^[96] was employed with $7 \times 7 \times 7$ and $7 \times 7 \times 1$ k-points for bulk and slabs calculations, respectively. The structures were fully optimized until the force acting on each atom was less than 0.01 eV Å^{-1} . The energy of convergence tolerance was set to $1 \times 10^{-6} \text{ eV}$. The electric dipole correction in the z direction was used to cut the spurious interaction between the repeated images of the slab model. The H_2 molecule was modeled using one free molecule inside a $20 \times 20 \times 20 \text{ Å}^3$ supercell with electric dipole correction implemented in all directions. To study the H diffusion mechanism, the CI-NEB approach was carried out to determine the minimum energy path of H diffusion. The CI-NEB method allows for ionic relaxation of each configuration along the diffusion path. The transition state (TS) is located at the saddle point of the reaction coordinate, where the energy difference between TS and the initial state yields the diffusion barrier.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

active sites, density functional theory, electrochemical scanning tunneling microscopy, hydrogen absorption, hydrogen evolution reaction, palladium, strain effect

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RESEARCH ARTICLE

Elucidating the Active Sites and Synergies in Water Splitting on Manganese Oxide Nanosheets on Graphite Support

Thorsten O. Schmidt, André Wark, Richard W. Haid, Regina M. Kluge, Shinya Suzuki, Kazuhide Kamiya, Aliaksandr S. Bandarenka,* Jun Maruyama,* and Egill Skúlason*

Photosystem II is nature's solution for driving the oxygen evolution reaction to oxidize water. A manganese-oxide cluster is this protein's active center for water splitting, while the most efficient man-made catalysts are costly noble metal-based oxides. Facing the climate change, research on affordable and abundant electrocatalysts is crucial. To mimic the biological solution, manganese oxide nanosheets are synthesized and deposited on highly-oriented pyrolytic graphite. This electrocatalyst is then examined with spectroscopic and electrochemical measurements, electrochemical noise scanning tunneling microscopy, and density functional theory calculations. The detailed investigation assigns the origin of its enhanced water-splitting performance to detected activity at the nanosheet edges which the proposed mechanism explains further. Therefore, the results provide a blueprint for how to design efficient electrocatalysts for water oxidation with abundant materials.

debate. Elucidating the OER mechanism is challenging due to, among other reasons, the complicated electronic structure of the Mn_4CaO_5 cluster and the complex environment of the protein matrix.^[7–9] Nevertheless, since researchers are seeking affordable alternatives for the most efficient electrocatalytic materials, which are expensive platinum group metals, some noble-metal free and manganese dioxide (MnO_2)-based photoelectrocatalysts have been inspired by PS II.^[10–12]

As the demand for clean and renewable fuel cells, for instance, has been increasing in the past years, MnO_2 -based heterogeneous catalysts (or functionalized variants of such as it has been done for, for instance, platinum^[13])

1. Introduction

Photosystem II (PS II) plays a key role in nature to drive the oxygen evolution reaction (OER) and can be found in plants and cyanobacteria.^[1–3] Herein, the active site in this protein is a molecular manganese oxide cluster Mn_4CaO_5 , embedded in a protein matrix, whose structure was elucidated only a decade ago.^[4,5] This molecular cluster drives the photoelectrochemical water-splitting reaction at very low overpotentials (about 0.3 V at pH 5),^[6] although the underlying mechanism is still under

can be considered as alternative material for photoelectrocatalysis.^[3] Generally, heterogeneous catalysts can better be used on a larger scale and are more persistent than homogeneous catalysts.^[14,15] Moreover, MnO_2 is an abundant material on earth with large deposits around the globe,^[16] unlike more precious transition metal oxides such as rutile IrO_2 , RuO_2 , or perovskites being utilized as the most efficient OER catalysts.^[17,18] Since MnO_2 has also shown to be a promising candidate as an OER catalyst,^[19] far-reaching basic research is desirable to better understand the origins of these catalysts' performance.

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To further reduce the complexity of research in this regard, the host or substrate of the catalyst must be simplified. The ideal candidate to address this requirement is carbon which has been extensively studied in experiments and theoretically.^[20–23] It is similarly abundant like MnO_2 ^[16] and especially in its crystalline structure as highly-oriented pyrolytic graphite (HOPG). It is a popular candidate as a support material, considering its conductivity,^[24] and electrochemical properties,^[25] which have already been studied in situ,^[26] and especially under OER conditions.^[27,28]

This work presents the experimental and theoretical characterization of the OER properties of the composite material MnO_2/HOPG consisting of MnO_2 nanosheets (MnO_2NS) on a HOPG support. The MnO_2NS consists of $\text{Mn}-\text{O}_6$ octahedral units connected by shared octahedral edges forming a highly anisotropic 2D layer with a thickness of approximately 0.7 nm and a typical lateral size in the micrometer range.^[29,30] Thus, the loading of MnO_2NS on HOPG forms a nearly ideal 2D model catalyst surface with broad terraces and NS step-edges with minimal height.^[31] First, we present the increase in total electrochemical activity due to the presence of MnO_2NS compared to pure HOPG using linear sweep voltammetry, illustrated in a Tafel plot. Subsequently, we show the nanosheets' nature of active sites using electrochemical noise scanning tunneling microscopy (n-EC-STM),^[32] which enables an in situ observation of the local activity^[33–36] as recently demonstrated by different groups.^[37–39] These observations are supported and systematically explained by the most probable reaction pathways using density functional theory (DFT) calculations. Herein, the MnO_2NS were modeled as a sheet of birnessite-type $\delta\text{-MnO}_2$ which has been shown to have similar features to the Mn_2CaO_5 in PS II.^[40,41] These findings allow a fundamental understanding of the chemical process of the OER on MnO_2NS , which can be used as a foundation for further research on MnO_x -based catalyst materials.

2. Results and Discussion

2.1. Electrochemical and Spectroscopic Characterization

The catalytic activity of the MnO_2NS for the OER was confirmed by higher currents for $\text{HOPG-MnO}_2\text{NS}$ compared to pure HOPG (Figure 1a and Figure S1, Supporting Information). Maruyama et al. previously examined the OER on HOPG with particulate Mn oxides deposited on the surface and found the enhancement of the OER current by the deposition.^[42] The enhancement was mainly observed above 0.65 V versus Hg/HgO . In this study, by contrast, the OER was clearly enhanced in the low overpotential region at $\text{HOPG-MnO}_2\text{NS}$ compared to HOPG. This effective OER enhancement was reasonably attributed to the morphology of MnO_2NS , which was characterized by the elongated edges. The Tafel slopes obtained by the semi-logarithmic plots in the high overpotential region were close to the conventional value, 0.12 V dec^{-1} , whereas those in the low overpotential region were exceptionally high. Such high Tafel slopes were also reported for the OER at polycrystalline $\gamma\text{-FeO}(\text{OH})$.^[43] The high Tafel slope might be due to the deviation of the transfer coefficient of the rate-determining step from the normal value, i.e., 0.5, although the detailed reason is unknown at present. The presence of the MnO_2NS was confirmed by the X-ray photoelec-

tron spectroscopy (XPS) after the electrochemical measurement (cf. Figure S2, Supporting Information). The low Mn/C ratio was associated with potential detachment of MnO_2NS upon immersion of $\text{HOPG-MnO}_2\text{NS}$ in the electrolyte and the limited number of Mn atoms within the XPS detection depth, in which the majority was C atoms of the HOPG substrate, and the Mn atoms were present only on the HOPG surface as the MnO_2NS . X-ray absorption near-edge structure (XANES) (Figure S3, Supporting Information) and the pseudo-radial structure function (RSF), being obtained by extended X-ray absorption fine structure (EXAFS) (Figure S4), further characterized the MnO_2NS . The peak at around 6.56 keV in the XANES spectrum and the two peaks at around 1.47 Å and 2.49 Å of the RSF indicate that the crystal structure of the MnO_2NS is a layered $\delta\text{-MnO}_2$ birnessite-type.^[31] Additionally, birnessite is known to occur when MnO_2 is present in an electrochemical environment.^[44] Consequently, it is also valid to assume that the structure of MnO_2NS is birnessite-typed. Therefore, this MnO_2 crystal structure was utilized in our DFT calculations to model the MnO_2NS .

2.2. Microscopic Measurements to Locate Active Centers

To understand these findings and to identify the most active sites for the OER, the in situ n-EC-STM technique was applied. The drawback of STMs is that it is generally unsuitable for distinguishing between different materials, and therefore, it is not straightforward to interpret the results on a composite material such as $\text{HOPG-MnO}_2\text{NS}$. However, using specific evaluation techniques and systematically performed measurements makes it possible to identify the observed material with a high probability. First, to study the behavior of the EC-STM signal on this sample and to exclude influences by the electrolyte, a measurement in the air was performed, illustrated in Figure 1b. Here, a NS with a size of several hundred nanometers and a height of approximately 0.7 nm is measured (cf. line scans below and Figure S5, Supporting Information), which agrees with other observations of MnO_2NS .^[44,45] The modeled height obtained from the DFT calculations is between 0.45 nm and 0.55 nm (Figure 1c and Figure S15, Supporting Information), which is close to the crystallographic thickness of 0.5 nm.^[31] Since the measurements in Figure 1b were carried out in air, while our calculations were performed in a vacuum and at zero temperature and water and cations as spacers between the layers^[41] were neglected for simplicity, both results are in reasonable agreement. Since the dimension of two overlying layers of HOPG ($2 \times 3.35\text{Å}$ ^[46]) is close to the one of a single layer of MnO_2 ($\approx 0.7\text{ nm}$), it is not possible to identify the material only by the observation of the height profile in Figure 1b.

A more precise determination of the materials and identification of the active sites at OER conditions is reached using the n-EC-STM technique. Like classical EC-STM, the partly insulated STM tip is engaged close to the sample surface surrounded by the electrolyte solution. When applying a reaction potential to the sample, electrochemical processes occur at catalytically active areas and locally alter the composition of the electrolyte solution, whereby the captured tunneling current fluctuates.^[32,47] This results in visible spikes in the STM signal while an increased noise level corresponds to an increased local electrochemical activity.

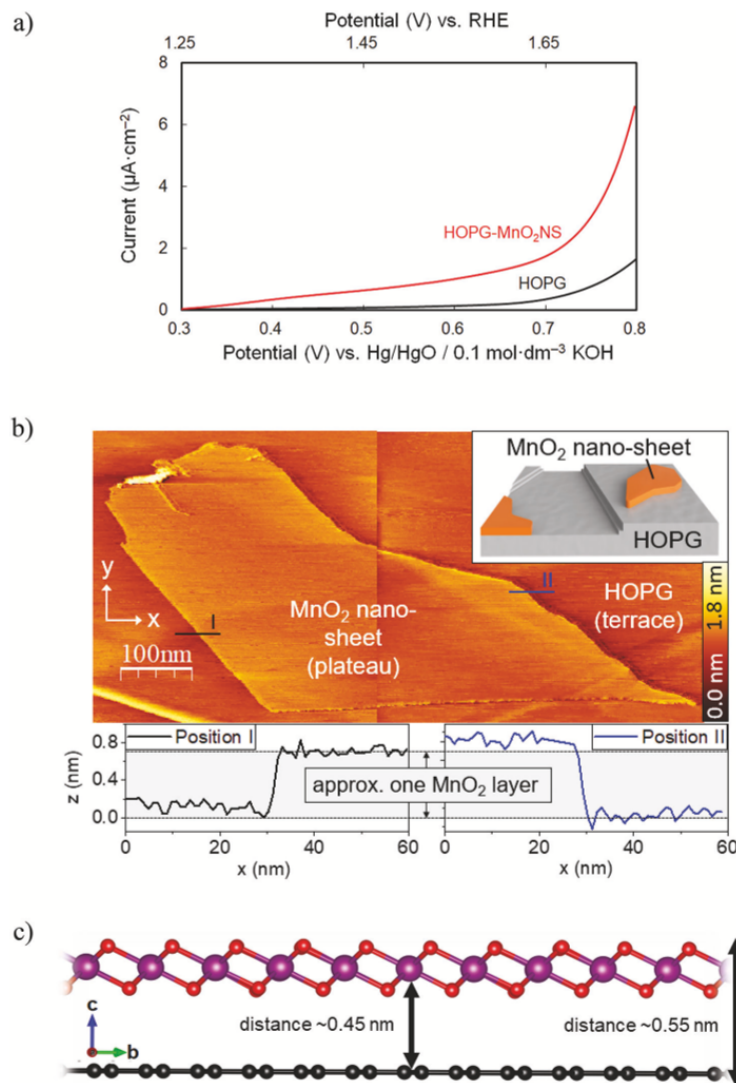


Figure 1. Characterization of the HOPG-MnO₂NS sample. a) Relationships between OER current and electrode potential at HOPG and HOPG-MnO₂NS in Ar-saturated 0.1 M KOH, at 25 °C. The potential scan rate was 10 mV s⁻¹. b) STM measurement of a supposed MnO₂NS in air and line scans of the sheet edges. Insert in the right top corner: Schematic model surface of HOPG-MnO₂NS. c) Model of the HOPG-MnO₂NS utilized in the DFT calculations. The predicted distances between the top graphene layer and the MnO₂NS are shown and represented by the arrows.

