

## O 10: Metal/Water Interfaces: Structure and Reactivity

Time: Monday 15:00–18:30

Location: HE 101

O 10.1 Mon 15:00 HE 101

**Adsorption of water and anions on noble metal electrodes: a surface vibrational spectroscopy study** — ●YUJIN TONG, MARTIN WOLF, and R. KRAMER CAMPEN — Fritz-Haber-Institut, Abt. Physikalische Chemie, 14195 Berlin, Germany

Reactions at noble metal electrode / electrolyte solution interfaces play a key role in electrochemistry. Despite their importance, our understanding of the mechanisms underlying this chemistry is still surprisingly limited. For example, the interpretation of the features of cyclic voltammograms for platinum single crystals in contact with various electrolyte solutions is still essentially speculative (*e.g.* see *Catalysis Today*, 202 (2013) 105). In these and similar systems the principle obstacle towards insight is a lack of an *in-situ* experimental probe of the population and structure of adsorbed hydrogen, hydroxyl groups, water and anions. Here we overcome this challenge by employing surface specific vibrational spectroscopy, Sum Frequency Generation (SFG), within a flow thin layer electrochemical cell, to concurrently characterize the potential dependent population and structure of surface hydroxyl, water, anions and reactive intermediates at Au and Pt surfaces during the electrochemical oxidation of formic acid. This approach allows the clear identification of bridge-bonded formate, interfacial hydroxyl and water and the evolution of each of these species as a function of potential.

O 10.2 Mon 15:15 HE 101

**On-line Detection of Different Concentrations of Organic Molecules Using a SERS Microfluidic Device** — ●OANA M. BUJA<sup>1,2</sup>, OVIDIU D. GORDAN<sup>1</sup>, NICOLAE LEOPOLD<sup>2</sup>, ANDREAS MORSCHHAUSER<sup>3</sup>, JÖRG NESTLER<sup>3</sup>, and DIETRICH R.T. ZAHN<sup>1</sup> — <sup>1</sup>Semiconductor Physics, Technische Universität Chemnitz, D-09107 Chemnitz, Germany — <sup>2</sup>Faculty of Physics, Babes-Bolyai University, Kogalniceanu 1, 400084 Cluj-Napoca, Romania — <sup>3</sup>Fraunhofer Institute for Electronic Nano Systems, Technologie Campus 3, 09126 Chemnitz, Germany

In recent years the integration of microfluidic technology with powerful spectroscopic techniques such as surface-enhanced Raman scattering (SERS), has become important for analytical studies of hazardous chemicals. Here, we propose a SERS microfluidic device used for on-line detection and monitoring of different concentrations of two model organic molecules (caffeine and malachite green). The SERS active silver spot was synthesized on the bottom of the capillary when the laser beam ( $\lambda = 514.7$  nm) was focused on a continuous flow of silver nitrate and sodium citrate<sup>1</sup>. Afterwards, different concentrations of selected analytes were injected and sequential SERS spectra were acquired. The adsorption of the molecules was investigated by monitoring the specific bands of caffeine ( $648\text{ cm}^{-1}$ ) and malachite green ( $1617\text{ cm}^{-1}$ ), respectively. By combining SERS and microfluidic technology a fast and reproducible on-line detection of organic molecules was achieved.

References: <sup>1</sup>N. Leopold, B. Lendl, *Anal. Bioanal. Chem.*, 2010, 396, 2341-2348.

O 10.3 Mon 15:30 HE 101

**Hydrogen Bonding Within Water/Hydroxyl Overlayers on Rh(111)** — ●CHRISTINE McMAHON, ALAN MASSEY, ANDREW HODGSON, and GEORGE DARLING — Surface Science Research Centre, Department of Chemistry, University of Liverpool, Liverpool, L69 3BX

At metal surfaces, water ice structures are determined by a competition between optimizing the bonding of molecules to the surface and optimizing the hydrogen bonding within the layer. On some metals the water overlayer is partially dissociated, this can be induced by preadsorbing oxygen, leading to a mixed OH+H<sub>2</sub>O overlayer on metals where dissociation is not spontaneous. We have used Density Functional Theory calculations to examine partially dissociated overlayers produced on Rh(111). Specifically we are looking to address questions that cannot be definitively answered by experiment: what is the optimum ratio of OH to H<sub>2</sub>O, and do the resultant structures favour Bjerrum defects (defects where H atoms point to each other rather than participating in hydrogen bonding or pointing into/away from the surface), as found on Cu surfaces.

