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## Report Title

Parameters for efficient fuel cell catalyst structures

### ABSTRACT

A rational design of the catalyst structure based on fundamental studies is the key to fuel cells with high performance. The focus of this project was to study anode as well as cathode reactions relevant to fuel cells such as the hydrogen oxidation reaction (HOR), the methanol oxidation reaction (MOR) and the oxygen reduction reaction (ORR). Also the hydrogen evolution reaction (HER) was under detailed investigation due to its importance as key reaction in hydrogen production via electrolysis. Major aspects of highly efficient catalysts are the morphology of the catalyst particles (e.g. particle size, particle height, inter-particle distance) and the influence of the support on their reactivity. The project followed the strategy of creating model electrode structures which allowed to fundamentally understanding the influence of the above mentioned parameters on the reactions. Electrochemical methods (e.g. potentiostatic and galvanostatic pulse techniques) were used in order to study the influence on HOR/HER, ORR and MOR. In-situ electrochemical scanning tunnelling microscopy (EC-STM), electrochemical atomic force microscopy (EC-AFM) and scanning electrochemical potential microscopy (SECPM) allowed investigating morphological and structural properties of the model catalysts. Single Pt particles were also locally investigated using an EC-STM.

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### List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

#### (a) Papers published in peer-reviewed journals (N/A for none)

H. Wolfschmidt, R. Bußar, U. Stimming; Journal of Physics, Condensed Matters 20 (2008) 374127 "Charge transfer reactions at nanostructured

Au(111) surfaces: influence of the substrate material on electrocatalytic activity"

T. Brülle, U. Stimming; Journal of Electroanalytical Chemistry 636 (2009), 10 "Platinum nanostructured HOPG – Preparation, characterization and reactivity"

H. Wolfschmidt, C. Baier, S. Gesell, M. Fischer, M. Schreck, U. Stimming, Materials, 3 (2010) 4196 "STM, SECPM, AFM and Electrochemistry on Single Crystalline Surfaces"

H. Wolfschmidt, D. Weingarth, U. Stimming, ChemPhysChem, 11 (2010) 1533 "Enhanced reactivity for hydrogen reactions at Pt nanoislands on Au(111)"

L. Wang, U. Stimming, M. Eikerling, Electrocatal., 1 (2010) 60 "Kinetic Model of Hydrogen Evolution at an Array of Au Supported Catalyst Nanoparticles"

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#### (c) Presentations

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- S. Pandelov, H. Wolf Schmid, R. Bussar, U. Stimming; "Reactivity of Pd-clusters on Au(111)-surfaces: Influence of cluster size and interparticle distance on the hydrogen evolution reaction" ICEI 2007, Saboro, Japan
- R. Bussar, U. Stimming; "Reactivity of Electrode Surfaces Modified with Nanoislands of Different Size and Distribution" ISE2007, 58th Annual Meeting, Banff, Canada
- U. Stimming; "Parameters for Efficient Fuel Cell Catalyst Structure" 2007 PI Meeting - Army Research Office, Chapel Hill, USA
- H. Wolf Schmid, R. Bussar, U. Stimming; "Catalysis of Nanostructured Surfaces for Hydrogen Related Reactions" ESF-FWF Conference Nanotechnology for Sustainable Energy 2008; Obergurgl, Austria
- H. Wolf Schmid, R. Bussar, U. Stimming; „Electrocatalytic Activity of Pt/Au(111) and Pd/Au(111) towards HER/HOR, ORR and MOR – Similarities and Differences" ISE Spring Meeting 2009, Szczecin, Poland
- H. Wolf Schmid, R. Bussar, O. Paschos, T. Brülle, U. Stimming; "Hydrogen Reactions on Pt supported on Au, Cu and HOPG - The influence of the Substrate on Electrocatalytic Activity" NACS 2009, San Francisco, USA
- T. Brülle, O. Paschos, H. Wolf Schmid, U. Stimming; "Substrate Effects in Electrocatalysis" 60th ISE Spring Meeting 2009, Beijing, China
- H. Wolf Schmid, U. Stimming; "Hydrogen, Oxygen and Methanol Reactions on Mono- and Submonolayers of Pd and Pt on Au(111)" 216th ECS Meeting 2009, Wien, Austria
- H. Wolf Schmid, T. Brülle, O. Paschos, U. Stimming; "Tutorials in Nanotechnology: Focus on Physical and Analytical Electrochemistry" 216th ECS Meeting 2009, Wien, Austria
- T. Brülle, U. Stimming "Preparation, Characterization and Reactivity of Sub-monolayers of Platinum on Graphite" ECS 216th Meeting, 2009, Vienna, Austria
- H. Wolf Schmid, O. Paschos, T. Brülle, U. Stimming; "Substrate Effects in Electrocatalysis" ICEI 2010, New York, USA
- H. Wolf Schmid, C. Baier, U. Stimming; "Scanning Probe Techniques (EC-STM, SECPM, AFM) and Electrochemistry on Single Crystalline Supports" GDCh – Electrochemistry 2010, Bochum, Germany
- H. Wolf Schmid, C. Baier, U. Stimming; "STM, SECPM, AFM and Electrochemistry on Single Crystalline Surfaces" 61st ISE Meeting 2010, Nice, France
- U. Stimming, H. Wolf Schmid; "Nanotechnology in Electrochemical Energy Conversion and Storage" International Workshop on Energy and Environmental Challenge 2010, Pretoria, South Africa

#### Poster presentation at conferences:

- S. Pandelov, R. Bussar and U. Stimming, "Reactivity of Pd-clusters on Au(111)-surfaces: influence of clusters size and interparticle distance on the hydrogen evolution reaction (HER)" Conference on "From Physical Understanding to Novel Architectures of Fuel Cells", 2007, Trieste, Italy
- H. Wolf Schmid, C. Baier, Ulrich Stimming; "Probing of single particle reactivity via EC-STM: dependence of reactivity on particle size" Conference "From Physical Understanding to Novel Architectures of Fuel Cells" 2007, Trieste, Italy
- H. Wolf Schmid, D. Weingarth, U. Stimming; "Reactivity Measurements with the Electrochemical STM" ICEI 2010, New York, USA

H. Wolschmidt, T. Brülle, O.Paschos, U.Stimming; "Hydrogen Reactions on Pt supported in Au, Cu and HOPG" ICEI 2010, New York, USA

H. Wolschmidt, T. Brülle, U.Stimming; "Hydrogen, Oxygen and Methanol Reactions on Pt Nanostructured Au(111) Surfaces" International Conference on Electrocatalysis 2010, Kloster Irsee, Germany

H. Wolschmidt, D. Weingarth, C. Ostermayer, U.Stimming; "Reactivity Measurements with the Electrochemical STM" International Conference on Electrocatalysis 2010, Kloster Irsee, Germany

H. Wolschmidt, C. Baier, U. Stimming; "STM, SECPM, AFM and Electrochemistry on Single Crystalline Surfaces" Nanoscale VIII 2010, Basel, Switzerland

H. Wolschmidt, D. Weingarth, U.Stimming; "Reactivity of Pt/Au(111) towards Hydrogen Related Reactions - Local vs. Large Scale Investigations" 61st ISE Meeting 2010, Nice, France

T. Brülle, A. Denisenko, U. Stimming; "Investigations of reactivity of catalyst nanostructures on planar carbon supports" 61st ISE Meeting 2010, Nice, France