The noise disappears as soon as the applied potential at the working electrode is set to an electrochemically “neutral” value. In this way, an identification of the nature of the active sites is possible, as shown in Figure 2. More information on this technique is available in the Methods Section and previous literature.^[26,27,32,48–52]

The presence of MnO₂NS during the n-EC-STM measurements is confirmed by an increased current density at the OER region compared to pure HOPG (cf. Figure S6a).

Figure 2a shows a MnO₂NS in 0.1 M KOH at a potential of 600 mV versus a Pt quasi reference electrode (mV_{Pt}) on the left

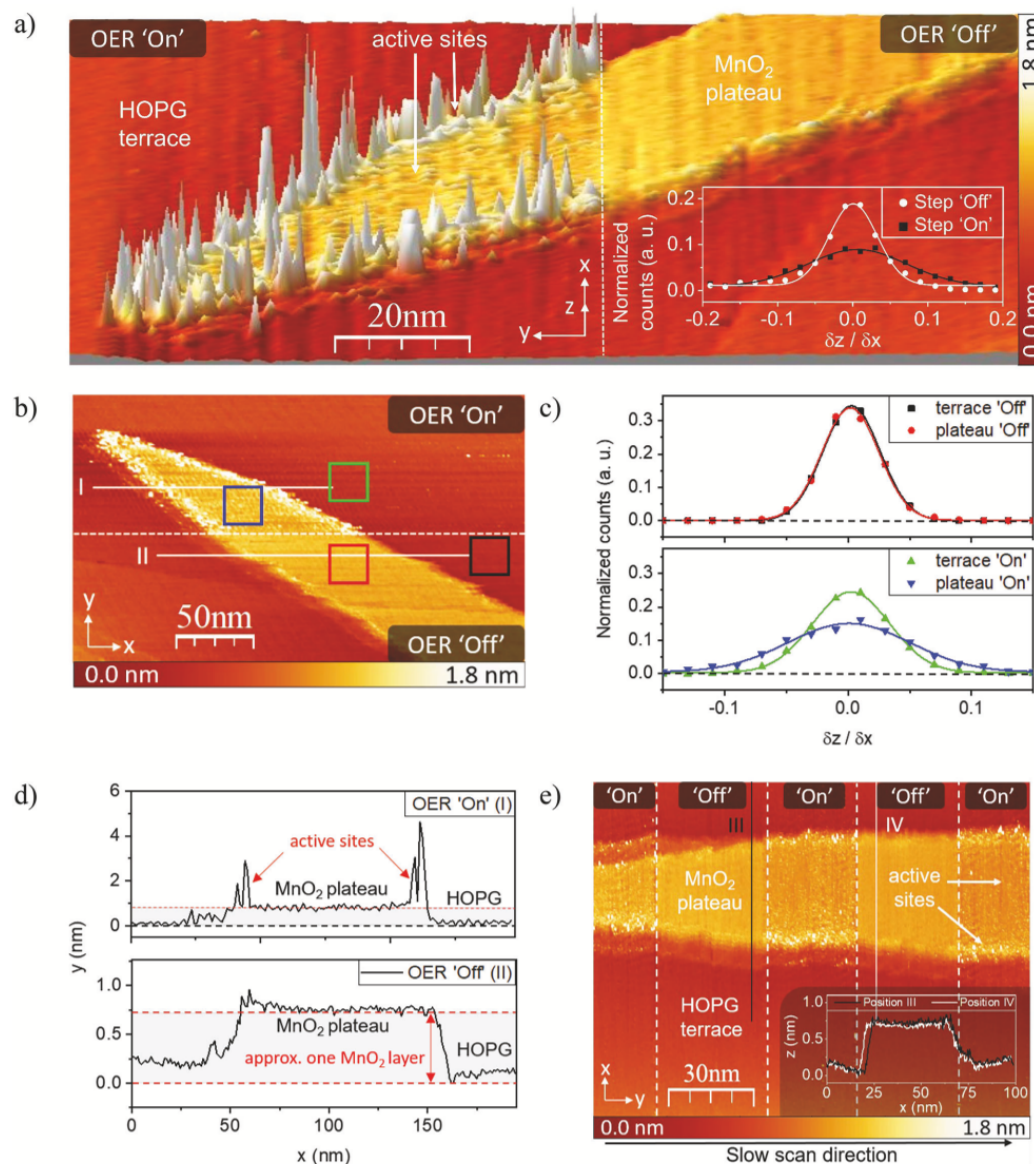


Figure 2. n-EC-STM measurement of an MnO_2NS in 0.1 M KOH. A minor noise level increase on the MnO_2 sheet and exceptional noise, and thus high activity near the sheet edges is visible. a) Three-dimensional view of an MnO_2NS (yellow area) on a HOPG support (red area). The graph in the right insert confirms a significant activity on the sheet edges for OER 'On'. b) Two-dimensional top view of a) illustrating an increased noise behavior on the plateau for OER 'On' while the surrounding HOPG terrace remains rather inactive. c) Roughness analysis of the four areas marked in b), demonstrating the difference in the noise behavior at the plateau and the surrounding terrace. d) Line scans for OER 'On' (I) and 'Off' (II) highlighted as white lines in b). The active sites are found predominantly close to the sheet edges (upper graph), while the profile is almost noise-free for OER 'Off' (lower graph). e) Demonstration of the reproducibility of the activity behavior, including a comparison of two line scans for reaction 'Off', illustrating the absence of significant corrosion effects during the measurements.

side (OER 'On') and at 0 mV_{Pt} on the right side (OER 'Off') (cf. Figure S6b, Supporting Information). The significant noise behavior on the edges of the nanosheet (white spikes) for OER 'On' indicates high activity. The increased noise level disappears at OER 'Off' on the right side, confirming the origin of the noise in electrocatalytic events. The visible ridge at the edge of the plateau for reaction 'Off' most likely results from the slightly increased STM's gain values required to visualize the noise on top of the plateau. However, the correlation becomes obvious in the inserted graph comparing the activity on the sheet edges at OER 'Off' (white) and OER 'On' (black). Here, by counting and normalizing the derivatives of the slopes of neighboring data points, one gets information about the captured roughness which is directly related to the activity. A lower amplitude and a larger full width at half maximum in OER 'On' than in OER 'Off' correspond to a higher distribution of derivative slopes and, therefore, to a higher activity. A more detailed explanation of this evaluation technique is available in the Methods Section and in references^[49] and^[53]. A white square in Figure S7a in the Supporting Information highlights the position of the evaluated area. One beneficial side effect of using the n-EC-STM technique is the opportunity to use insights on the relative activity of surface structures to draw conclusions on the observed material. For comparison, Figure S8 in the Supporting Information shows an area that consists only of the support material HOPG without any MnO₂. The active centers are equally distributed on steps and terraces and not dominantly on steps as observed in Figure 2. These findings on HOPG steps with similar experimental conditions indicate once more the correct differentiation of the materials in Figure 2a. Note that the observed noise on HOPG became visible by increased gain settings (see Table S1, Supporting Information) and is in good agreement with the findings of a previous study.^[27] Another interesting result is that, under reaction conditions, the surface on top of the NS (plateau) also shows a slight activity while the surrounding HOPG is largely inactive (cf. Figure 2a,b), which is confirmed and explained below by our DFT calculations. By comparing the normalized number of different slopes on top of the plateau and on the surrounding terrace for OER 'On' and 'Off', a miscellaneous noise behavior is observed. While the roughness on the plateau and on the terrace is very similar for OER 'Off' (cf. upper graph in Figure 2c), it is significantly more pronounced on top of the plateau in contrast to the terrace for OER 'On' (cf. lower graph). It is likely that this difference in the noise behavior for OER 'On' results from a difference in the materials, which once more indicates MnO₂ as the NS material and HOPG as the subjacent layer.

Further, Figure 2d provides a side view of the activity in representative line scans for OER 'On' (upper graph) and OER 'Off' (lower graph) with respect to the sheet height. In Figure 2e, starting on the left side of the image for OER 'On', the potential was switched 'Off' and 'On' multiple times. Neither the noise behavior nor the morphology of the sheet changed. We observed this process as reversible and did not find any evidence of corrosion during these experiments (cf. Figure S9, Supporting Information). In summary, we can experimentally identify active sites on the entire MnO₂NS with its highest activity close to the sheet edges, which is in accordance with the increased activity by MnO₂NS illustrated in the Tafel plot in Figure 1a. To further elucidate the origin of the enhanced activity by MnO₂NS and to

identify the chemical moieties causing the higher performance at their edges (Figure 2a), we performed DFT calculations as demonstrated in the following.

2.3. Density Functional Theory Calculations Reveal Chemical Moieties and Pathway

Figure 3 summarizes the key results of the DFT calculations. Various model systems are constructed to model the complexity of the hybrid material. To identify the synergistic effects of the hybrid material, the system is first deconvoluted into the HOPG support and the MnO₂ components separately as shown in Figure S10–S14, Supporting Information, respectively. Our test calculation shows that using a single graphene layer is sufficient to model the HOPG support (Figure S13 and S19, Supporting Information). The differences in the energetic landscape are negligible (Figure S19, Supporting Information), and the charge-density-difference plots also reveal that the charge transfer from the graphite to the MnO₂ sheet only originates from one graphene layer, while the other layers do not contribute to the charge transfer (Figure S38 and S39, Supporting Information). After these calculations on the pristine components of the hybrid material, the hybrid material itself is modeled by basically two different approaches to capture the experimental situation: One model system consists of a graphene layer which is completely covered by a MnO₂ sheet (Figure S16, Supporting Information, MnO₂NS@G) to simulate the conditions on the MnO₂ plateau on which some low OER activity was detected in the n-EC-STM experiments (Figure 2a). The second model illustrated in Figure 3a,b (and Figure S24 and S25, Supporting Information) also contains a graphene and MnO₂ layer, but some space ("vacuum") is made between the MnO₂ sheets to model the interface region (see also the results of our test calculations in Figure S20–S23, Supporting Information). Within this model, we can study the catalysis of the edges of the MnO₂ nanosheet (or nanoribbon) and the graphene layer. Figure 3a,b and Figure S24, Supporting Information show a model system with one site being oxygen-terminated and the other being Mn-terminated (MnO₂NS-1ox@G), while Figure S25, Supporting Information shows a model with oxygen termination on both sites (MnO₂NS-2ox@G). Further, Figure 3c summarizes the thermodynamics of all optimal OER pathways for each of the model systems considered in this work, while a constant applied potential of 1.23 eV was used for each investigated site.

Figure 3a,b reveal that a charge transfer occurs from the support material to the MnO₂ sheet. The same is found for other model systems like when a full sheet of MnO₂ completely covers the graphene support (MnO₂NS@G sheet) for which Bader analysis reveals that about 0.02 e[−] per carbon atom are transferred to the MnO₂ sheet (cf. the charge density difference plot in Figure S38, Supporting Information). For the supercell we use as a model system (50 carbon atoms), this corresponds to a total of 0.81 e[−] being transferred to the MnO₂ sheet. This finding is in agreement with intuition as the oxygen in the MnO₂ sheet is more electronegative than the carbon in the graphene support. The carbons are, therefore, more likely to be positively charged in the presence of more electronegative oxygen moieties. It is also evident from the charge-density-difference plots in Figure 3a,b