O 10.4 Mon 15:45 HE 101

**Free energy assessment of water structures and their dissociation on Ru(0001)** — ●GUILLEM REVILLA-LÓPEZ, PIOTR BŁOŃSKI, and NÚRIA LÓPEZ — Institute of Chemical Research of Catalonia, ICIQ, Av. Països Catalans 16, 43007 Tarragona, Spain

The structure and dissociation degree of the first water and heavy water adlayers on hexagonal close-packed metals is a keystone in disciplines such as catalysis, and surface science. Ru(0001) is considered as a model for such interactions since hexagonal Ice patterning and variable water dissociation are present on it. We have assessed the free energy landscape of the adsorption of different water motifs experimentally reported on Ru(0001). Our work provides computational results rationalizing the driving forces of Ice-like bilayer formation on Ru(0001) by describing thermodynamically feasible pathways. The key role of both electrostatics as a driving force and the recently discovered Chains-4a motif as a key intermediate structure have been revealed in the formation of molecular and dissociative Ice-like bilayers and other complex patterns. Thus, new routes for bilayer formation are proposed based on non-cluster structures like Rosette and Island. Further on, the isotopic and temperature dependent balance of dissociation degrees for the Ice-like bilayer and their troubled experimental determination are rationalized by configurational entropy contributions.

O 10.5 Mon 16:00 HE 101

**Water adsorption structures on the step edge of Pt(533) and Pt(553)** — ●MANUEL KOLB<sup>1</sup>, JASPER WERMINK<sup>1</sup>, JON DEROUIN<sup>2</sup>, RACHEL FARBER<sup>2</sup>, DAN KILLELEA<sup>2</sup>, LUDO JUURLINK<sup>1</sup>, and MARC KOPER<sup>1</sup> — <sup>1</sup>University Leiden, Leiden, The Netherlands — <sup>2</sup>Loyola University Chicago, Chicago, USA

The water-metal interface is being studied intensively today, due to its importance for electrochemistry and fuel cell applications. Many fundamental studies in the past have targeted the Pt(111)-Water system, however this model has clear deficits, namely the absence of step edges, corners and kinks, when comparing it to nano-particles which are important for industrial applications.

In this study we present DFT (density functional theory) calculations of water adsorption structures on the Pt(533) and Pt(553) surfaces at coverages significantly beyond the ones studied previously for these systems.

We compare the adsorption geometries and energies on the Pt(533) and Pt(553) surface to elucidate the influence of the type of step edge on the preferred adsorption geometries. We furthermore report the clear tendency of water to adsorb in an H-down configuration similar to the situation on Pt(111), however with significantly increased driving force towards this configuration. To verify the approach taken, we plan to compare our results to STM measurements performed on stepped single-crystal surfaces of the same orientation.

O 10.6 Mon 16:15 HE 101

**Neural Network-Based Molecular Dynamics Simulations of the Water-Copper Interface** — ●SURESH KONDATI NATARAJAN, TOBIAS MORAWIETZ, and JOERG BEHER — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany

The interaction of water with metal surfaces is an important research topic in electrochemistry and surface science. However, realistic structural models of solid-liquid interfaces including surface defects like adatoms and steps are notoriously difficult to describe by efficient atomistic potentials. High-dimensional neural network (NN) potentials [1-2] have been demonstrated to provide an efficient and accurate way to construct interatomic potentials with close to first-principles quality. Here, we present an application of NN potentials to study the water-copper interface. preliminary results are discussed and compared to density functional theory data.

O 10.7 Mon 16:30 HE 101

**Comparing density functionals in modeling electrode-electrolyte interfaces** — ●SUNG SAKONG and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

Atomistic modeling of electrode-electrolyte interfaces requires an accurate description of electrode-water interactions in which dispersion interactions play a crucial role. Because of the lack of van der Waals interactions in conventional density functionals, pair-wise semi-empirical

corrections or non-local functionals with an approximated dispersion interactions are necessary to improve the descriptions of the interfaces. Tonigold and Groß [1,2] demonstrated that the RPBE+D3 [3] method reproduces adsorption properties of water layers and structural properties of liquid water correctly. We extend these studies to address electrode-electrolyte interfaces using both explicit and implicit water models. The implicit water model in which water is described by a polarizable dielectric continuum is assumed to act as a thermodynamic reservoir. This allows to quantify the contribution of the electrode potential and solvation effects on the water-electrode interaction. Formation enthalpies of simple adsorbates such as H, O or OH on Pt in the presence of an electrolyte are derived using a combination of explicit and implicit water models. Here, several density functionals with/without dispersion corrections will be compared.