C. Ostermayr, U. Stimming; "Activity of Platinum Submonolayers on Oxidized Gold" DGCh Electrochemistry 2010, Bochum, Germany

T. Brülle, H. Wolschmidt, U. Stimming; "Reactivity of platinum on carbon supports" DGCh Electrochemistry 2010, Bochum, Germany

H. Wolschmidt, D. Weingarth, U. Stimming; "Reactivity Measurements with the Electrochemical STM" International Workshop on Energy and Environmental Challenge, 2010, Pretoria, South Africa

H. Wolschmidt, T. Brülle, O. Paschos, U. Stimming; "Hydrogen Reactions on Pt Supported on Au, Cu and Carbon" International Workshop on Energy and Environmental Challenge, 2010, Pretoria, South Africa

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T. Brülle, A. Denisenko, H. Sternschulte, U. Stimming; "Catalytic activity of platinum nanoparticles on highly boron doped and 100-oriented diamond towards HER and HOR" in preparation

H. Wolschmidt, M. Hantel, D. Weingarth, U. Stimming; "A transfer of fundamental results to fuel cell catalyst for Pd/Au system" in preparation

P. Quiano, H. Wolschmidt, E. Santos, U. Stimming, W. Schmickler, Catal. Today, "Pd and Pt on Au(111) for hydrogen catalysis – Theory and Experiment" submitted

**Number of Manuscripts:** 4.00

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## Patents Submitted

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## Patents Awarded

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### Awards

Second prize for outstanding contributed talk at ESF-FWF-LFUI Conference on Nanotechnology for Sustainable Energy, Holger Wolfschmidt, 2008, Obergurgl, Austria

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Methrom/Autolab Poster Award at GDCh Conference, Holger Wolfschmidt, 2010, Bochum, Germany

Electrochimica Acta Gold Medal of International Society of Electrochemistry 2010, U. Stimming, 2010

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### Graduate Students

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| T. Brülle              | 0.28                     |
| S. Bugarski            | 0.04                     |
| C. Du                  | 0.15                     |
| D. Horsch              | 0.06                     |
| M. Möst                | 0.06                     |
| C. Ostermayr           | 0.06                     |
| M. Salehiravesh        | 0.04                     |
| T. Walter              | 0.06                     |
| H. Wolfschmidt         | 0.07                     |
| <b>FTE Equivalent:</b> | <b>0.82</b>              |
| <b>Total Number:</b>   | <b>9</b>                 |

### Names of Post Doctorates

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| R. Bußar               | 0.10                     |
| O. Paschos             | 0.10                     |
| S. Malkhandi           | 0.17                     |
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### Names of Faculty Supported

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|------------------------|--------------------------|
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| <b>Total Number:</b>   |                          |

### Names of Under Graduate students supported

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> |
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| M. Discher             | 0.06                     |
| I. Kunze               | 0.02                     |
| T. Mittermeier         | 0.15                     |
| E. Plante              | 0.07                     |
| U. Stützel             | 0.06                     |
| F. Selmeier            | 0.08                     |
| K. Tu                  | 0.06                     |
| D. Weingarth           | 0.41                     |
| S. Zimnik              | 0.06                     |
| <b>FTE Equivalent:</b> | <b>1.15</b>              |
| <b>Total Number:</b>   | <b>10</b>                |

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 2.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 2.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 2.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ..... 0.00

### Names of Personnel receiving masters degrees

| <u>NAME</u>          |
|----------------------|
| D. Weingarth         |
| H. Wolfschmidt       |
| <b>Total Number:</b> |

2

### Names of personnel receiving PHDs

| <u>NAME</u>          |
|----------------------|
| <b>Total Number:</b> |

### Names of other research staff

| <u>NAME</u>            | <u>PERCENT SUPPORTED</u> |
|------------------------|--------------------------|
| J. Figueiredo          | 0.06 No                  |
| <b>FTE Equivalent:</b> | <b>0.06</b>              |
| <b>Total Number:</b>   | <b>1</b>                 |

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## **Inventions (DD882)**

### **Scientific Progress**

Please see the attached WORD-file for the final technical report. During the funding no subcontractors are involved and there were no inventions made.

### **Technology Transfer**

ARO Final Report  
Grant No. W911NF-06-1-0483

## Parameters for Efficient Fuel Cell Catalyst Structure

Holger Wolfschmidt, Tine Brülle, Cornelia Ostermayr,  
Sauradip Malkhandi, Petra Bele, Ulrich Stimming

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## **1 Introduction**

Catalysis in fuel cells is still a challenging task in order to enhance the overall efficiency and simultaneously decrease the amount of noble metal. A rational design of the catalyst structure based on fundamental studies is the key to fuel cells with high performance. The focus of this project was to study anode as well as cathode reactions relevant in fuel cells such as the hydrogen oxidation reaction (HOR), oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR). Also the hydrogen evolution reaction (HER) was under detailed investigation due to its importance as key reaction in hydrogen production via electrolysis. Major aspects for high efficient catalysts are morphology of the catalyst particles (e.g. particle size, particle height, inter-particle distance) and the influence of the support on reactivity. Therefore, the project followed the strategy of creating model electrode structures which allowed to fundamentally understand the influence of the above mentioned parameters in the reactions. The deposition of different reactive nanoparticles such as Pt or Pd onto unreactive model substrates such as Au (111), Cu(hkl), Ru(0001), highly oriented pyrolytic graphite (HOPG) and diamond was performed. Thus, by varying the substrate and the deposited catalyst a more detailed insight into important parameters was achieved and optimized catalyst support system could be obtained. Electrochemical methods (e.g. potentiostatic and galvanostatic pulse techniques) were used in order to study the influence on HOR/HER, ORR and MOR. In-situ electrochemical scanning tunnelling microscopy (EC-STM), electrochemical atomic force microscopy (EC-AFM) and scanning electrochemical potential microscopy (SECPM) allowed investigating morphological and structural properties of the model catalysts. Single Pt particles were also locally investigated with an EC-STM. This combined approach revealed a more detailed picture of the major structural and morphological parameters having an influence on electrocatalytic activity.

## **2 Literatur overview and scientific goals**

Several parameters determine the activity of the noble metal catalysts such as particle size [1-3], particle dispersion [4, 5], density of low coordinated surface atoms [6, 7] and influence of the substrate material [8-17]. Fast transport due to spherical diffusion for small, isolated catalyst particles resulting from a fine particle dispersion might also be an important parameter [5, 18].

One distinct property of nanometer sized particles is their large specific surface area and the large number of low coordinated sites on the surface, which may have a direct impact on their reactivity. For example, the variation of platinum nanoparticle size results for several reactions in considerable changes in the particle reactivity, e.g. specific activity towards the hydrogen evolution/hydrogen oxidation [4, 5, 18-21], oxidation of methanol [22, 23] and formic acid [23] and the reduction of oxygen [24, 25]. But it was also found that nanoparticles can not be described just by the sum of the behavior of the adsorption sites they provide determined by the coordination of the atoms. This is for example evident from infrared stretching frequency, from nuclear magnetic resonance studies of linearly adsorbed CO on Pt nanoparticles of different size and from density functional theory calculations [3, 26-29]. One reason, why nanoparticles are ‘more than the sum of their active centers’, could be, that the electronic structure of supported nanoparticles may differ significantly from the according electronic structure of the bulk material. According to theoretical calculations from the group of Nørskov [9, 30-36], the group of Groß [11, 12, 37] and the group of Schmickler [38-42] the electronic structure of metals influences their reactivity when supported on or alloyed with other metals. Density Functional Theory (DFT) is the approach to calculate activation energies and adsorption energies of species and reaction intermediates on surfaces [35]. For example the electrocatalytic properties of Pd islands on Au(111) are modified due to strain in the lattice of Pd by about 4.8% resulting in a shift of the d-band centre of Pd to higher energies and thus a change in the interaction with reaction intermediates, e.g. with atomic hydrogen [21]. Similar conclusions were taken by Roudgar and Gross [11] who investigated theoretically the adsorption energies of hydrogen and CO.