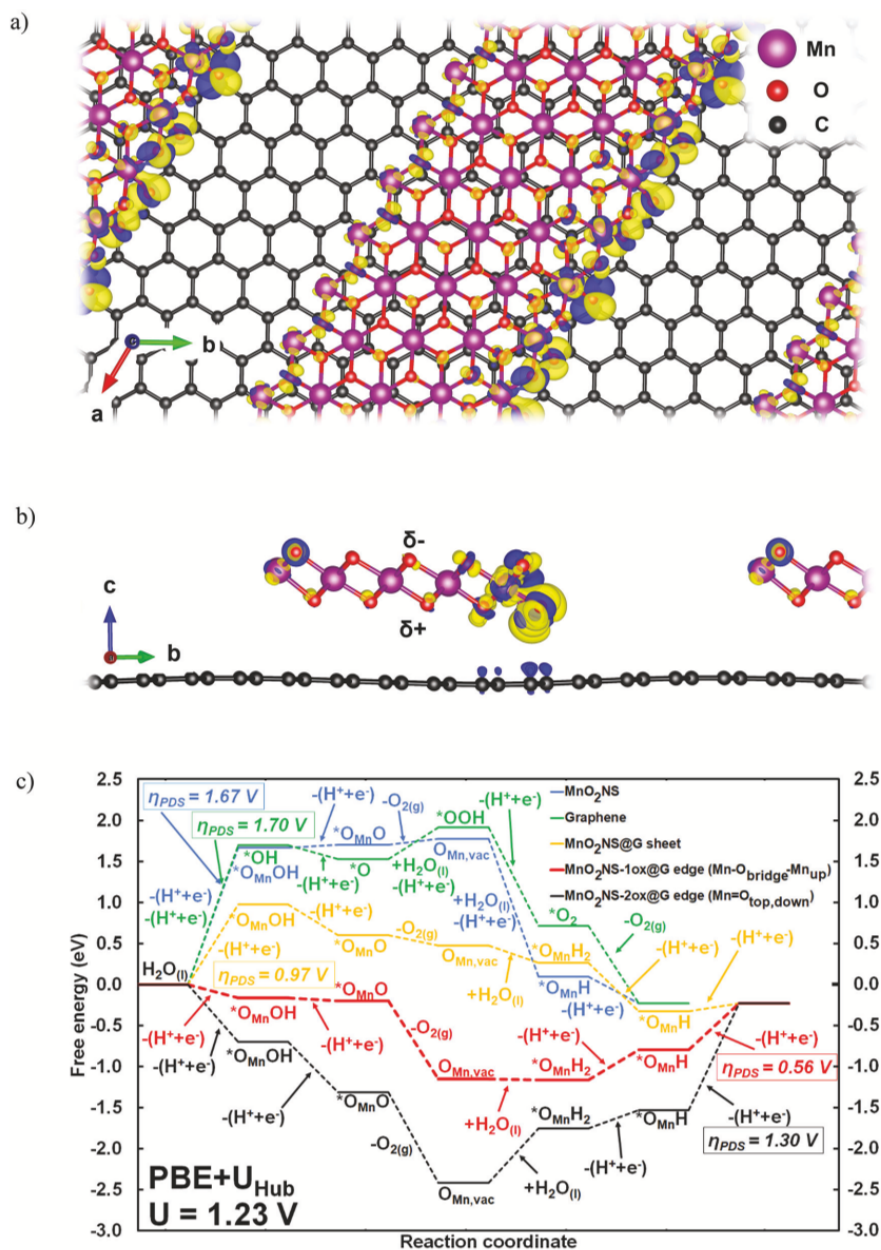


Figure 3. Results of the DFT calculations. a) shows the top and b) the side view of the MnO₂NS-HOPG interface model with oxygen termination on one side and Mn termination on the other side (MnO₂NS-1ox@G). Manganese, oxygen, and carbon are indicated as purple, red, and black spheres, respectively. The blue and yellow charge isosurfaces (isovalue: 0.02 e Å⁻³) illustrate charge depletion and charge accumulation regions, respectively. The free energy diagram in c) shows the calculated optimal free energy landscape of the OER of each model systems at the equilibrium potential 1.23 V vs RHE (cf. the catalytic cycle in Figure S18, Supporting Information): MnO₂NS (blue; shown in Figure S14, Supporting Information); graphene (green; shown

that much charge density is rearranged due to the presence of the support. The charge is depleted from some Mn-O bonds and accumulates at the oxygen atoms at the edge of the nanosheet, enhancing the OER activity of hybrid material (Figure 3c). Furthermore, most charge transfer occurs from the support material to the MnO_2NS around its edges (Figure 3a,b). The charge is therefore stored inside the terminal Mn-O bonds, increasing their activity even more (Figure 3c).

To justify the prediction being made by the charge-density-difference plots, the OER was modeled at various locations of the hybrid material. Basically, probing the material, like in an STM experiment, is done here by carrying out calculations in which the energetic landscape of various OER pathways at different locations or in different model systems is explored. The thermodynamics of the OER pathways at these locations in the material are summarized in Figure 3c. To identify synergistic effects within the hybrid material, the OER pathways are modeled on a pristine graphene and MnO_2 sheet, shown as the green and blue pathways, respectively. It is clear from these two pathways that the OER is unlikely to happen at these locations in the system, which is in agreement with the experimental observations (Figures 1a and 2a). The first proton-electron transfer step of the considered OER pathway has to surpass a high thermodynamic barrier in both cases (about 1.7 eV at $U = 1.23$ V), where that step is also potential-determining for both systems. The given picture of the activity from the calculations agrees with the result in Figure 2a, in which it is evident that the HOPG shows negligible activity compared to other areas in the hybrid material. More activity, however, is seen on the terraces of MnO_2 by the n-EC-STM measurements. This situation was modeled by the model system presented in Figure S16, Supporting Information, and the obtained OER pathway is shown in Figure 3c (yellow pathway). The first step is still potential-determining, but the overpotential is reduced by about 0.8 eV compared to the pristine components. This result indicates that the synergistic effects between the carbonaceous substrate and MnO_2 sheet reduce the overpotential and enhance the activity of the hybrid material. Nevertheless, the overpotential is still around 1 eV, and therefore high, and only some activity at this location would be expected. It should be noted that the model system is only an idealized case of the experimental situation in which oxygen vacancies, for instance, could further reduce the barrier and make the hybrid material more active. However, such a situation is beyond the scope of our study and is therefore not investigated here. Nevertheless, the results already captured the qualitative trend correctly in which the hybrid material at the MnO_2 plateau is shown to be more active than its pristine components.

The OER at the interface region or at the edges between the carbonaceous substrate and MnO_2 nanosheet is also explored to complete the analysis on finding the most active sites of the over-

all catalyst. Here, three possible active sites can be considered: A carbon of the substrate, an oxygen which is bonded to a single manganese atom ($\text{Mn} = \text{O}_{\text{top}}$), and an oxygen moiety which bridges two manganese atoms ($\text{Mn}-\text{O}_{\text{bridge}}-\text{Mn}$). The subscripts “down” and “up” indicate whether an OER intermediate is oriented in a direction to or away from the substrate, respectively, as exemplified in Figures S26–S30, Supporting Information for the $\text{Mn} = \text{O}_{\text{top,down}}$ site and Figures S31–S35, Supporting Information for the $\text{Mn}-\text{O}_{\text{bridge}}-\text{Mn}_{\text{up}}$ site. The optimal OER pathways of $\text{MnO}_2\text{NS-1ox@G}$ and $\text{MnO}_2\text{NS-2ox@G}$ are shown in Figure 3c in red and black, respectively, while all the others are summed up in Figures S36 and S37, Supporting Information. These results clearly identify the oxygen moieties at the edges of the MnO_2 nanosheet as the most active sites in the hybrid system. The first proton-electron transfer step of the OER on the substrate is still thermodynamically challenging and potential-determining (Figure S36, Supporting Information). This result was expected from the calculated OER pathway on pristine graphene (see the blue pathway in Figure 3c) and was confirmed by tests on $\text{MnO}_2\text{NS-1ox@G}$ (see the green pathway in Figure S36, Supporting Information). On top, the MnO_2NS are spatially more available for the reactants than HOPG as the MnO_2NS are deposited on HOPG. Consequently, the steric hindrance for the reactants to reach the edges of the MnO_2NS and to react at the interface is less than to reach HOPG. Therefore, the two oxygen moieties are shown to be the most active sites in the hybrid material (black and red pathways in Figure 3c and also Figure S36 and S37, Supporting Information). The formations of the first OER intermediate ($^*\text{O}_{\text{Mn}}\text{OH}$) at the edges require no additional potential at $U = 1.23$ V but are downhill in free energy, except for the $\text{Mn} = \text{O}_{\text{top}}$ site in $\text{MnO}_2\text{NS-1ox@G}$ (cf. Figure S36, Supporting Information). It should therefore be facile to form this intermediate from a thermodynamic point of view. Significant overpotentials were found for many systems in the pathways at the edges of MnO_2NS . The OER pathway with the lowest overpotential (1.30 V at $U = 1.23$ V) on $\text{MnO}_2\text{NS-2ox@G}$ is shown in Figure 3c, and the step is the last deprotonation step towards the pristine hybrid system. Note that this particular step is potential-determining for all edge sites on $\text{MnO}_2\text{NS-2ox@G}$, but with higher overpotentials than at $\text{Mn} = \text{O}_{\text{top,down}}$ (up to 2.0 V at $U = 1.23$ V; Figure 3c and Figure S37, Supporting Information). These results raise the concern that the catalytic cycles would not be closed. Nevertheless, they can explain the activity shown in Figure 2a. Since the first step requires no extra potential to be driven, the detected current or activity is predicted to be higher than at the other investigated locations. However, it is more likely that the reaction follows at the $\text{Mn}-\text{O}_{\text{bridge}}-\text{Mn}_{\text{up}}$ sites in the $\text{MnO}_2\text{NS-1ox@G}$ which is shown by the red pathway in Figure 3c. Note that the MnO_2NS in the $\text{MnO}_2\text{NS-1ox@G}$ preserve the chemical formula of MnO_2 , while $\text{MnO}_2\text{NS-2ox@G}$ is higher oxidized. The

in Figure S10, Supporting Information); the MnO_2NS on graphene in which the MnO_2 fully covers the graphene (Figure S16, Supporting Information; yellow); the $\text{MnO}_2\text{NS-HOPG}$ with one side (red, 1ox and shown in a) and b) and Figure S24, Supporting Information) and both sides (black, 2ox, shown in Figure S25, Supporting Information) being oxygen terminated. The first proton-electron transfer step of the OER on a MnO_2NS sheet, graphene, and $\text{MnO}_2\text{NS@G}$ sheet are potential-determining on all these model systems. However, the first proton-electron transfer step on the edge site at the MnO_2 -graphene interface is downhill in free energy and will therefore result in small currents and low overpotentials in the experiments, as shown in Figures 1a and 2. However, the potential-determining steps of the hybrid-edge models are the last proton-electron transfer steps to complete the catalytic cycle. The terminal oxygen atoms bound to manganese could therefore explain the detected OER activity in the experimental measurements.

formation of the $^*\text{O}_{\text{Mn}}\text{OH}$ intermediate at the $\text{Mn}-\text{O}_{\text{bridge}}-\text{Mn}_{\text{up}}$ sites in $\text{MnO}_2\text{NS-10x@G}$ (illustrated in Figure S31, Supporting Information) is less downhill in free energy than at most sites of the $\text{MnO}_2\text{NS-20x@G}$ system. However, the further pathway follows steps which require less overpotential. The overpotential of the potential-determining step, which is deprotonation of $^*\text{O}_{\text{Mn}}\text{H}$, is 0.56 eV (red pathway in Figure 3c). The potential-determining step at the other possible site $\text{Mn} = \text{O}_{\text{top,down}}$ is the first deprotonation of adsorbed water and requires, however, 1.05 V overpotential at $U = 1.23$ V (black pathway in Figure S36, Supporting Information). Hence, the OER pathway at the $\text{Mn}-\text{O}_{\text{bridge}}-\text{Mn}_{\text{up}}$ sites in $\text{MnO}_2\text{NS-10x@G}$ and this model system explain the experimental observations in Figure 1a and 2a best. Unlike the other possible reaction sites being considered in this hybrid material, this pathway's first step is thermodynamically favored at OER equilibrium potential and features a surmountable overpotential at ambient conditions. Additionally, this overpotential (0.56 V at $U = 1.23$ V) is less than for the pristine components (about 1.70 V at $U = 1.23$ V for both HOPG and MnO_2), as it is shown in Figure 3c. These findings explain the enhanced activity (Figure 1a) and are in agreement with the n-EC-STM measurements (Figure 2a), but located the active centers even further.

Our calculations, however, do not include kinetic effects, which can determine whether the rate of an electrochemical reaction is high enough to be feasible. Particularly, the formation of peroxide intermediates ($^*\text{OOH}$) has been proven to be rate-determining, which is the first step in our investigated pathways.^[54] Given the system size of our models, calculations on the kinetic barriers, like by utilizing the Nudge Elastic Band^[55] method, are challenging and computationally demanding. Grand-Canonical DFT calculations on the OER on other materials could, however, reveal that also the kinetic barrier of an electrochemical reaction is reduced when the potential is applied.^[56–59] Hence, and given the fact that the first step of the OER is already very downhill in energy, a kinetic barrier is assumed to be surmountable. The Bell–Evans–Polanyi principle on the nature of transition states allows to expect a late transition state at reaction conditions and, additionally, a surmountable barrier. To conclude, our DFT calculations could reveal and explain not only the origin of the increased macroscopic activity but also the microscopic picture attributed to the source of activity at the edges at the interface between HOPG and the MnO_2NS . Our calculations identified the oxygen atoms bound to manganese as the source of the electrochemical activity found in the experiment.