- [1] K. Tonigold and A. Groß, *J. Comput. Chem.* **33**, 695 (2012)  
 [2] K. Forster-Tonigold and A. Groß, *JCP* **141**, 064501 (2014)  
 [3] S. Grimme *et al.*, *J. Chem. Phys.* **132**, 154104 (2010)

O 10.8 Mon 16:45 HE 101

#### Equilibrium coverage of halides on metals electrodes —

•FLORIAN GOSSENBERGER, TANGLAW ROMAN, and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Under acidic conditions, the specific adsorption of anions is an integral part of the formation of the electric double layer at electrochemical metal/electrolyte interfaces. We studied the adsorption of the halides  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  on Pt(111) and Cu(111) using density functional theory calculations [1]. Based on a thermodynamic approach, the stable equilibrium coverage is linked to the electrode potential without taking the electrochemical environment explicitly into account. Although there are still some quantitative discrepancies with experiment, the qualitative trends derived from the calculations are consistent with experimental observations, in particular as far as the stability of high-coverage halide structures is concerned.

However, under more realistic conditions and low electrode potentials, platinum is always covered with hydrogen, which is always available in an aqueous electrochemical environment. Therefore, mixed coverages of the halides with co-adsorbed hydrogen are considered in the next step to simulate the double layer and the solid-liquid interface at the electrode surface.

- [1] Florian Gossenberger, Tanglaw Roman, and Axel Groß, *Surf. Sci.* **631** (2015), doi: 10.1016/j.susc.2014.01.021 .

O 10.9 Mon 17:00 HE 101

#### $\text{H}_2\text{O}$ adsorption on bimetallic Pt-Ru(0001) surfaces - a low-temperature UHV-STM investigation —

•MARTIN SCHILLING, ALBERT K. ENGSTFELD, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

Profound knowledge of the elementary electrochemical/-catalytic processes on catalytically relevant electrode materials requires a detailed understanding of the solid | liquid interface, including the water | metal interaction. The latter has been investigated in detail in earlier studies, using model systems consisting of ice layers adsorbed on monometallic single crystal surfaces.<sup>[1,2]</sup> Where in former studies only  $\text{H}_2\text{O}$  adsorption on monometallic surfaces were subject of investigation, we present results on the interaction of  $\text{H}_2\text{O}$  with 2D bimetallic PtRu model electrodes.  $\text{H}_2\text{O}$  was deposited under well defined conditions in ultra high vacuum (UHV) at low sample temperatures (100 K - 130 K) on Pt modified Ru(0001) single crystal surfaces. The structures have been investigated with scanning tunnelling microscopy (STM) in a temperature range of 100 K to RT. Depending on the Pt layer thickness on Ru(0001) and the dosing conditions of  $\text{H}_2\text{O}$ , a variety of molecular arrangements are observed, which vary from total disorder to well-ordered domains. The influence of substrate | molecule and molecule | molecule interactions are discussed based on the Pt modified Ru(0001) substrate.

- [1] P.A. Thiel and T.E. Madey, *Surf. Sci. Rep.* **7** (1987) 211-385.  
 [2] M.A. Henderson, *Surf. Sci. Rep.* **46** (2002) 1-308.

O 10.10 Mon 17:15 HE 101

#### Two-dimensional bimetallic molecular networks as electrocatalyst for oxygen reduction and evolution —

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Inspired by catalytically active bimetallic centers commonly found in biology we prepared bimetallic coordination networks and studied their electrocatalytic properties. Two different functional groups for metal coordination of 5,10,15,20-tetra(4-pyridyl)porphyrin (TPyP) were used to selectively incorporate different metals in the structures. The samples were prepared under ultra-high vacuum (UHV) conditions by evaporating TPyP containing the first metal (Cu, Fe, or Co) in the pyrrolic macrocycle. The second metal (Fe or Co) was sublimed in an additional step and is coordinated by the pyridyl groups. The metal-organic networks were characterized by scanning tunneling microscopy in UHV prior to studying their electrocatalytic activity towards oxygen reduction and evolution in alkaline media. Linear voltammetry experiments show that the electrocatalytic response in the oxygen reduction can be altered by choosing different combinations of metals. The incorporation of the second metal led to a higher oxygen evolution, while the stability of the electrochemical signal was influenced by the central metal within TPyP.

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#### Solvent Effects in Co-Catalyzed Oxygen Evolution: Efficient First-Principles Treatment —

•MARKUS SINSTEIN<sup>1</sup>, HARALD OBERHOFER<sup>1</sup>, VOLKER BLUM<sup>2</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Technische Universität München, Germany — <sup>2</sup>Duke University, USA

Photoelectrochemically driven redox reactions like water splitting or  $\text{CO}_2$  reduction are prominent examples for energy-conversion from abundant sunlight into solar-fuel type chemical compounds. A detailed analysis of the involved elementary processes via first-principles calculations requires to simultaneously account for the extended semiconductor photocatalyst and the liquid electrolyte. Beyond traditionally assumed proton-coupled electron transfer (PCET) mechanisms the latter is particularly important in order to address charged reaction intermediates that are likely stabilized by the polar liquid environment. Aiming for a computationally efficient approach that allows for catalyst screening, we implement an implicit solvation scheme based on the Multipole Expansion (MPE) method into the all-electron DFT package FHI-aims. We define the cavity within the dielectric continuum from an iso-density surface which is sampled in a constraint dynamics scheme. As a first step towards modelling the full water splitting reaction, we apply this scheme to the oxygen evolution reaction on gold co-catalysts. These calculations indicate non-negligible solvent effects already for neutral intermediates in PCET mechanisms.