It was experimentally shown by the groups of Kolb [14, 43-45], Kibler [13] and Uosaki [46, 47] that the physical and chemical properties of thin Pd overlayers change with respect to the Pd bulk material. Baldauf and Kolb [44] as well as Kibler et al. [45] investigated the catalytic behaviour regarding formic acid oxidation. The reactivity is obviously dependent on the thickness of the Pd layer, the crystallographic orientation and also on the chemical identity of the substrate. The oxygen reduction reaction (ORR) was investigated by Naohara et al. [46, 47] who found a dependence on the thickness of the Pd overlayer. Kibler et al. [13, 48, 49] reported on the parameters influencing the hydrogen evolution reaction (HER) which can change the catalytic activity; most of the observed experimental results can be explained by a lateral strain of thin Pd films on Au(111) electrodes according to the Nørskov model [36]. Pandelov and Stimming [17] more recently reported an increased specific reactivity of Pd submonolayers on

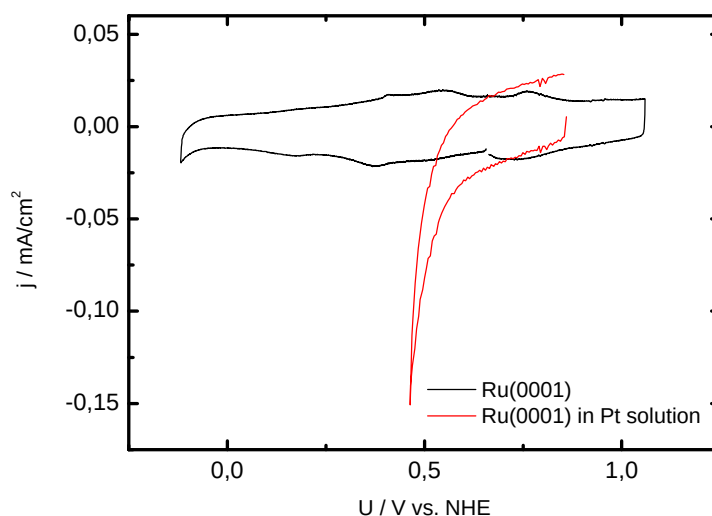
Au(111) which is two orders of magnitude higher compared to bulk Pd. This result may indicate a significant involvement of the gold substrate in the activity of Pd/Au(111). A spill-over mechanism of the adsorbed hydrogen during the HER from the Pd sites to the Au substrate was able to explain the results for submonolayer coverage [16]. Local reactivity measurements and combined DFT calculations of Pd nanoparticles on Au electrode surfaces were performed by Meier et al. [19, 21]. Experimentally it was first demonstrated by Meier et al. [21] that with decreasing particle size from 200nm to 6nm the specific electrochemical activity of single nanoparticles for hydrogen evolution reaction (HER) is increased by more than two orders of magnitude. This result was tentatively explained by a strain effect on the isomorphically deposited Pd particles induced by the Au(111) substrate with larger lattice constant.

All above mentioned work contributes to a better understanding of the parameters influencing the electrocatalytic properties of catalysts, which is important for a rational design of catalysts. As already mentioned parameters may be the interparticle distance, particle morphology, chemical composition and influence of the support. In an effort to better separate the various parameters, this project follows the approach of depositing nanoislands of different reactive materials such as Pd and Pt onto nonreactive model surfaces, for instance Au(111), Ru(0001), Cu(hkl), highly oriented pyrolytic graphite (HOPG) and diamond. The electrocatalytic behaviour of Pt and Pd nanoparticles on Au(111), HOPG and diamond systems concerning the HOR/HER, ORR and MOR were investigated in detail. Electrochemical methods (e.g. potentiostatic pulse techniques and cyclic voltammetry) are used in order to study the influence of the above mentioned parameters on HOR/HER, ORR and MOR. With *in-situ* electrochemical STM (EC-STM) and AFM morphological and structural properties of the model catalysts were investigated in parallel to reactivity measurements. New supports for electrochemical investigations were characterized with standard techniques and a new developed method called scanning electrochemical potential microscopy (SECPM). Also a local pH sensor for investigations in the nm range was developed.

### **3 Results from last funding period**

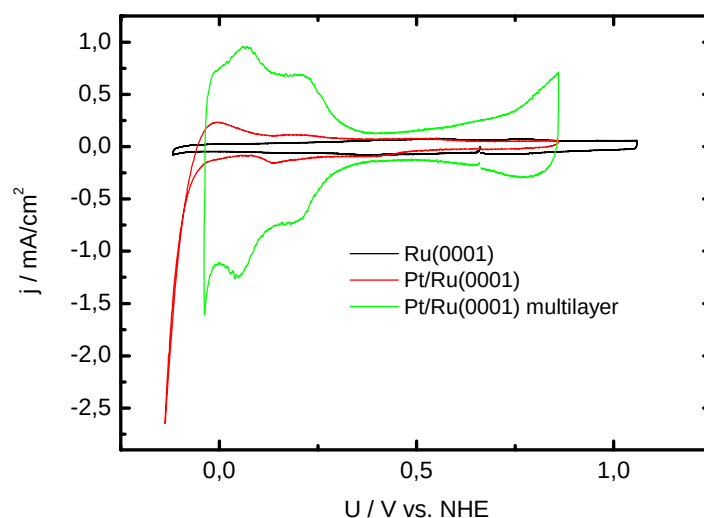
#### **3.1 Pt Deposition on Ru(0001)**

First experiments on Pt deposition on Ru(0001) were conducted to investigate the suitability of the single crystalline substrates for electrochemical purposes. Therefore Pt deposition was performed in 1M HClO<sub>4</sub> and 0.5mM K<sub>2</sub>PtCl<sub>6</sub> using cycling voltammetry. Starting at the initial potential of 860mV vs. NHE and sweeping with 100mV/s to 460mV vs. NHE leads to a deposited charge of 25μC which is equal to 0.15ML on the exposed 0.2cm<sup>2</sup> area of Ru(0001) shown in Figure 1. According to hydrogen adsorption on the Pt surface a charge from the CV of 9μC was determined after correcting the Ru background for the Pt/Ru(0001) sample. The deposition was continued with cyclic voltammograms to further grow Pt to multilayers. A constant initial potential of 860mV vs. NHE was used with a final potential of 0mV vs. NHE with scan rates of 100mV/s and 10mV/s. In both cases the cycles were repeated ten times and a diffusion controlled deposition was observed. The total amount of Pt could not be determined by integration of the deposition cycles due to large overlapping with Ru features and hydrogen adsorption on already deposited Pt.