3. Conclusions

In this work, we aimed to elucidate the active centers of a HOPG- MnO_2 hybrid material by utilizing macroscopic and microscopic methods as well as DFT calculations. After validating and characterizing the material, the Tafel plots revealed an increased catalytic performance of the hybrid material compared to pristine HOPG. To shed light on the origin of the enhanced OER activity, n-EC-STM measurements and DFT calculations were carried out. The n-EC-STM technique can assess the local activity of surface features by a distinct increase in the STM signal's noise

level under reaction conditions, while the DFT calculations can further locate the active centers and the corresponding reaction pathway with atomistic resolution. The HOPG substrate remains largely inactive, as monitored by n-EC-STM images which is explained by DFT calculations by a thermodynamic barrier of 1.70 eV for the formation of the first OER intermediate. In contrast, the MnO_2NS plateau is active towards the OER for a constant potential of 1.23 eV which was used for all investigated sites, however, to a lesser extent than the sites near the edges. In both cases, the formation free energy of the $^*\text{O}_{\text{Mn}}\text{OH}$ intermediate is decreased compared to pristine MnO_2 . While a significant overpotential is still calculated for the $^*\text{O}_{\text{Mn}}\text{OH}$ formation on the plateau, this thermodynamic barrier vanishes at the edges of the MnO_2NS and a surmountable overpotential of 0.56 V at OER equilibrium potential is found there. It explains the difference in activity at both locations in the n-EC-STM experiments. Similar structural features like $\text{Mn}-\text{O}_{\text{bridge}}-\text{Mn}$ and $\text{Mn} = \text{O}_{\text{top}}$ at the edge of our hybrid material are also found in the active cluster of PS II Mn_4CaO_5 . Therefore, our work on the simpler HOPG- MnO_2NS hybrid system may provide further insights and ideas into the more complex nature of PS II. Due to the simplicity of HOPG- MnO_2NS hybrid system, we could clearly assign the origin of the catalytic activity, which could help to clarify the mechanism of the OER in PS II and design future catalysts made of abundant materials.

4. Experimental Section

MnO_2NS Preparation: The MnO_2NS were synthesized with a method similar to those reported previously.^[60–62] First, KMnO_4 was heat-treated in an alumina crucible at 800 °C in the air for 10 h. The product was washed with distilled water, dried, and heat-treated again at 800 °C in the air for 20 h. An aliquot of 1 g of the obtained powder was added to 200 cm³ of 1 mol dm^{−3} HNO_3 and shaken for 1 day at ambient temperature. The solution was replaced with 1 mol dm^{−3} HNO_3 and shaken again for 1 day. This shaking process to exchange the cations in the obtained powder was carried out for 5 days in total. After removing the solution, an aqueous solution of 200 cm³ containing 2.6 g of $[\text{CH}_3(\text{CH}_2)_3]_4\text{NOH}$ was added, shaken for 10 days at ambient temperature, and finally centrifuged at 5000 rpm to obtain the MnO_2NS dispersion as the supernatant. The measurement of X-ray absorption fine structure (XAFS) was performed in air at room temperature in transmission mode using synchrotron radiation at the BL01B1 beamline of SPring-8 at the Japan Synchrotron Radiation Research Institute. The MnO_2NS dispersion was dried in vacuum and mixed with BN. The mixture was pressed to form a pellet as a sample to measure the XAFS. The RSF was obtained through Fourier transformation of the k^3 -weighted EXAFS spectra using the REX2000 program (Rigaku).

MnO_2NS Loading on HOPG: MnO_2NS were loaded on HOPG as substrates using a Langmuir-Blodgett trough (USI-3-22; trough volume, 250 cm³; trough area, 344 mm × 100 mm, USI) with a Wilhelmy plate tensiometer.^[63] The trough was filled with 250 cm³ of the MnO_2NS dispersion diluted to 7 mg dm^{−3}, in which typically 1 cm³ of a 10% $[\text{CH}_3(\text{CH}_2)_3]_4\text{NOH}$ solution was added. After leaving the dispersion still at 20 °C for 30 min, the surface was compressed up to the surface pressure of typically 17 mN m^{−1} with the barrier swept at 0.5 mm s^{−1}. Then the pressure was kept for further 30 min. The Langmuir film was transferred to the surface of the substrate, dipped vertically, and raised at 0.02 mm s^{−1} to obtain the MnO_2NS -loaded HOPG (labeled HOPG- MnO_2NS).

Electrochemical Measurement of OER Current: The HOPG and HOPG- MnO_2NS surface was masked using adhesive tape made of polytetrafluoroethylene (PTFE) with a hole of 6-mm diameter to expose the surface

of 0.283 cm² and to form the working electrode. The electrochemical measurements were performed at 25 °C using an electrochemical analyzer (660B, ALS) and a three-electrode glass cell. The electrolyte was 0.1 M KOH prepared by diluting 3 M KOH (Ultrapur, Kanto Chemical) with high-purity water. The counter electrode was carbon cloth (EC-CC1-060T, ElectroChem), and the reference electrode was Hg/HgO (0.1 M KOH). The potential was repetitively scanned between 0.3 V and −0.9 V at 50 mV s^{−1} in an Ar atmosphere until a stable voltammogram was obtained. The OER current–potential relationship was measured in an Ar atmosphere at 10 mV s^{−1} from 0.3 V to 0.8 V. After rinsing the working electrode surface with high-purity water and drying it in air at room temperature, XPS was performed using an AXIS ULTRA DLD system (Kratos Analytical) with Al K α radiation (1486.6 eV).

n-EC-STM: The EC-STM setup consists of a Nanoscope III SPM Multimode (Veeco Instruments) device, a Veeco Nanoscope Universal bipotentiostat and a Nanoscope IIID controller. The MnO₂/HOPG sample was clamped between a Teflon ring and a metal base plate, fixed by screws, and served as a miniature electrochemical cell. Next to the platinum reference electrode (wire, $\varnothing$ = 0.5 mm, 99.99%, MaTeck, Germany) and a carbon rod counter electrode (rod, $\varnothing$ = 0.5 mm, 99.95%, Goodfellow GmbH), a mechanically cut STM-tip (wire, Pt80/Ir20, $\varnothing$ = 0.25, 99.9+%, Goodfellow GmbH), insulated with Apiezon wax was used. The electrolyte employed for the STM measurements at room temperature was mixed from ultrapure water (Evoqua Milli-Q®, 18.2 M Ω cm) and potassium hydroxide pellets (99.99%, Sigma Aldrich). The applied potential of 600 mV_{pt} for OER 'On' and of 0 mV_{pt} for OER 'Off' was chosen according to the significant increase of the current at approximately 550 mV_{pt} and the low current close to 0 mV_{pt} illustrated in Figure S6b. Crucial STM settings such as the integral gain, proportional gain, and the current setpoint were optimally calibrated to provide the best possible visualization of the local activity, while mapping the surface morphology as unadulterated as possible. The specific settings used for each measurement are listed in Table S1, Supporting Information.

The evaluation of the images was performed by using the WSxM 5.0 Develop 9.4 software^[64] and a Python script deriving the neighboring data points in the slow scan direction by using the function "numpy.gradient()" of the library NumPy and counting its relative number (cf. reference^[49] and^[53]). The normalized sums are plotted against the derivatives of the slopes with a bin size of 0.02 for 30 bins.

Density Functional Theory Calculations: All spin-polarized calculations were carried out utilizing the Vienna Ab-initio Software Package (VASP; version 5.4.4).^[65,66] A dipole correction was utilized to avoid interactions between adjacent images. The functional of Perdew, Becke, and Ernzerhof (PBE) was applied to carry out all simulations.^[67,68] In order to account for the self-interaction error of highly localized *d*-electrons in manganese, the Hubbard correction with the parameter U_{Hub} was applied and set to 3.90 eV.^[69–71] We used the projector augmented-wave (PAW) method to describe the ion-core interactions,^[72] choosing the following potentials: C (2s²2p², ENMAX = 400.0 eV); H (1s¹, ENMAX = 250.0 eV); O (2s²2p⁴, ENMAX = 400.0 eV) and Mn (3p⁶4s²3d⁵, ENMAX = 269.9 eV). The cut-off was set to 450 eV for all simulations. Convergence criteria of 10^{−7} eV and 0.01 eV Å^{−1} were used for the total energies and forces, respectively. All atoms were allowed to relax to their optimal position. Gaussian smearing with a width of 0.05 eV was applied in all cases. The following gamma point meshes were utilized for each model system:^[73] 6 × 6 × 1 for graphene and graphite (two and three graphene layers) models and the hybrid material in which graphene and graphite are fully covered by a manganese oxide sheet; 6 × 2 × 1 for the interface models and 9 × 9 × 1 for a single manganese oxide sheet. All model systems with their cell constants are illustrated in Figure S10–S12, S14, S16, S17, S24, and S25, Supporting Information S1 and further described there. Furthermore, it explains the procedure to build the model systems of the hybrid material as graphene/graphite and MnO₂ of the birnissite type crystallize in different structures: The pathway shown in Figure S18, Supporting Information was assumed for the OER on manganese oxide and the hybrid material, while the conventional mechanism is assumed for pristine graphene and graphite. To calculate the free energy of these OER pathways, the computational hydrogen electrode was utilized.^[74] The free energies were ob-

tained by correcting the DFT energies with zero-point energies (ZPEs), the entropic contribution (−TS) and the heat capacity $C_p dT$ which are listed in Table S2, Supporting Information. To visualize the initial and final geometries and to calculate the charge density difference plots, the VESTA program was used.^[75] Bader charges were calculated utilizing the Bader program.^[76]

Resource availability—Materials Availability: This study did not generate new unique reagents.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

T.O.S. and A.W. contributed equally to this work. J.M. performed the conceptualization; J.M., S.S., and K.K. performed the methodology, electrochemical and spectroscopic measurements; T.O.S., R.W.H., R.M.K., and A.S.B. performed the electrochemical scanning tunneling microscopy; A.W. and E.S. performed the density functional theory calculations; J.M., E.S., and A.S.B., acquired the funding; J.M., E.S., and A.S.B. administrated the project; E.S. and A.S.B. supervised the study of A.W., T.O.S., R.W.H., and R.M.K.; T.O.S., A.W., and J.M., wrote the original draft; E.S., J.M., A.S.B., T.O.S., and A.W. review and edited the original manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

highly-oriented pyrolytic graphite, manganese oxide, n-EC-STM, noble metal-free electrocatalysts, oxygen evolution reaction, photosystem II

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Structure-Dependent Electrical Double-Layer Capacitances of the Basal Plane Pd(*hkl*) Electrodes in HClO₄

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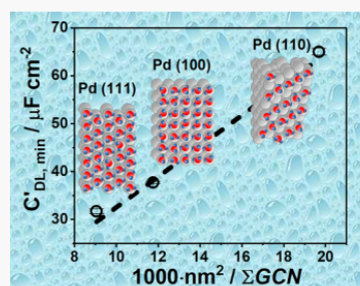
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ABSTRACT: Electrical double-layer capacitance (C_{DL}) measurements are among the key experiments in physical electrochemistry aimed to understand the properties of electrified solid/liquid interfaces. C_{DL} serves as a critical parameter for developing physical models of electrochemical interfaces. Palladium (Pd) electrodes are among the most widely used functional materials in many applications, including (electro)catalysis. In this work, we report on double-layer capacitances of the basal plane Pd(111), Pd(100), and Pd(110) electrodes in aqueous HClO₄ electrolytes measured using electrochemical impedance spectroscopy. Importantly, we find that the C_{DL} values estimated at the minima of the capacitance vs electrode potential curves can be correlated with the density-functional-theory (DFT)-calculated adsorption energies for water molecules and the coordination of electrode surface atoms. Our results thus suggest that it might be possible to find simple descriptors of the electrical double layer (EDL) analogous to those used for functional electrode materials. Taken together, such descriptors could be employed for efficient high-throughput screening of various electrode/electrolyte interfaces, such as in supercapacitor and electrocatalytic systems.



INTRODUCTION

The knowledge of basic parameters characterizing the electrified solid/liquid interface is of great importance to understanding its functionality, such as catalytic properties.^{1–6} The capacitance of the electrical double layer (C_{DL}) is one of those critical parameters.⁷ For example, the position of the C_{DL} minima is often associated with the so-called potential of zero charge or maximum entropy, indicating which electrolyte compositions are beneficial for promoting electrocatalytic reactions.^{8–14} However, despite their importance, the C_{DL} values of model single-crystal electrodes are available only for a relatively small amount of systems (see, e.g.,^{15–17}). This can be partly explained by the challenges in preparing single-crystal electrodes and fundamental issues related to the measurements, for example, due to the so-called frequency dispersion of the double-layer capacitance,^{18–20} even for flat single-crystal electrodes in electrolytes, which do not contain specifically adsorbing ions.

Palladium(Pd) is a versatile material with a wide range of applications. In electrocatalysis, it is considered among the so-called energy materials, catalyzing the hydrogen evolution, hydrogen oxidation, and oxygen reduction reactions.²¹ In this work, we report on the double-layer capacitances of the basal plane Pd(*hkl*) single-crystal electrodes, namely, Pd(111), Pd(100), and Pd(110). The utilized electrolyte is 0.1 M HClO₄, a standard medium used in multiple electrocatalytic and other physicochemical applications. Furthermore, we

establish the hypothesis on the intrinsic correlations between the energy adsorption characteristics of electrolyte components, the structure of the Pd(*hkl*) surfaces, and the double-layer capacitances found close to the potential of zero charge (PZC). We suggest that these correlations can be used to improve or supplement the rational design of new materials for various energy conversion and storage applications.