O 10.12 Mon 17:45 HE 101

#### Electrocatalytic activity and stability of structurally well defined $\text{AgPt/Pt(111)}$ surface alloys-correlation between structure and reactivity —

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Bimetallic surface often show electrochemical and catalytic properties different from those of the individual metals. This is evident, e.g., in the oxygen reduction reaction (ORR), where Pt is known to be the most active single metal catalyst. However, in previous studies it was shown that this high activity can be enhanced by modifying Pt with transition or noble metals, such as Ni, Co or Cu.[1] We show results on the electrochemical and electrocatalytic properties of well defined  $\text{Ag}_x\text{Pt}_{1-x}$  surface alloys on Pt(111) with increasing Ag content (0%-100% Ag). The surface alloys were prepared under ultra high vacuum (UHV) conditions by physical vapor deposition of Ag on Pt(111), followed by an annealing step to 900 K. Via scanning tunneling microscopy (STM) the atomic distribution in the topmost layer, as well as the abundance of catalytic relevant ensembles (e.g.  $\text{Pt}_1\text{Ag}_2$ ,  $\text{Pt}_2\text{Ag}_1$ ) is determined. Subsequently the surfaces are characterized in an electrochemical flow cell attached to the main UHV system with respect to their stability and their ORR activity in  $\text{H}_2\text{SO}_4$ . To validate the stability of the surface alloys, they are re-analyzed by STM after the electrochemical measurements. Finally, the experimental results are compared to simulated activities based on DFT calculations.

- [1] J. Greeley and J.K. Nørskov, *J. Phys. Chem.* **113** (2009) 4932.

O 10.13 Mon 18:00 HE 101

#### First-principles reaction barriers for the splitting of water on Au nanocatalysts —

•THOMAS STECHER, HARALD OBERHOFER, and KARSTEN REUTER — Technische Universität München

First-principles modeling of electrocatalytic surface reactions is still

largely defined by the computational hydrogen approach. This approach evaluates free energy differences between consecutive reaction steps and therewith accounts only for possibly existing thermodynamic barriers. In order to access additional kinetic barriers in the photocatalytic oxidation of water we present an approach based on *ab initio* molecular dynamics (AIMD) simulations and umbrella sampling. For the proton transfer steps we hereby specifically use path-integral AIMD to also capture nuclear quantum effects. As a first showcase system we consider water splitting at a Au<sub>3</sub> co-catalyst, which was previously studied within the computational hydrogen electrode approach [1]. This allows to disentangle thermodynamic and kinetic contributions to the individual reaction barriers, as well as to assess the relevance of quantum effects by comparing classically and quantum-mechanically calculated barriers. [1] H. Oberhofer and K. Reuter, *J. Chem. Phys.* **139**, 044710 (2013).

O 10.14 Mon 18:15 HE 101

**Size dependent electrocatalytic activity of Pt nanoparticles on Ru(0001) supported graphene - hydrogen evolution reaction** — •JENS KLEIN, ALBERT K. ENGSTFELD, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chem-

istry and Catalysis, D-89069 Ulm, Germany

In water electrolyzers and fuel cell technology, carbon supported Platinum nanoparticles are the state-of-the-art catalyst for the hydrogen evolution reaction. The performance of this catalyst depends sensitively on the size, density, shape and stability of the Pt nanoparticles.<sup>[1]</sup> To get a more detailed understanding on the structure | activity relationship of this particular system, we present results of a model catalyst study on Pt nanoparticles on Ru(0001) supported graphene, investigated in a combined ultra high vacuum (UHV) - electrochemical flow cell setup. The graphene layer was prepared under UHV by ethylene decomposition on Ru(0001) at 1050 K. Lateral Pt nanoparticle arrays with well defined size distributions were grown by physical vapor deposition and characterized by scanning tunneling microscopy (STM). The sizes of the Pt nanoparticles are below 3 nm and they consist of 10-80 atoms in average. After structural analysis, the model electrodes were transferred to an electrochemical flow cell, attached to the UHV system, to investigate their electrocatalytic activity during the hydrogen evolution reaction (HER) by cyclic voltammetry. Finally, to assure that the particles are stable in the electrocatalytic environment, the model electrodes were again characterized by STM in UHV afterwards. [1] M.T.M. Koper, *Nanoscale* **3** (2011) 2054.