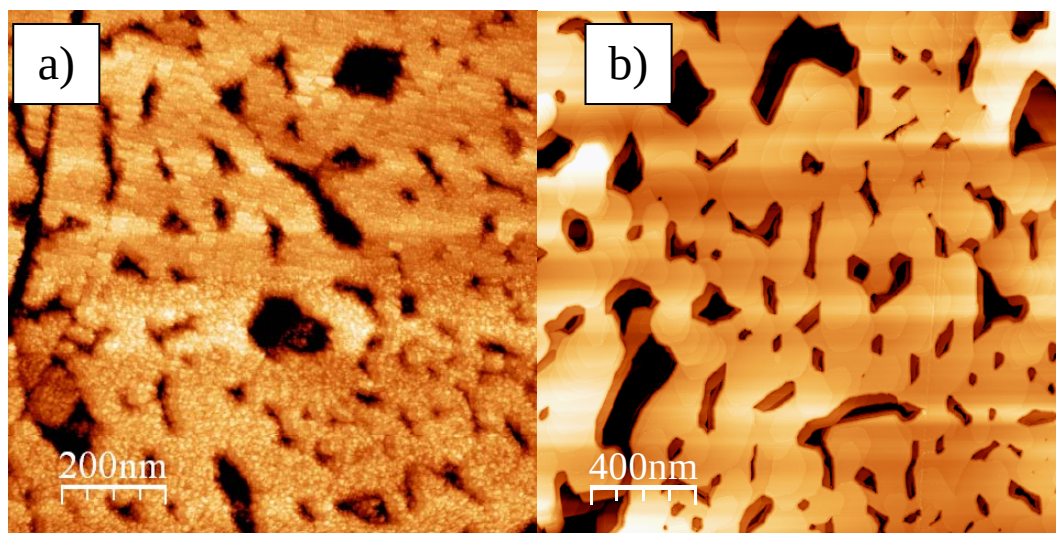
**Figure 1 CV on Ru(0001) in 1M HClO<sub>4</sub> with and without Pt**

Figure 2 shows three different Ru(0001) surfaces. The black line is without Pt, the red line with 0.15ML Pt on Ru(0001) and the green line with multilayers of Pt on Ru. The surfaces for the multilayer determination via adsorbed hydrogen lead to a charge of 80μC which can be calculated to an area of 0.38cm<sup>2</sup> assuming a charge of 210μC per cm<sup>2</sup>. This also shows a surface roughness of about 1.9 compared to the smooth Ru(0001) support with a geometrical area of 0.2cm<sup>2</sup>.



**Figure 2 CV of Ru(0001) and Pt decorated Ru(0001) between hydrogen and oxide formation of the surface in 1M HClO<sub>4</sub>**

In order to investigate the multilayer deposition and to obtain a morphology of the surface STM was performed on these Pt/Ru(0001) samples and hydrogen adsorption to determine the Pt surface. The multilayer structure of Pt on Ru is shown with STM in Figure 3 on the left side and compared to the bare Ru(0001) on the right side. As it can be clearly seen the Pt deposits are on the Ru and roughened the whole surface via a three-dimensional growth. Calculating the image surface area with evaluation software (Nanoscope 7.30) the smooth Ru shows an area of  $4.04\mu\text{m}^2$  for  $2\mu\text{m} \times 2\mu\text{m}$  scan resulting in a surface area difference of 0.9%. The Pt decorated Ru surfaces shows an image surface area of  $1.47\mu\text{m}^2$  for  $1\mu\text{m} \times 1\mu\text{m}$  scan resulting in a 47% surface area difference compared to a flat undecorated surface. Although there is a difference in STM and hydrogen adsorption evaluation the results show the same tendency.



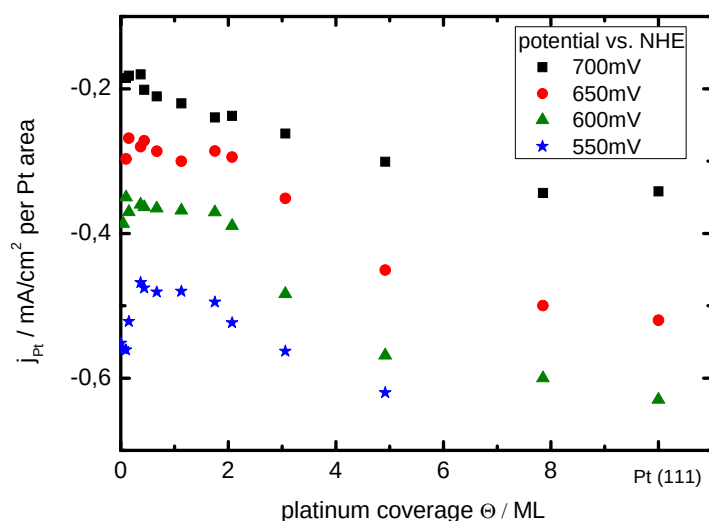
**Figure 3** a) Pt decorated Ru(0001), scan area  $1\mu\text{m}^2$ , image surface area  $1.47\mu\text{m}^2$ ; b) Ru(0001) scan area  $4\mu\text{m}^2$ , image surface area  $4.04\mu\text{m}^2$

### 3.2 ORR on Pt/Au(111)

The deposition and characterization experiments of Pt submonolayers were carried out as described in previous reports.. After purging the electrolyte with oxygen, the initial potential was set to 820mV vs. NHE and cyclic voltammograms for the Pt/Au(111) system were performed between 820mV vs. NHE and 250mV vs. NHE. The obtained results for the Pt/Au(111) system were summarized in a Tafel plot. For a better comparison with results for the hydrogen und methanol reaction the current density for a given potential was plotted versus the coverage of Pt on Au(111), shown in Figure 4. All current densities are referred to the amount of platinum to compare specific current densities of the active Pt catalyst. Results obtained on a Pt(111) single crystal surface are added for comparison. It can be seen that the reactivity of the Pt(111) surface is similar to the reactivity of 7.8ML Pt on Au(111) and shows the highest activity in all cases.

Lower coverages show an increasing current density with increasing Pt coverage for a potential of 700mV vs. NHE. At lower potentials a similar behaviour for coverages larger than 30% is shown. A slightly different behaviour for the reduction of oxygen was found for coverages smaller than 30% for the potentials for 550mV vs. NHE. The current densities are somewhat higher compared to larger coverages. This behaviour was not investigated in detail but diffusion effects may play a key role when lowering the coverage and thus providing island

catalysts with a changed transport mechanism of educts and products in contrast to extended catalyst surfaces. Summarized, the Pt/Au(111) shows an activity increasing with increasing amount of deposited Pt regarding ORR for low overpotentials. Higher overpotentials result in two different behaviours for the activity. For coverages larger than approx. 30% the activity is increasing with increasing amount of Pt. Coverages smaller than approx. 30% show an increasing behaviour but with decreasing amount of Pt for high overpotentials. This results in a current density minimum at about one ML.