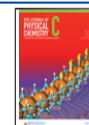
EXPERIMENTAL SECTION

The Pd(111), Pd(100), and Pd(110) disk electrodes (Ø: 5 mm, 99.999%, MaTecK, Jülich, Germany) were oriented more precisely than 0.05° and polished to a nominal roughness of less than 30 nm. Before the cyclic voltammetric (CV) and electrochemical impedance spectroscopy (EIS) experiments, the crystals were annealed for 2 h in an Ar (S.O. Westfalen, Germany) atmosphere at 950 °C in a furnace (Heraeus Instruments RO 7/50, Germany), cooled down overnight, and transferred into a standard three-electrode cell. To avoid an oxidation during the transportation by exposing the sample to the air, the electrode surface was protected by a droplet of

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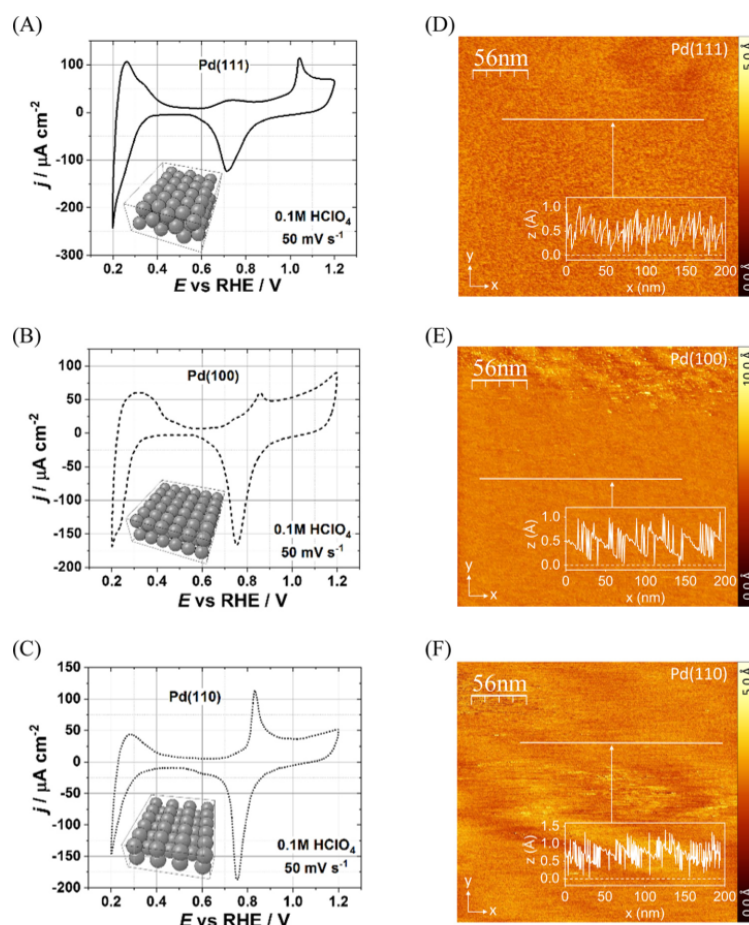


Figure 1. (A–C) Typical cyclic voltammograms (first cycles) and (D–F) corresponding EC-STM pictures of freshly annealed (A, D) Pd(111), (B, E) Pd(100), and (C, F) Pd(110) in 0.1 M HClO₄. Scanning rate for CVs (A–C): 50 mV s^{−1}.

ultrapure water (Evoqua Milli-Q, 18.2 MΩ cm). Electrochemical scanning tunneling microscopy (EC-STM) imaging was performed under potential control (0.0 V vs platinum) to prevent electrochemical surface reactions. In all experiments, 0.1 M HClO₄ (Suprapur, Merck, Germany) was used as an electrolyte. The measurements were performed using a VSP-300 potentiostat (BioLogic, France).

Electrochemical Voltammetric and Impedance Measurements. All glassware and Teflon cell parts were cleaned in a piranha solution, a 1:2 mixture of 30% H₂O₂ (Suprapur, Merck, Germany) and 96% H₂SO₄ (Suprapur, Merck, Germany), and treated/washed with boiling ultrapure Milli-Q water with a resistivity of 18.2 MΩ·cm before the experiments. The standard three-electrode configuration cell was operated with a mercury-mercurous sulfate electrode (MMS) (SI Analytics, Germany) and Pd wire (Ø 0.25 mm, 99.95%, MaTeck, Germany) as the reference and counter electrode, respectively. A starting potential of 0.57 V_{RHE} was used to avoid possible electrochemical surface processes before

the actual measurement started. The quality of the annealed single crystalline surface was verified by cyclic voltammetry (CVs) in Ar-saturated 0.1 M HClO₄ at a potential range between 0.2 and 1.2 V_{RHE} and a scan rate of 50 mV s^{−1}.

The electrochemical impedance spectroscopy (EIS) measurements were performed within a frequency range between 50 kHz and 1 Hz using a perturbation amplitude of 10 mV. To suppress possible potentiostat- and reference electrode-related artifacts, a shunt capacitor was connected between the reference and a dummy electrode. The dummy electrode was placed close to the Luggin capillary. For the EIS data analysis, the housemade software “EIS Spectrum Analyzer 1.3” was used.^{22,23} The quality of the recorded spectra was ensured by a Krammer–Kroenig check.

Electrochemical Scanning Tunneling Microscopy. Electrochemical scanning tunneling microscopy (EC-STM) imaging was performed using a Nanoscope III SPM Multi-mode (Veeco Instruments), connected to a Veeco Nanoscope Universal bipotentiostat and a Nanoscope IIID controller in

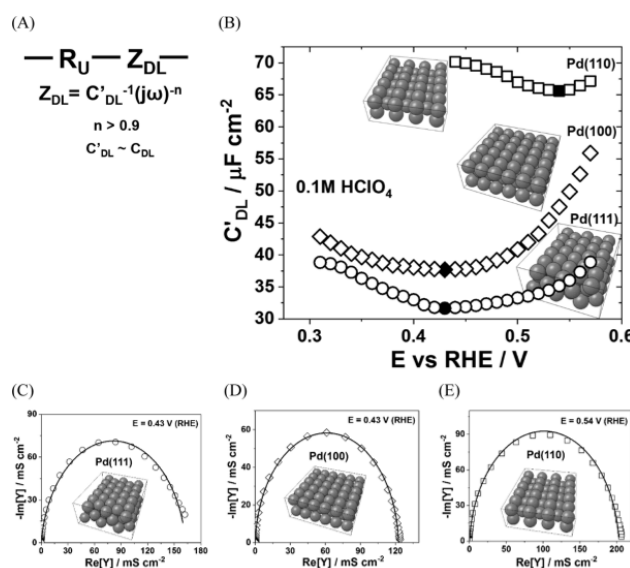


Figure 2. Characterization of Pd(*hkl*) electrodes using electrochemical impedance spectroscopy. (A) Equivalent electric circuit. (B) Dependences of the double-layer capacitance on the electrode potential. (C–E) Examples of impedance spectra together with the fitting (solid lines) to the equivalent circuit for the (C) Pd(111), (D) Pd(100), and (E) Pd(110) electrodes.

0.1 M HClO₄. For all EC-STM measurements, the single crystals were clamped between a stainless steel plate and a Teflon ring acting as the case of the miniature electrochemical cell. A Pt wire (Ø 0.5 mm, 99.99%, MaTeck, Germany) was used as a quasi-reference electrode and a curled Pd wire (Ø 0.25 mm, 99.95%, MaTeck, Germany) as the counter electrode. The STM-tips were mechanically cut from a Pt/Ir wire (Pt80/Ir20, Ø 0.25, Goodfellow, Germany) and insulated by Apiezon wax. Detailed information on this technique can be found in refs 24–27. The visualization of the EC-STM data was implemented by using WSxM 5.0 Develop 9.4.²⁸

Computational Approach. The atomic structures of the Pd surfaces with converged computational parameters were taken from the Materials Project²⁹ and used for adsorption calculations.

Ab initio simulations were performed using the density-functional-theory (DFT) plane-wave VASP code.^{30–33} The revised Perdew–Burke–Ernzerhof (RPBE) exchange–correlation functional³⁴ together with the PAW Pd, O, and H potentials³⁵ was employed. The D3 approach within Grimme’s formalism was used to correct for nonlocal van der Waals interactions.^{36,37} A cutoff energy of 520 eV was employed in all calculations. The structures were optimized until the total energies and atomic forces were converged to within 10^{−5} eV and 0.03 eV/Å, respectively. The (100), (110), and (111) surfaces of Pd were modeled using the periodic slabs consisting of eight, eight, and ten atomic layers, respectively, taken from the Materials Project.²⁹ The dimensions of the cells employed to estimate the adsorption energies for H₂O, H, and OH species were 8.38 × 8.38 Å², 8.38 × 11.86 Å², and 8.38 × 8.38 Å², respectively, with a vacuum gap of at least 13 Å. The Monkhorst–Pack *k*-point mesh of 5 × 5 × 1 was used in all slab calculations. The adsorption energies were computed considering water, proton, and hydroxyl species as adsorbates. All

calculations were performed for charge-neutral supercells. The negative adsorption energies correspond to attractive interactions between the adsorbate and the metal surface.

All potentials presented in this work for CV, EIS data, and DFT calculations have been referred to the reversible hydrogen electrode (RHE).

RESULTS AND DISCUSSION

Figure 1 summarizes the results of voltammetric and EC-STM characterization of the Pd(111), Pd(100), and Pd(110) electrodes. The samples demonstrate typical CV profiles (Figure 1A–C)^{38,39} with (i) the underpotential deposition of the hydrogen region between *ca.* 0.2 and 0.5 V, (ii) the double-layer region, and (iii) the region of adsorption of the oxygenated species at the electrode potentials more positive than *ca.* 0.6 V. The corresponding EC-STM images (Figure 1D–F) generally reveal smooth surfaces with atomically flat terraces consisting of thousands of Pd atoms.

Figure 2 shows typical examples of the electrochemical impedance spectroscopy data of the investigated palladium electrodes. The equivalent electric circuit (EEC) shown in Figure 2A was found to adequately describe the impedance response of the systems within the double-layer regions (further analysis details are shown in Figure S1 of the Supporting Information). It consists of two elements: the uncompensated resistance associated with the electrolyte, *R*_U, and the impedance of the electrical double layer, *Z*_{DL}, given by the formula presented in Figure 2A. With the exponent *n* approaching 1, *Z*_{DL} is close to the impedance of an ideal capacitance. Therefore, the corresponding parameter *C*_{DL} is further considered as the double-layer capacitance in this study.

The dependences *C*_{DL} vs (*E* The dependence *C*_{DL} vs (*E* vs RHE)) for the three freshly annealed Pd(*hkl*) electrodes are

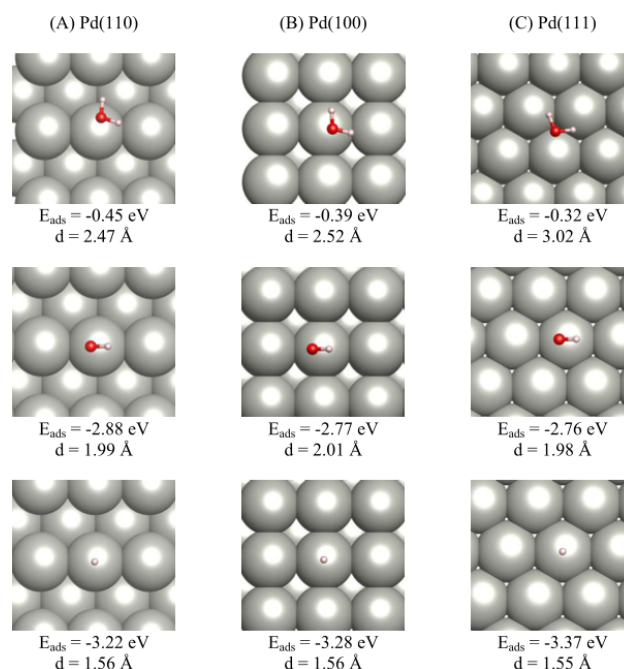


Figure 3. (A–C) Adsorbate configurations (top view) and DFT-calculated binding energies for H_2O , hydroxyl, and H^+ species at $\text{Pd}(hkl)$ surfaces with the corresponding Pd–O and Pd–H bond lengths indicated in the pictures.

shown in Figure 2B in the potential regions where no significant side electrochemical reactions occur. Typical fitting examples of the admittance spectra to the EEC are shown in Figure 2C–E, confirming that the model describes the experimental data pretty well, with the root-mean-square deviations of less than 2%. It is remarkable in Figure 2B that the double-layer capacitances are drastically different for all three palladium electrodes, considering that they represent examples of very flat model surfaces. In each of the curves in Figure 2B, one can identify the C'_{DL} minima, $C_{\text{DL,min}}$, at different electrode potentials and with different corresponding capacitance values. These minima should typically be close to the so-called potentials of zero charges (PZCs), where the net charge of the surface approaches zero.

Somewhat surprisingly, even close to the PZC point, the double-layer capacitances drastically depend on the basal plane surface structure. While classical and recent⁴⁰ theories of the double layer do not consider the nature of the electrode and its structure, the experiments show that the electrical double-layer (EDL) capacitance significantly depends not only on the electrolyte composition but also on the electrode structure and its chemical composition.^{2,3} Therefore, elucidation of the structure-capacitance relations is an essential part of developing more comprehensive theories of the double layer. As $C_{\text{DL,min}}$ also plays a significant role in understanding the electrified interface and the electrocatalytic interfacial charge transfer, in the following, we analyze these data in more detail.

First of all, we hypothesize that $C_{\text{DL,min}}$ reflects the intrinsic interactions between the surface and the electrolyte components with minimal influence of the excessive electrode

charge. DFT calculations were used to quantify the adsorption energy for the most important strongly interacting species. Three types of species were considered: water molecules, H^+ , and OH^- species. The results of these calculations are summarized in Figure 3.

It can be seen that H^+ species are characterized by the strongest adsorption on the top sites of the Pd surfaces, followed by OH^- and then H_2O . Moreover, the corresponding Pd–H and Pd–O bond lengths for the H^+ and OH^- adsorbates are almost unaffected by the surface structure (<1%), while for H_2O , the bond length is significantly stronger influenced by the surface structure. Therefore, one can assume that the most critical interacting species for the C_{DL} analysis are water molecules. Further, they are likely to significantly impact the overall thickness of the inner Helmholtz layer in the double-layer structure. In turn, this should be reflected by variations of the double-layer capacitance for different surfaces.

For the detailed study of this effect, it is essential to parametrize the $\text{Pd}(hkl)$ structures to correlate structure-related information with the double-layer capacitances. One can do that using the so-called generalized coordination numbers (GCNs).^{41–43} GCN is a parameter that can be considered as a simple quantitative measure related to the structure linking it with an electron density function at the surface. Therefore, GCN is a useful descriptor for the affinity of the surface to the electrolyte components. It considers the first and the second nearest neighbors of the accessible adsorption sites and can be calculated using the eq 1, weighting each first-nearest-neighbor atom (j) by its conventional coordination number ($cn(j)$)⁴³

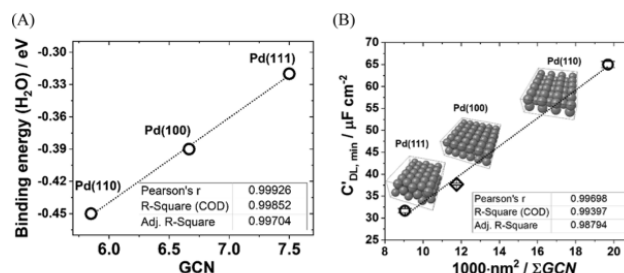


Figure 4. (A) DFT-calculated binding energies for H₂O molecules for different Pd(*hkl*) surfaces correlated with the GCNs. (B) Double-layer capacitances found at the minima of the capacitance/electrode potential curves correlated with the F_e parameter defined via surface area normalized generalized coordination numbers.

$$\text{GCN} = (1 + S)^{-1} \left[\sum c_n(j) / c_{n_{\max}} \right] \quad (1)$$

where S is the percentage of strain (negative or positive for compressive or tensile strain) and $c_{n_{\max}}$ is the maximum number of the direct neighbors in the bulk phase, which is defined as 12 on *fcc* and *hcp* crystals, and as 8 for the *bcc* ones (examples of GCN calculations for the 111, 100, and 110 palladium surfaces are given in the Supporting Information, Figure S2). By assuming zero strain for the freshly annealed surfaces, one can calculate $\text{GCN}(\text{Pd}_{111}) = 7.5$, $\text{GCN}(\text{Pd}_{100}) = 6.6(6)$, and $\text{GCN}(\text{Pd}_{110}) = 5.85$.

Remarkably, the DFT-calculated binding energies for H₂O molecules scale linearly with the GCNs of the investigated palladium planes (Figure 4A), enabling further parametrization of the surfaces in energetic and structural terms simultaneously. In other words, one can use GCNs to characterize and quantify the affinity of the surface toward electrolyte components (in the following, only H₂O is considered) in simple terms.

To correlate the GCN with the $C_{\text{DL,min}}$, consider that the generalized coordination number is a measure of “unsaturated surface electron density.” One can assume that the higher this value, the lower the densities and the longer the effective distances between the surface atoms and the first layer of water molecules (see, e.g., Figure 3). One should also consider the different numbers of accessible surface sites for the water molecules per unit area, S , for different basal surfaces (see Figure S2 in Supporting Information). Therefore, it is reasonable to define a new function, F_e , which should be connected to $C_{\text{DL,min}}$ in a first approximation

$$F_e = S / \sum \text{GCN} \quad (2)$$

Figure 4B reveals an excellent quasi-linear correlation between $C_{\text{DL,min}}$ and F_e , where $C_{\text{DL,min}}$ increases with decreasing $\sum \text{GCN}$, as follows: Pd(111) < Pd(100) < Pd(110).

There must be, of course, not only purely structural reasons, which affect the double-layer capacitances close to the potential of zero charge. For example, one can compare the values for the double-layer capacitances of flat Pd(111) and Pt(111) electrodes at corresponding minima in 0.1 M HClO₄ being ca. 31.7 μF/cm² and ca. 60 μF/cm²,⁴⁴ respectively. This is an indicator that also the chemical nature (via dissimilar surface electronic properties) of the electrode is important, and this requires further investigations.

CONCLUSIONS

In conclusion, we carried out EIS, voltammetric, and electrochemical scanning tunneling microscopy characterizations of the Pd(111), Pd(100), and Pd(110) electrodes. The EIS measurements revealed a strong surface dependence of the double-layer capacitance close to the potential of zero charge, being ca. 31.7 μF/cm² for Pd(111), ca. 37.7 μF/cm² for Pd(100), and ca. 65 μF/cm² for Pd(110). We were also able to correlate the capacitance data with the surface adsorption energies for water species and the generalized coordination numbers of the Pd surfaces. The results of this work thus suggest that it may be possible to characterize the EDL properties such as the double-layer capacitance using simple physical descriptors. Further joint experiment–theory investigations are necessary to generalize the obtained results to other electrochemical systems.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.2c03117>.

Estimations related to the generalized coordination numbers. Additional analysis of electrochemical impedance spectroscopy data at the potentials of the C_{DL} minima (PDF)

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Notes

The authors declare no competing financial interest.

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ORIGINAL PAPER



Electrochemical Scanning Tunneling Microscopy as a Tool for the Detection of Active Electrocatalytic Sites

Thorsten O. Schmidt¹ · Richard W. Haid¹ · Elena L. Gubanova¹ · Regina M. Kluge¹ · Aliaksandr S. Bandarenka^{1,2}

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Abstract

To advance meaningful guidelines in the design of electrocatalytically active catalysts, a knowledge of the nature of active sites is the starting point. However, multiple factors such as material composition, site coordination, electrolyte effects, the support material, surface strain, and others influence catalytic behavior. Therefore, the identification of active sites can be complex. A substantial contributor can be in-situ experiments, which are able to identify active centers in a specific system while the reaction takes place. An example of such a technique is electrochemical scanning tunneling microscopy (EC-STM), which relates locally confined noise features to local electrocatalytic activity. In this work, we spotlight recent achievements of this technique with respect to palladium (Pd) surfaces for the hydrogen reduction reaction, where strain due to hydride formation comes into play in addition to surface coordination. Secondly, we demonstrate the high resolution of the technique on graphite-based surfaces. Here, edge sites are particularly active. Thus, with the EC-STM technique, we take strain effects (like on Pd) or effects of coordination (like on carbon) into account. Therefore, we can determine active sites with great accuracy under reaction conditions.

Keywords Active site · Hydrogen evolution reaction · Electrochemical scanning tunneling microscopy · In-situ method · Palladium · Carbon

1 Introduction

Renewable energy is inevitable for a more sustainable and worldwide accessible energy provision. However, due to intermittency, energy storage is necessary. Due to its large energy density, hydrogen is considered a promising candidate [1]. Electrocatalytic water splitting is a major element for large-scale production of ‘green’ hydrogen from renewable electricity [2]. Among the involved electrochemical half-cell reactions is the cathodic hydrogen evolution reaction (HER). The HER requires an active, stable, and low-cost electrocatalyst to increase the electrolyzer efficiency. State-of-the-art materials are platinum (Pt) and palladium

(Pd) [3], but also cheap materials such as carbon [4, 5] are considered. Hydrogen adsorption and subsequently also the HER can depend on the structure of the catalyst surface [6, 7]. Therefore, to design an effective catalyst, it is essential to know which sites on the catalytic surface are active.

For active site identification, ex-situ methods such as scanning electron microscopy, Raman spectroscopy, Fourier-transform infrared spectroscopy, x-ray photoelectron spectroscopy, and x-ray diffraction are employed [8]. Beyond, in-situ techniques like scanning electrochemical cell microscopy, where a miniature electrochemical cell assesses the local reactivity [9], and electrochemical scanning tunneling microscopy (EC-STM), in which structural changes or self-activation can be observed under reaction conditions [10] are versatile techniques. The major difficulty is that the nature of active sites can depend on coordination, ligand and strain effects, particle size, electrolyte interactions, and many more [11].

Therefore, assessing the local activity of different surface sites under reaction conditions, paired with high resolution, is a strong approach. We first introduce an EC-STM technique that can do so via the analysis of noise features.

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Afterward, we showcase the ability of the technique for the HER. As model systems, we chose Pd, known as a complex system and for its ability to form hydrides. Besides, we demonstrate on highly oriented pyrolytic graphite (HOPG) that active sites can be distinguished with atomic resolution.

2 Method: Electrochemical Scanning Tunneling Microscopy for Active Site Identification

In scanning tunneling microscopy (STM), an atomically sharp scanning probe moves across a conductive sample to provide the electronic topology. Depending on the mode, the tip-sample distance is adjusted to the tunneling current, or the tunneling current is recorded at a fixed tip-sample distance. The tunneling current is highly sensitive to the width of the tunneling gap (exponential dependence). Therefore, it was the first technique capable of achieving atomic resolution of a surface in real space [12, 13].

EC-STM profits from this high resolution and combines the ‘conventional’ STM with an electrochemical cell, including a reference (RE) and a counter electrode (CE). Instead of a vacuum or air, an electrolyte serves as the tunnel medium. A bi-potentiostat controls the potentials between tip and sample, influencing the tunneling current, and between the sample and RE, allowing control over electrochemical reactions at the sample/electrolyte interface. The tip itself is insulated with an inert material, preventing any Faradaic reactions on the tip, which could falsify the tunnel current emanating from the sample.

In addition to the sample and tip work function, tip-sample distance, tunneling voltage, etc., the tunneling current depends on the tunneling medium, such as the electrolyte structure, movement of chemical species across the tunneling gap and adsorbed species on the surface [14–20]. Considering those dependencies, it becomes understandable why EC-STM provides valid information when performed under electrocatalytic reaction conditions. An ongoing reaction persistently changes the composition and structure of the tunneling medium. Consequently, fluctuations of the tunneling current caused by the resulting changes in the electrochemical properties within the tunneling barrier lead to a temporary retraction of the STM tip. Due to the temporal random occurrence of electrochemical events, a noise-like behavior of the STM signal is observed. These changes are the most pronounced at the position where the electrocatalytic reactions occur: at the active centers. Therefore, information about the local activity can be extracted by evaluating the noise features appearing during such a reaction.

Figure 1a sketches the working principle of the noise-EC-STM (n-EC-STM) technique. As described above, the electrolyte between the tip and sample serves as the tunneling medium while the tip is scanning across the surface. Dependent on the chosen sample potential with respect to the RE, the reaction of interest is either enabled (‘On’) or not (‘Off’). If the reaction is hindered, the signal is recorded without distortion, and, e.g., the morphology of a step edge can be mapped (black curve sketched in the tunneling gap). If the reaction is ongoing, distinct noise features appear at the position of the active sites. In the example, the blue atoms at the top of the step edge are active. Therefore, the signal under reaction conditions (blue curve sketched in the tunneling gap) is a superposition of the step edge morphology and the distinct noise features at the active step-top sites. The reason for the distinct noise features is the dependence of the changes in the electrolyte on the tunneling barrier, as discussed above. The n-EC-STM technique can be used to monitor active areas and quantify local activity values. An example is given in Fig. 1b, c on the model system Pt(111) for the oxygen reduction reaction (ORR) in 0.1 M perchloric acid (HClO₄) [23]. For this system, the sites with higher coordination in the vicinity of step edges were identified as active [21, 22], which is in accordance with the higher noise level at the step sites in Fig. 1b.