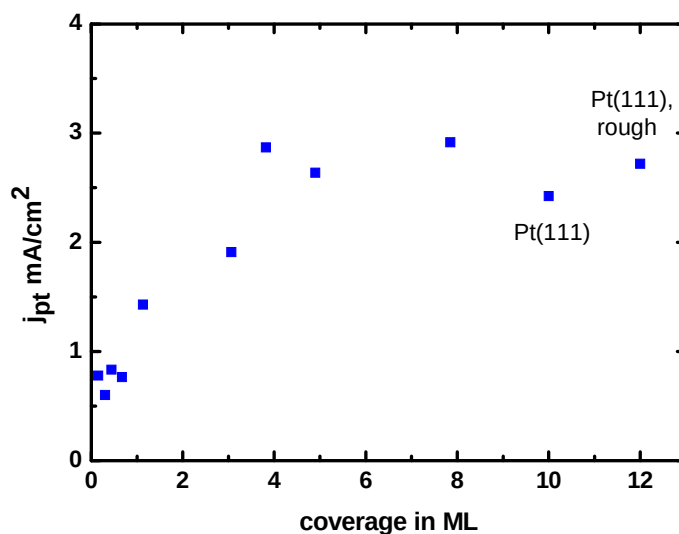


**Figure 4** Specific current density of Pt for oxygen reduction versus platinum coverage on Au(111) for different potentials. The values were obtained from CVs in O<sub>2</sub> saturated 1M HClO<sub>4</sub>.

### 3.3 MOR on Pd/Au(111) and Pt/Au(111)

The methanol oxidation reaction was measured in 1M HClO<sub>4</sub> + 1M CH<sub>3</sub>OH Ar purged electrolyte using cyclic voltammograms with a scan speed of 100mV/s. A typical double peak structure was obtained. The maximum current and the potentials of the forward and the reverse peak were determined. The results of the evaluation of the maximum current are summarized in Figure 5, showing a strong dependence of the Pt coverage on the activity towards methanol oxidation. For very low coverages in the range smaller than 0.15 monolayers no reliable currents could be determined from the CVs. It was found that an increase of the maximum current with increasing Pt coverage on Au(111) up to approx. 3ML occurs. Increasing the amount of Pt leads in a constant maximum current. This is in line with results obtained on single crystal surfaces. For comparison a Pt(111) well oriented and a rough Pt(111) single crystal are shown, indicating

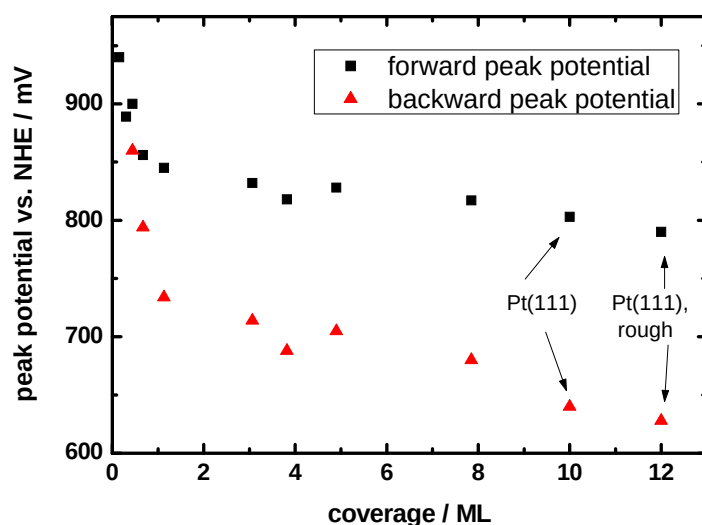
that the Pt(111) is less reactive compared to more polycrystalline surface of the roughened Pt(111). The measured maximum current density of  $3\text{mA}/\text{cm}^2$  is in line with literature [50, 51].



**Figure 5: Specific peak current density of Pt for methanol oxidation versus platinum coverage on Au(111). The values were obtained from CVs in Ar saturated 1M  $\text{CH}_3\text{OH}$  + 1M  $\text{HClO}_4$ .**

For comparison of the peak potentials the forward and the reverse peak potential of the methanol oxidation was evaluated and plotted versus the Pt coverage on Au(111) (see Figure 6). Due to the high scan velocity of  $100\text{mV/s}$  the forward and the reverse peak potentials are separated whereas the forward potential has the higher value. The separation of the peak potentials depends on the Pt coverage and is at least  $100\text{mV}$ . The rough Pt(111) has the lowest onset potential slightly lower compared to the well prepared Pt(111). Starting at  $7.8\text{ML}$  of Pt on Au(111) the peak potential increases with decreasing coverage up to  $1\text{ML}$  in a moderate way. A strong increase of the peak potential is observed below one ML of Pt on Au(111) resulting in a total shift of at least  $150\text{mV}$  compared to the submonolayer regime with the roughed Pt(111).





**Figure 6: Peak potential of methanol oxidation for forward and reverse cycle versus platinum coverage on Au(111). The values were obtained from CVs in Ar saturated 1M CH<sub>3</sub>OH + 1M HClO<sub>4</sub>.**

The methanol oxidation was also investigated on the model surface Pd/Au(111). Even monolayers and multilayers were inactive towards the methanol oxidation at the standard experimental conditions. The investigation of Pd towards the MOR was therefore not investigated in detail.

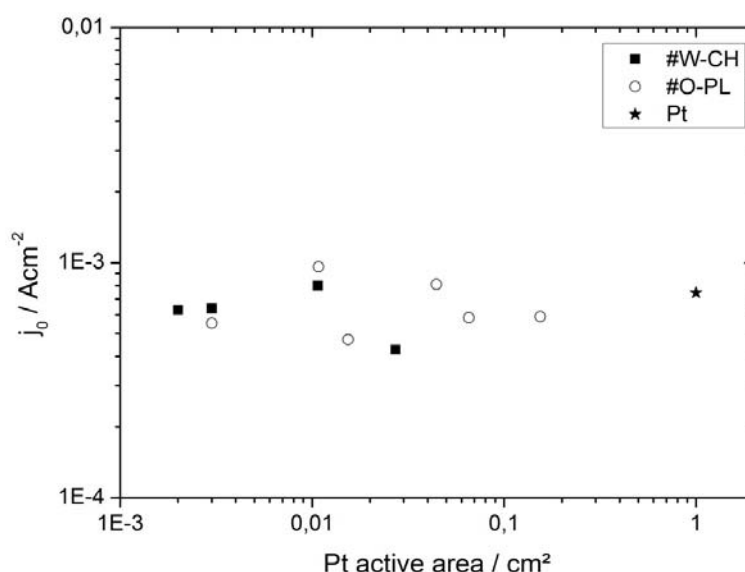
### 3.4 Pt on Diamond

Pt nanostructured monocrystalline diamond(100) surfaces were investigated as model systems in order to study the influence of particle size, particle density and surface treatment of the support on activity regarding catalytic reactions. A homogenous distribution of particles and control the particle density and size was achieved using the potentiostatic double pulse technique. Monocrystalline diamond is particularly suitable for this application due to the homogeneous surface and the apparent lack of preferred nucleation sites. The 3-dimensional nanoparticles form an ohmic contact with the substrate and therefore act as nanoelectrodes. The electrochemical and the morphological analysis of the Pt/diamond surface shows clearly a difference in the deposition process for the two different diamond surfaces used as supports

(#W-Ch : wet chemical oxidation; #O-Pl : oxygen plasma treatment). This difference however is limited to the process of particle nucleation, while the growth does not seem to be affected. On the plasma-treated surface of sample #O-PL, the Pt particle density is larger than on the smoother surface of sample #W-CH. This could be ascribed to two different effects of the plasma treatment. On the one hand, plasma-induced electronic defect might result in a higher effective nucleation potential which causes a faster nucleation of particles. Also, the higher nucleation rate might be due to the higher availability of sites for the formation of stable Pt nuclei on the rougher surface.