To quantify the noise level for each data set (reaction ‘On’/‘Off’, step or terrace sites), the STM signal was derived with respect to adjacent data points, according to

$$\left(\frac{\partial z}{\partial x}\right)_{t_i} = \frac{1}{2} \left[\frac{z_2 - z_1}{x_2 - x_1} + \frac{z_1 - z_0}{x_1 - x_0} \right]$$

where (x₀, z₀), (x₁, z₁) and (x₂, z₂) are three successive data points with scan direction x and tip-sample distance z. In the next step, histograms were compiled from the signal derivatives, as shown in Fig. 1c. To compare data sets of unequal sizes, each histogram was divided by the number of data points to ‘normalized counts’. The histograms were fitted by Gaussian curves, and the full width at half maximum (FWHM) and the height of the Gaussian fit served as descriptors of the noise level. If spikes are present in the scan, a large number of different slopes arise. Consequently, for an elevated noise level in the STM signal, the derivatives are scattered widely around zero. The corresponding histogram is broader and of lower intensity. Analog, this quantification is possible in constant current mode using the derivative of the height signal with respect to adjacent data points. With this approach, it is possible to assign a number to the noise level of a certain signal. Applied to the Pt(111) example for the ORR, step sites are indeed more active as they show a broader histogram than the terrace sites

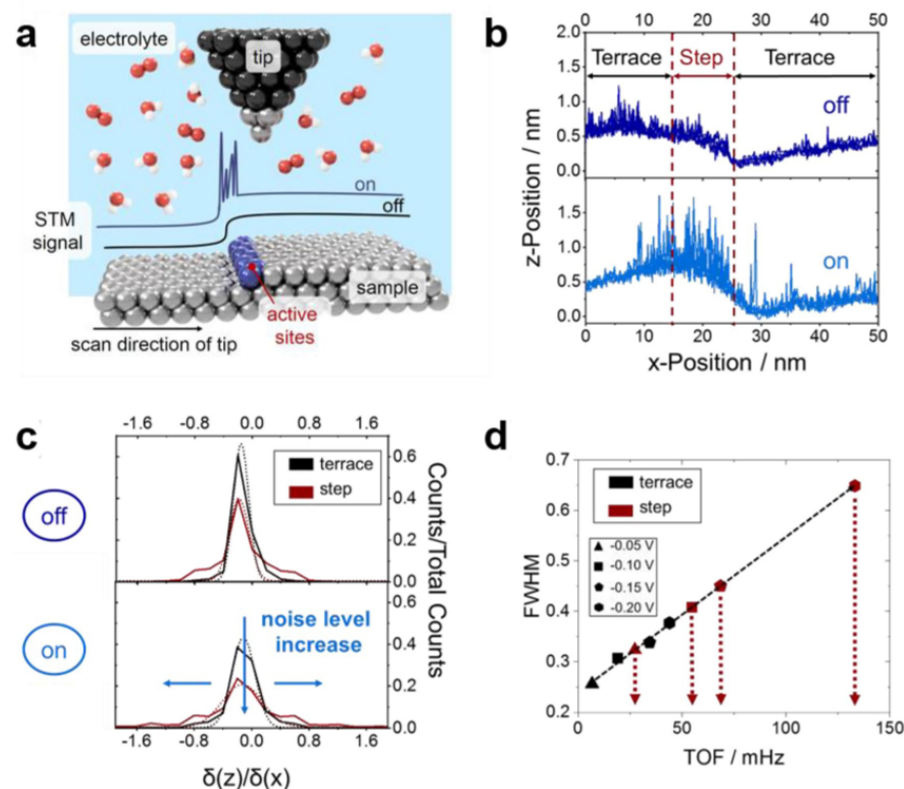


Fig. 1 n-EC-STM principle for the detection and quantification of local activity. **a** The EC-STM signal is obtained by a tip scanning across a conductive sample with the tunneling gap in-between filled by the electrolyte. The tip is insulated against chemical reactions e.g. by a layer of wax. If the potential between the sample and RE is chosen such that no reaction takes place ('Off'), the signal is unperturbed (black line in tunneling gap). However, if a reaction is allowed ('On'), distinct noise features appear at the position of the active sites. In this example, the active sites are colored in blue at the top of the step edge. **b** Example of an n-EC-STM measurement under ORR conditions on a Pt(111) surface in 0.1 M HClO_4 . An increased noise level is observed near the step for reaction 'On'. Therefore, step sites are

more active than terrace sites for this system. **c** Histograms for the data in **(b)** confirm that step sites are more active than terrace sites because the histogram for step sites under reaction conditions (red curve in the lower graph) is broader and less intense than for terrace sites (black curve). Details can be found in the main text. **d** Further experiments for the same system as **b**, **c** confirm that the FWHM of the histogram, quantifying the noise level, is linearly related to the local TOF. This instant serves as means for a local quantification of activity using EC-STM. Data in **(b–d)** and the applied potentials published in reference [23]. © 2020 The Authors Published by Wiley-VCH GmbH

in Fig. 1c. This kind of experiment was repeated for various step sites and various applied sample potentials. The FWHM served as a descriptor for the noise level. As a descriptor for the activity, the turnover frequency (TOF), defined as the number of reaction events per active site and per time unit for a fixed set of reaction conditions [24], was chosen. For the terrace sites, the TOF was calculated from the overall sample current, assuming a low overall number of non-terrace sites (step and defect sites) on the annealed Pt(111) surface. Importantly, a linear trend could be established

between FWHM and TOF from a set of applied potentials within one measurement series. By assessing the noise level of the step edges and using the noise-activity relation from adjacent terrace sites, one can extrapolate the local activity of the step sites. The relation between FWHM and TOF is shown in Fig. 1d for the same data set as in Fig. 1b, c. The noise-activity relation did not only serve to very locally extract the activity of a certain category of surface sites but also confirms that the noise features in the EC-STM signal are indeed caused by an electrocatalytic activity. These

findings were confirmed by Agnoli et al. [25, 26], who state that the electrocatalytic influence on the tunneling current takes the form of a first-order perturbation at low overpotentials. With their quantification approach, they can assess the onset potential, the Tafel slope, and the TOF locally for different surface geometries.

In summary, the EC-STM technique serves as a viable tool to identify active sites with high resolution while at the same time being able to assess the surface morphology.

3 Experimental Details

The samples investigated in this work were Pd(111) and Pd(100) single crystals (both Ø 5 mm, 99.999%, MaTeCK, Germany), and HOPG (mosaic spread value 3.5°, mosaic spread accuracy $\pm 1.5^\circ$, sample size 10×10×1 mm³, Nano-AndMore GmbH, Germany).

A Nanoscope III SPM Multimode (Veeco Instruments) connected to a Nanoscope IIID controller and a Veeco Nanoscope Universal bipotentiostat was used for the n-EC-STM experiments. The sample was clamped between a stainless steel plate and a polytetrafluoroethylene (PTFE) ring. This resulted in a miniature electrochemical cell, which can host the electrolyte. For all measurements, 0.1 M HClO₄ (70% HClO₄, Suprapur, Merck, Germany) was used as the electrolyte and prepared by the dilution with ultrapure water (18.2 MΩ cm, Evoqua Milli-Q). Two wires were immersed into the electrolyte and acted as RE and CE. The RE was Pt (Ø 0.5 mm, 99.99%, MaTeCK, Germany). The CE was a carbon rod (Ø 0.5 mm, 99.95%, Goodfellow GmbH) or a curled palladium wire (Ø 0.25 mm, 99.95%, MaTeCK, Germany) for the measurements on HOPG or the palladium single crystals, respectively. The STM tips were mechanically ripped from a platinum-iridium wire (Pt80/Ir20, Ø=0.25, 99.9 + %, Goodfellow GmbH) with a side cutter. The tip was insulated with Apiezon[®] wax [27].

Since STM is not an element-sensitive technique, well-defined model surfaces are needed for profound findings. Therefore, specific preparations are required to clean and smoothen the sample. For the palladium single crystals, a controlled annealing temperature of approximately 950° C under the exclusion of oxygen was required. For this purpose, two different heating systems were applied: a high-frequency induction heater (20–80 kHz, 15 KW–EQ-SP-15A, MTI, USA) and a tube furnace (Heraeus Instruments RO 7/50). In both, the Pd surfaces were annealed in an argon atmosphere (Argon 5.0, Westfalen, Germany). The annealed surface was protected by a drop of electrolyte before the electrochemical measurements. The HOPG surface was

prepared by removing the first layers with adhesive tape. More details are available in references [28, 29].

4 Results & Discussion: n-EC-STM Measurements for the HER

In the following, we demonstrate the in-situ technique for the HER. First, we focus on Pd(111) and Pd(100) model surfaces and showcase the different noise behavior on sites of different coordination. Second, we demonstrate the atomic resolution of the technique on a graphite material.

4.1 Palladium Catalyst Surfaces: In-Situ Imaging and Identification of Active Sites

For structure-sensitive reactions, the local activity strongly depends on the coordination of the surface sites. The reason is that surface site coordination is for many reaction intermediates directly related to the binding strength between the surface site and the reaction intermediate [30]. The Sabatier principle concludes that binding strength should be optimal at active sites and thus also coordination. Therefore, n-EC-STM measurements can contribute to finding the optimal surface geometry by relating step and terrace sites in the same image. In the case of Pd hydride formation, strain plays a role, which can also influence the nature of active sites [28]. In the here-presented study, cyclic voltammetry measurements in Ar-saturated 0.1 M HClO₄ provided enough hydrogen absorption and the subsequent release of strain to convert an atomically flat surface of a freshly annealed Pd crystal into a ‘hilly’ surface. Figure 2 illustrates this change in morphology by STM measurements for reaction ‘Off’ on Pd(111) (Fig. 2a, b) and Pd(100) (Fig. 2c, d) before (Pd) and after 8 or 5 cycles (Pd_c), respectively.

This restructured morphology also leads to a change in the location of the active sites (cf. ref. [28]). However, to keep it simple, under reaction conditions, we only consider surface coordination without strain by measuring a freshly annealed sample and performing n-EC-STM measurements at the onset of the HER to avoid the influence of hydride formation.

The nature of active sites on Pd surfaces was investigated on the two model surfaces with orientations (111) and (100). For the n-EC-STM experiments, the surfaces were freshly annealed and protected from oxygen as described in the section ‘3’. The used electrolyte was 0.1 M HClO₄. The STM measurement in Fig. 3a, b includes two steps on Pd(111) with a height of 2.2 nm, which corresponds to approximately eight Pd layers

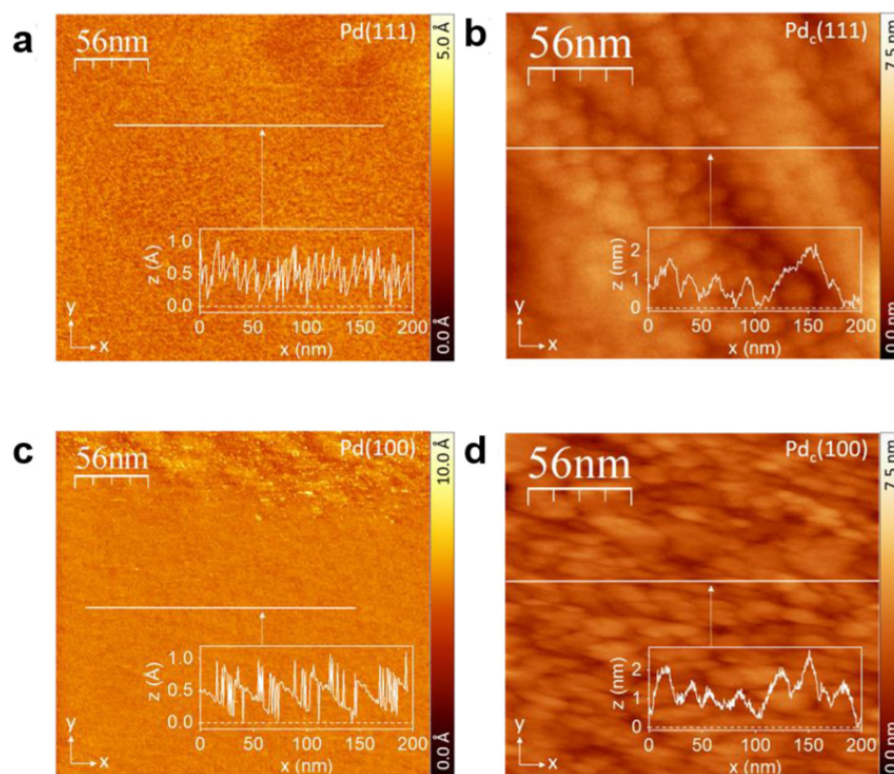


Fig. 2 STM measurements for reaction ‘Off’ of annealed Pd before (a, c) and after (b, d) cyclic voltammetry (8 or 5 cycles, respectively) performed at a potential between 0.2 and 1.2 V versus a reversible hydrogen electrode (RHE) and a scan rate of 50 mV s^{-1} . The inset line scans show the height profile of each surface at the position indicated with the solid white line. While the freshly annealed surfaces

(a, c) are mostly atomically flat, the surfaces after cycling (Pd_c) in b, d show a hilly morphology with a height difference of several nanometers. Here, the upper part of (c) exhibits a single atomic roughness. a, c are reprinted with permission from [31]. Copyright © 2022 American Chemical Society

[32]. During the recording of the image, the sample potential (with respect to the RE) was switched such that the HER was allowed (‘On’) or hindered (‘Off’). The latter is achieved at a potential in the double-layer region. For reaction ‘On’, locally distinct noise features occur, which can be used to assess the geometry of active areas. More details on the working principle of the technique are given in Section ‘2’. In Fig. 3a, b, near the step sizes, the noise level is higher compared to the Pd(111) terraces. Therefore, we can assume a higher electrochemical activity of these structures. In contrast, the terraces have fewer noise peaks, which indicates lower activity. For the reaction ‘Off’, which is shown in the middle part of the measurement, the overall noise level of the image

is low. This provides a reference to assign noise to electrochemical activity; and not to a change in morphology. Combining several EC-STM measurements with further mentioned evaluation techniques makes a conclusion on the nature of active sites possible. Here, on Pd(111), we identify the highest accumulation of active sites on the top of the step edges and a lower one on the terrace (cf. reference [28]).

Figure 3c, d provides an analog measurement for Pd(100) in 0.1 M HClO_4 . During the recording of the image, the sample potential was switched between reaction ‘On’ and ‘Off’. The bottom part of the image shows an elevated structure with rich noise behavior. In contrast, at first glance, the terrace in the upper part exhibits no

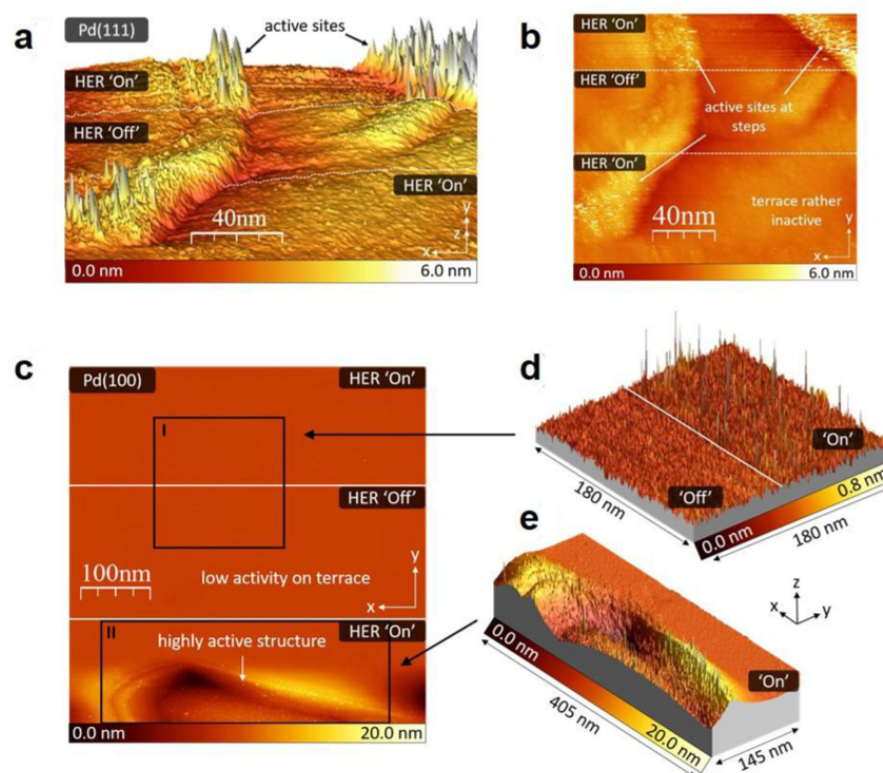


Fig. 3 n-EC-STM measurements on Pd surfaces under HER conditions. **a** Three-dimensional view of an n-EC-STM measurement of freshly annealed Pd(111) in 0.1 M HClO₄. By comparing the signal between reactions 'On' and 'Off', we encounter distinct noise spikes at the active sites. While the flat areas remain mostly inactive, a high

accumulation of active sites is visible on the step edges. **b** Two-dimensional view of (a). **c** n-EC-STM measurement of annealed Pd(100) in 0.1 M HClO₄. **d** Comparison of reaction 'On' and 'Off' for terrace sites. **e** Active structure, including step sites.

noise level. However, at a closer look at the terrace sites in Fig. 3d, a noise level increase is visible between 'On' and 'Off'. Since the noise level of the terrace is orders of magnitude lower than at the step, the terrace noise is less easily visible in the overall image of Fig. 3c, but can be detected by an individual investigation of this area. Here, it is important to note that a comparison of the noise is only possible within an individual image or a series of line scans, but not between different measurements since several influences like feedback settings, tip properties, or electrolyte concentration can alter the intensity of the noise. From previous measurements (cf. reference [28]), we know that the highest activity on Pd(100) is located on step-edges, while a lower but also significant one is spotted on the terrace as well. This is in good agreement with Fig. 3c–e, as the structure in the lower third of the images

might consist of multiple steps while the activity on the terrace is also elevated.

In summary, for unstrained, as-prepared Pd(111) and Pd(100) surfaces, step sites show higher activity than terrace sites. The explanation is an activity-coordination dependence, which is mentioned at the beginning of the section. For the inclusion of strain effects during hydride formation and for more details on the applied potentials, we refer to reference [28].

4.2 Carbon Surfaces: High-Resolution Imaging Under Reaction Conditions

It has been well-known for a long time that, in principle, the STM is capable of resolving the electronic structure of surfaces with a sub-nanometer resolution. In many cases,

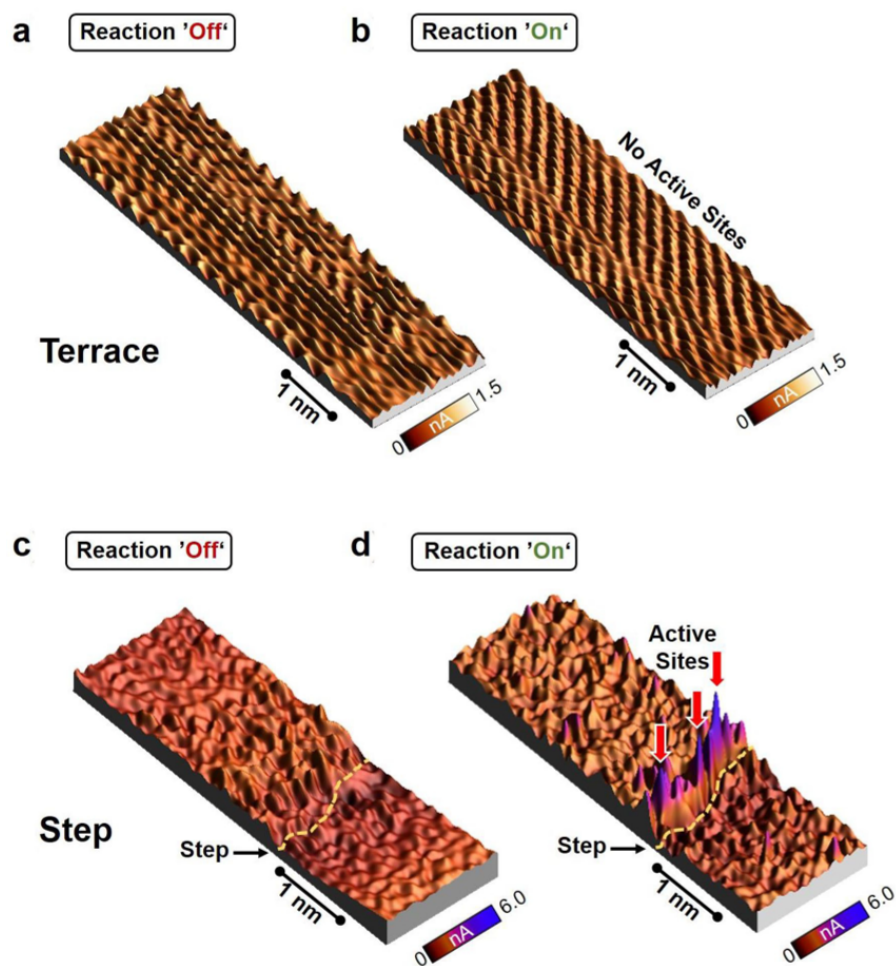


Fig. 4 Atomic-resolution images of HOPG under HER conditions. **a**, **b** Measurement of a HOPG terrace (basal plane) while the applied potential corresponds to **a** reaction 'Off' and **b** reaction 'On' (cf. reference [37] for more information on the applied potentials). No active sites can be detected under the reaction conditions. **c**, **d** represent a

repetition of the experiment at a position including a step edge. In this case, the reaction causes noise spikes (in purple color) along the upper edge of the step, indicating the presence of active sites. Reproduced from reference [37] with permission from the Royal Society of Chemistry

the resulting STM image relates to the atomic configuration and is, therefore, often called atomic resolution. One of the first successful applications is the visualization of the Si(111) reconstruction by Binnig and Rohrer, just a few months after their introduction of the STM technique [33]. Naturally, being able to replicate this functionality

under reaction conditions to identify active sites would be a valuable resource. Consequently, we carried out a study specifically targeting achieving the best possible resolution of active sites by using the n-EC-STM method. We selected a simple model system so that the evaluation of the images is straightforward. The sample material was

HOPG, which possesses a highly periodic configuration and is, for this reason, a typical calibration surface for STM measurements. Importantly, it is, for several reasons, also an interesting material for energy conversion devices. First of all, carbon is one of the most abundant materials on earth, and HOPG can be seen as a model system for many carbon-based catalyst structures [34]. Moreover, carbon has good electronic conductivity properties and is often used as a support for nanoparticulate catalysts [35]. Additionally, graphite is employed as an anode material in some batteries, such as Li-ion batteries. In this case, it is desirable to suppress any interfering reactions [36]. Taking these considerations into account, it is clear that knowing the nature of the active sites is the fundament for designing a functional material that, depending on the application, maximizes or minimizes the activity toward a reaction. The reaction we investigated was the HER in an acidic medium (0.1 M HClO₄). The advantage of this reaction is a relatively simple mechanism involving only one intermediate (*H). Additionally, it is currently predominantly catalyzed using platinum group metals which are scarce, and it is one of the most common interfering reactions at graphite electrodes in batteries.

To start, we focused on the HOPG basal plane by imaging a section of a large terrace on the sample. The resolution was increased so that the periodic structure of the sample was visible. Then, the same area was captured once with the reaction ‘Off’ (Fig. 4a) and once with the reaction ‘On’ (Fig. 4b). In the images, the periodic surface pattern is represented in a 3D view. From this data, it becomes apparent that there are no active sites on the terrace, as there are no noise spikes in the image under reaction conditions. However, certain surface sites need to be active at the applied potential, causing the HER current in the macroscopic cyclic voltammogram (see e.g. reference [35]). Therefore, we investigated another typical structural motif on the HOPG surface, a step edge. The previous experiment was repeated and is displayed in Fig. 4c (reaction ‘Off’) and Fig. 4d (reaction ‘On’), which illustrate excerpts of the measurements published in reference [37]. Here, also 2D views of the entire images are provided. Under reaction conditions, the upper edges showed clear signs of activity in this case, reflected by the noise spikes at these positions (purple color shade in the image). The spikes appear directly or very close to the upper edge of the step, indicating that the first one or two rows of atoms along the edges should contain the most active atomic configurations. The terraces (i.e., the basal plane) remain almost completely inactive. Minor signs of activity could be caused by defects or other structural deviations from the ordered atomic arrangement.

The results were supported by density functional theory calculations, which suggested the most favorable binding conditions for the *H intermediate should be found within the first two rows of atoms along HOPG edges and in the vicinity of carbon vacancies (more details in reference [37]). This is in good agreement with the observations from the n-EC-STM images. Other literature reports on related carbon materials, using both experimental and theoretical approaches, similarly find the most active sites at the edge planes [38–41]. Consequently, it can be assumed that the n-EC-STM technique is indeed capable of the successful identification and visualization of active sites with down to atomic resolution.

5 Conclusion

In the field of electrocatalysis and its applications, such as water electrolysis, the acceleration of the involved reaction kinetics is vital. For structure-sensitive reactions, optimized binding conditions between reaction intermediates and catalyst surface lead to maximal performance. Therefore, for catalyst design strategies, knowledge about the nature of the active sites, which means their electronic and geometric configuration, is important. In doing so, in-situ techniques with high resolution can provide valuable information. One approach is to evaluate noise features in the EC-STM signal to track local activity changes. As an example, we investigated Pd and HOPG surfaces for the HER. For Pd(111) and Pd(100) in 0.1 M HClO₄, a significant activity occurs on step edges while a marginal one appears on flat areas. Besides the capabilities of qualitatively identifying the position of active sites and obtaining quantitative information on their relative activities, it is also possible to achieve an atomic resolution with this technique. This was showcased for the HER on HOPG in an acidic medium, where the most active sites were located within the first two rows of atoms along the upper edge of steps. Depending on the experimental conditions, the n-EC-STM technique allows a targeted and comprehensive in-situ investigation of active sites on well-chosen systems down to atomic resolution by selecting the scan size, the examined surface structures, the electrochemical reaction, and the catalyst materials.

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Data availability The data supporting the results of this review are available on reasonable request from the last corresponding author A. S. B.

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