The prepared Pt/diamond(100) substrates were used to investigate the activity for the HER and HOR in dependence of particle size and particle density using different electrochemical methods. The specific current density for both reactions was not found to be dependent on coverage of substrate treatment. The values for the exchange current densities were around  $0.8 \text{ mA cm}^{-2}$  which is in agreement with values for bulk platinum surfaces [51].

For Pt/diamond-surfaces also the particle size does not influence the catalytic activity and shows the specific activity of bulk platinum (Figure 7). We conclude from this that platinum mass loading reduction at the anode is a good strategy when using carbon as a support, without deteriorating the intrinsic electrocatalytic process.



**Figure 7:** Exchange current density normalized to platinum surface area versus coverage.

### 3.5 Nanotransfer Printing and Nanoimprint Lithography

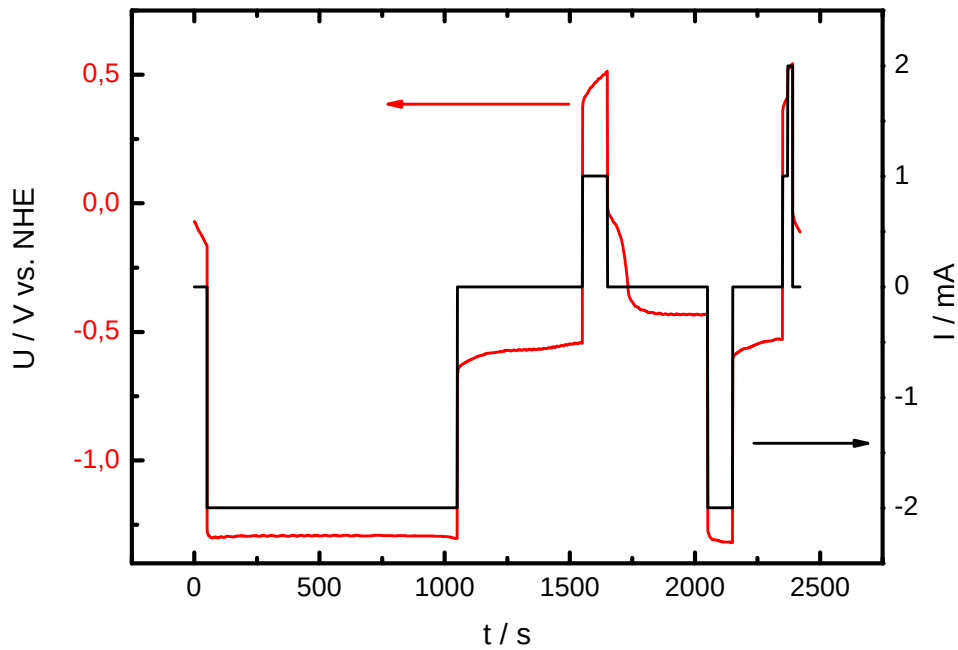
Recent collaborations allow new nanostructuring techniques within the running project. Using surface nanopatterned printing stamps, metallic structures such as Au, Pd and Pt can be deposited on flat substrates and used as electrodes for the investigation of electrocatalytic activities. Two different structuring techniques, nanotransfer printing (nTP) and nanoimprint lithography (NIL), provide a specific variation of the parameters (diameter, height and spacing of the nanoparticles) between 5 and 250 nm. These ordered nanostructures will contribute to a better understanding of the physical properties of electrocatalytically active systems.

### 3.6 Local pH Sensor, Pd/H Electrode

It was shown in the past, that the EC-STM tip can be used as a local sensor to measure the reactivity of single Pd [19, 21] or Pt nanoparticles [52] via the tip. That method detects at the tip the reaction products of a catalytic active particle on a surface. In the cited cases a Pd or Pt particle deposited on Au(111) evolves hydrogen which is then oxidized at the tip and induces a current flow.

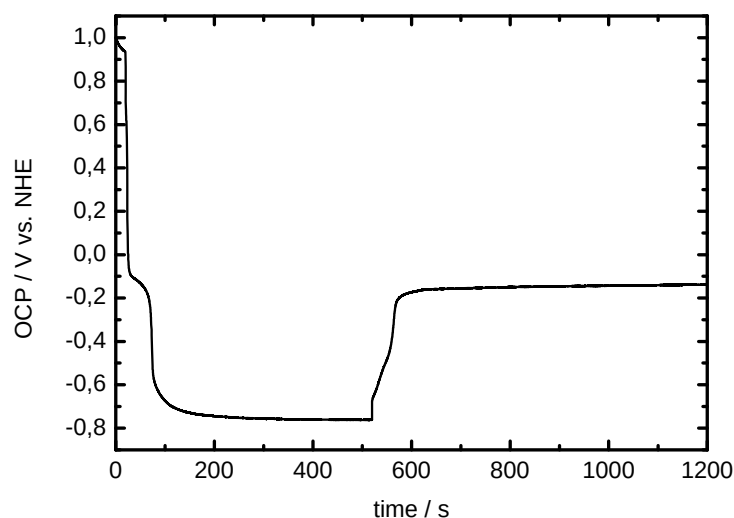
This idea was transferred to locally determine also the proton concentration which varies for several reactions generating or consuming protons. The SECPM offers this possibility due to the potentiometric measurement technique using the tip as a local potential sensor which is held at open circuit potential (OCP). Since a change in proton concentration changes the local pH a proton sensitive tip senses a potential shift of 59 mV per pH value. Thus, hydrogen evolution or oxidation can be directly detected at the SECPM tip by a shift of its OCP. Therefore pH sensitive tips such as Pt and Pd were used to determine their behaviour on the required nanometre length scale. Due to their ability to store hydrogen, Pd tips were favoured and investigated in detail.

Polycrystalline palladium was loaded with hydrogen by galvanostatic pulses to form palladium hydride electrodes in an electrochemical glass cell according to [178]. A hydrogen adsorption and desorption process is shown in Figure 8. The applied current is shown in black with the axis on the right side and the measured potential is shown in red with the axis on the left side. Applying a negative current in the neutral 1M NaClO<sub>4</sub> electrolyte leads to a negative potential at -1.3V vs. NHE where hydrogen evolution and hydrogen absorption occur in parallel. At 1100s the OCP of the tip is measured for about 400s. The OCP is not stable and increasing with time. The short positive current pulse for duration of 100s causes a high OCP which stabilizes after several ten seconds. Repeating the procedure with a negative current pulse leads again to unstable OCP, seen in the time range between 2150s and 2350s. The last positive current pulse which was applied with two different current steps shows the same beginning of the transient as compared to the first positive current pulse.



**Figure 8: Galvanostatic pulses on Pd electrode; Potential response due to the galvanostatic hydrogen ad- and absorption, hydrogen desorption and OCP measurements.**

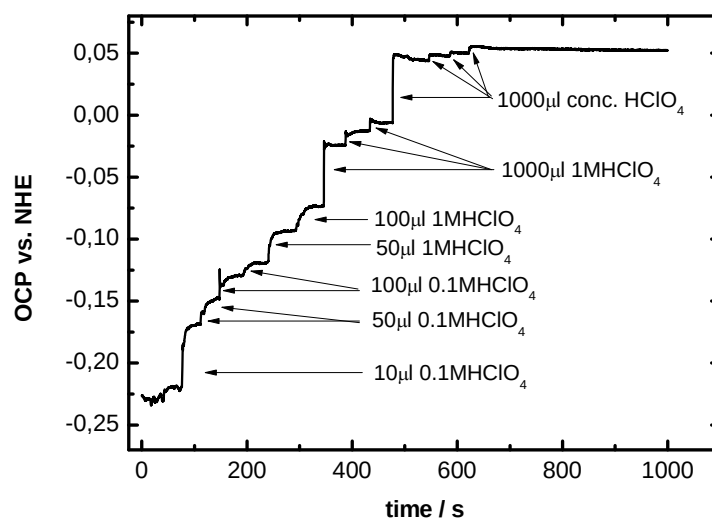
A closer look into the steps forming a stable Pd/H electrode can be seen in Figure 8. The initial potential drop includes double layer charging, hydrogen adsorption and Pd hydride formation. The completion of the hydride phase is at the end of the first potential plateau. The further potential decay and thus the increase in overpotential is attributed to hydrogen evolution and further hydrogen absorption into the palladium. These results are comparable to potential step experiments for form Pd/H and detecting current transients in [53]. The OCP measurement after the hydrogen loading starting at 610s already shows the very high stability of the produced electrode.



**Figure 9: Formation of Pd/H electrode and subsequent OCP measurement. The applied negative current for hydrogen loading was  $-500\mu\text{A}$  for 500s.**

As already shown in Figure 8 also positive galvanostatic pulses were applied to obtain stable OCP values of the Pd/H electrode. Based in the work of Flanagan and Lewis [54, 55] the electrochemically loading of palladium electrodes can lead to a higher concentration of surface hydrogen than hydrogen in the bulk for the hydrogen/palladium ratio larger compared to 0.4. Therefore, a positive pulse after hydrogen loading was applied to the Pd/H electrode in order to remove excess surface hydrogen and relieve concentration gradients [56].

Titration experiments in order to investigate the pH sensitivity of the Pd/H electrodes were performed in standard glass cells. The Pd/H electrode was prepared in 1M  $\text{HClO}_4$  Ar purged electrolyte as described above. Starting at a pH value of approximately 5.8 in 1 M  $\text{NaClO}_4$  (80 ml) electrolyte the proton concentration was increased by adding stepwise  $\text{HClO}_4$  in different concentrations ranging from 0.1M to concentrated  $\text{HClO}_4$ . During the whole experiment the OCP of the Pd/H electrode was recorded. The potential transient of the Pd/H electrode versus time is shown in Figure 9. Due to the strong dependence of the OCP to the proton concentration and the low concentration of protons in a pH 5.8 electrolyte only  $10\mu\text{l}$  of 0.1M  $\text{HClO}_4$  was added in the first step. This already leads to a potential step of about 100mV. Continuous adding of perchloric acid in different amounts and concentrations is shown of Figure 10. The OCP shifts to more positive values. At the end of the experiment the pH of the electrolyte was 0.36 determined with a pH meter. From the amount and concentration of added  $\text{HClO}_4$  the pH value of the electrolyte can be calculated after each step.

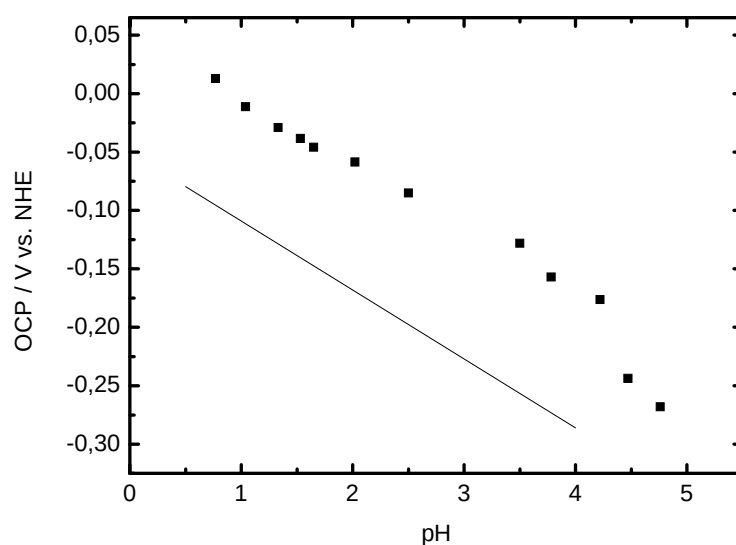


**Figure 10: Titration curve of Pd/H electrode. OCP vs. time**

This experiment was also done adding alkaline NaOH electrolyte in different amounts and different concentrations. A shift of the OCP towards more negative potentials was recorded and is in line with the results found in acidic environment.

In order to apply all the results of the Pd/H electrode the surface of the Pd has to be minimized for use in an EC-STM or SECPM. This was achieved by insulating the etched Pd electrodes with Apiezon wax as described in chapter three. The surface of the Pd tips was determined with different techniques such as double layer charging method,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple method and hydrogen adsorption. All methods are used in a limit range of their field of application. Nevertheless the results of the determined surface areas are for each experiment in the same order or magnitude which implies that the radii of the free tip apex only varies of a factor three assuming a hemispherical shape.

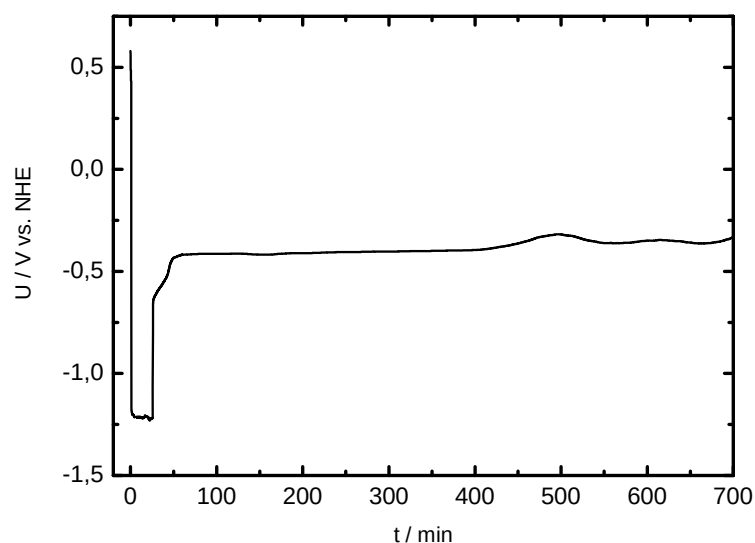
The relation between the OCP of an insulated Pd/H tip and the pH value is shown in Figure 12. The black curve is a guide for an eye with a slope of 59mV/decade as theoretical value [53, 57]. Although the measured data are not on a perfect line the slope of 60mV/decade is very close to the theoretical value. The intersection point with the y-axis is at 60mV vs. NHE which is also very close to the literature value of 50mV vs. NHE [56, 58].



**Figure 12: pH sensitivity of the Pd/H electrode OCP**

The stability of the OCP for the nano pH sensitive electrode was a challenge to investigate. As shown above large Pd/H electrodes show good stability and behave as already described in literature. Figure 13 pointed out that also an insulated with hydrogen loaded Pd STM tip is comparable to a large electrode towards its OCP. The potential starts with a positive value which is undefined. A negative current of  $-10\mu\text{A}$  was applied and leads to potential drop due to forming a Pd hydride phase, hydrogen evolution and hydrogen absorption. A subsequent measurement of the OCP when applied 0A shows after a short relaxation time a stable value for about 4 hours. After this time a slight increase in potential is seen which then requires a new loading with hydrogen showing a stable potential behaviour and thus suitable to investigate pH changes over a long time period.





**Figure 13 OCP vs. time for a hydrogen loaded Pd tip**

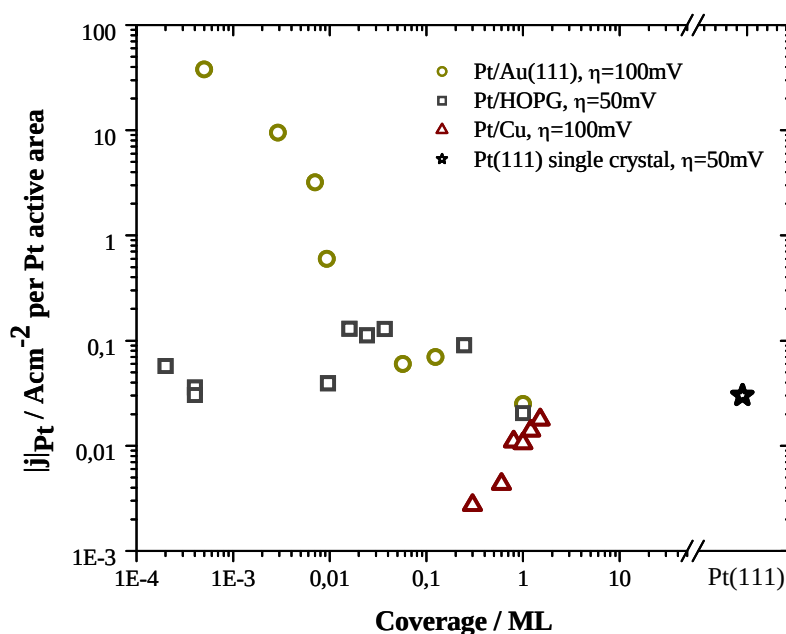
## 4 Summary of Results in the Project

Short statements which summarize the behaviour of the investigated systems:

- The specific activity for HER/HOR increases with decreasing amount of noble metal for Pd/Au(111) and Pt/Au(111) nanostructured electrodes as well as single Pt and Pd particles deposited on Au(111).
- The geometric current density for HER/HOR increases with decreasing amount for Pd/Au(111) surfaces whereas for Pt/Au(111) the geometric current density is decreasing with decreasing amount of noble metal.
- The specific activity for ORR increases with increasing amount of noble metal for Pd/Au(111) and Pt/Au(111) nanostructured electrodes.
- The specific activity for MOR increases with increasing amount of noble metal for Pt/Au(111) nanostructured electrodes. The peak potential of the MOR is shifted to more negative potentials for higher coverages. There was no measurable activity found for Pd/Au(111) electrodes for MOR.
- The results for ORR and MOR are in contrast to the results obtained for the HER/HOR whereas the specific activity for hydrogen reactions increases with

decreasing amount of noble metal on Pd/Au(111) and Pt/Au(111) nanostructured electrodes.

- Pt on HOPG and Pt on diamond behave as Pt bulk for hydrogen oxidation and hydrogen evolution reaction.
- Pt on diamond for ORR shows a slight increase in activity for decreasing amount of noble metal.
- Pt on diamond for CO oxidation shows no effect when varying the amount of noble metal.
- The hydrogen evolution is slowed down for the system Pt/Cu(hkl).
- A Pd/H nanoelectrode was developed for local investigations in the SECPM and shows linear correlation of potential and pH in the nanometer regime.
- Models with theoretical groups were developed and applied to the investigated systems for hydrogen reactions.
- Single crystalline surfaces were found to be new supports for model system studies.
- Nanotransfer Printing and Nanoimprint Lithography was explored to be a promising tool for nanometer structuring.



**Figure 1: Plot of specific current density versus coverage for the three investigated systems showing the effect of substrate on the electrocatalytic activity.**

## 5 Conclusion/Summary

The focus of this project was the investigation of substrate effects in electrocatalysis ranging from large nanostructured surfaces down to single particles deposited on single crystals for various reactions. An increased activity with decreasing amount of Pd and Pt deposited on Au(111) was found for hydrogen related reactions; hydrogen evolution as well as hydrogen oxidation. In contrast to that result, the oxygen reduction and the methanol oxidation show an increasing activity with increasing amount of Pd and Pt. These findings can be discussed in terms of low coordinated atoms, support effects, mass transport effects and a direct involvement of the support. It became clear, that the Au support plays a major role in catalytic behavior by causing a strain in the Pd and Pt overlayers. In clear contrast to that finding, HOPG and diamond behave as supports which do not affect the activity of the noble metal catalyst and Cu as support does even slow down the hydrogen reactions.

Various models obtained from different theoretical groups agree well with the experimental findings in this thesis. Density Functional Theory provided a theoretical insight into binding energies and proposed reaction pathways. Studies on bare single crystals, alloys of different metals and the influence of the support on foreign overlayers theoretically showed a strong impact in the behavior of the catalysts deposited in various supports as compared bare catalyst surfaces. Also a direct involvement of the support material as storage of intermediate reactions products seems possible. Reviewed systems ranging from model surfaces to applied systems from experimental groups also show the same trends towards the investigated hydrogen, oxygen and methanol reactions. Detailed studies on further model systems changing the support material will thus lead to a further insight into substrate effects and modifying catalytic activity specified on individual reactions.

A new kind of single crystalline surfaces were investigated with STM, SECPM, AFM and cyclic voltammetry to evaluate the quality and suitability of these surfaces for electrochemistry. All investigated heteroepitaxially grown Ru, Rh and Ir single crystalline surfaces show high quality. Therefore they are suitable for a wide range of investigations under electrochemical conditions. Especially, the use as support material in electrocatalysis where foreign metals are deposited onto the substrates will clarify the influence of the support in more detail. Basic studies of Pt deposition on Ru(0001) has already underlined the applicability of these supports.

During these studies the SECPM technique based on the potential difference between two electrodes in electrolytes was investigated. A resolution which is comparable to AFM and STM in air and under electrochemical conditions on the investigated surfaces was elaborated although the physical background is quite different.

Also a new local pH sensor in order to measure the changes in proton concentration in the nanometer scale was developed. The successful use of a STM tip as a current sensor to locally measure single particle reactivity was the initial point to explore also a local potential technique. Based on the possibility to measure the OCP of the tip in the SECPM setup a potential sensitive tip was developed. Etched Pd tips with insulation to the very end of the apex and galvanostatically loaded with hydrogen acted as electrodes. These minimized electrodes are sensitive to proton concentration and thus change their OCP according to the pH of the solution surrounding the tip.

Summarized, based on principle studies on different supports the electrocatalytic activity was investigated on Pd and Pt nanostructured Au(111), Cu(hkl), HOPG and diamond surfaces towards hydrogen, oxygen and methanol reactions. A strong influence of the support was found enhancing the hydrogen reactions and restraining the oxygen and methanol reactions. Also single Pt particles on Au(111) were generated and investigated towards their activity for hydrogen evolution showing an increase in activity for lower particles. New single crystal supports were found to be excellent supports for electrochemical investigations. Principle studies regarding resolution and practicability of the SECPM were performed and a local potentiometric sensor for measurements of pH changes with a nanometer tip was developed.

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