

CPP 15: Solid-liquid interfaces: Reactions and electrochemistry I (joint session O/CPP)

Time: Monday 15:00–16:30

Location: MA 144

CPP 15.1 Mon 15:00 MA 144

Towards size-selected supported Pd clusters in aqueous environment — ●NICOLAS BOCK, ASTRID DE CLERCQ, CLARA RETTENMAIER, UELI HEIZ, and FRIEDRICH ESCH — Chemistry Department & Catalysis Research Center, Technische Universität München, Garching, 85747, Germany

Supported Palladium nanoparticles have been widely investigated as efficient electro- and photo-electro-catalysts. However, for the smaller sub-nanometer Pd clusters, little is known about their size-dependent catalytic properties and stability in aqueous environments. Since this non-scalable size regime bears the potential of high catalytic activity, we aim at finding new ways to prepare and study size-selected Pd clusters via controlled electrochemical decomposition.

To this purpose we have investigated the controlled decomposition of Pd-polyoxo-metalates [1] under specific electrochemical potential and pH conditions, taking advantage of their precise stoichiometry and redox properties. The investigation bases on Electrochemical Scanning Microscopy (ECSTM) and Rotating Disk Electrode (RDE) measurements. Reactivity measurements on single clusters using the STM tip as a microelectrode for hydrogen evolution monitoring are work in progress.

[1] P. Yang, Y. Xiang, Z. Lin, B. S. Bassil, J. Cao, L. Fan, Y. Fan, M.-X. Li, P. Jiménez-Lozano, J. J. Carbó, et al., *Angewandte Chemie International Edition* 2014, 53, 11974-11978.

CPP 15.2 Mon 15:15 MA 144

Probing ultrafast processes at electrode-aqueous solution interfaces with laser induced photovoltage measurements — ●YUJIN TONG, FRANÇOIS LAPOINTE, MARTIN WOLF, and R. KRAMER CAMPEN — Fritz-Haber-Institut, Abt. Physikalische Chemie, 14195 Berlin, Germany

A conventional potentiostat that typically employed for a three electrode electrochemical system has a time resolution of, at best, 1 μ s (bandwidth above 1MHz) [Bard, A.J., *Electrochemical methods: fundamentals and applications*, New York: Wiley, (1980), Chapter 15]. However, many charge transfer processes happen on pico- to femtosecond time scales. To measure such fast kinetics, all-optical pump probe techniques using ultrafast lasers are usually adopted. In this contribution, we demonstrate that, using a sequence of two ultrashort laser pulses of different photon energies and detection of the laser induced photovoltage by a slow potentiostat as a function of the delay between the two incident pulses, ultrafast charge transfer kinetics on femtosecond timescales can be resolved. For example, we used a UV laser to trigger electron transfer from a gold electrode to Na₂SO₄ aqueous solution and then a second laser in middle or near infrared region was employed to interact with the species that generated by the freshly generated electron. The life time as well as the spectrum of the transient species is consistent with the solvated electron at the interface.

CPP 15.3 Mon 15:30 MA 144

The Reactivity of Individual ‘Defect’-Sites on Electrochemically Roughened Pt(111) — ●LEON JACOBSE¹, MARCEL J. ROST², and MARC T.M. KOPER¹ — ¹Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands — ²Huygens-Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands

Platinum is arguably the most stable, highly active electrocatalyst under oxidizing conditions in acidic media. Nonetheless, the poorly understood electrode degradation process strongly limits the economic feasibility of large scale applications.

Previously, we have shown by combination of simultaneous cyclic voltammetry and in-situ EC-STM that the total electrochemical signal of Pt(111) is directly correlated to its surface roughness [1]. This analysis, however, did not yet provide a rationale for this correlation. A detailed analysis of the EC-STM images provides information on the atomic-scale structure of the formed Pt nano-islands and their evolution. Correlating the resulting density of specific surface sites to the different hydrogen adsorption features in the voltammetry, allows us to determine the electrochemical reactivity of formed step and kink sites on the roughened surface. This finally delivers an insight on how to describe the electrochemical reactivity not only of the observed nano-islands but also of Pt nanoparticles in general.

[1] L. Jacobse, Y.-F. Huang, M.T.M. Koper, M.J. Rost, *Nature Mate-*

rials, accepted (2017)

CPP 15.4 Mon 15:45 MA 144

Correlation of Surface Site Formation to Nano-Island Growth in the Electrochemical Roughening of Pt(111) — LEON JACOBSE¹, YI-FAN HUANG¹, MARC KOPER¹, and ●MARCEL ROST² — ¹Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands — ²Huygens-Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands

Platinum plays a central role in a wide variety of electrochemical devices. Electrode degradation, especially under oxidizing conditions, forms an important barrier for the widespread of applications. Although it is known that repeated oxidation and reduction of platinum electrodes results in irreversible surface structure changes, over thirty years of research did not yet yield to a conclusive description of this process on the atomic level; even not for well-defined single crystal surfaces.

Using a special EC-STM, which is capable of measuring the electrochemical signals simultaneously during imaging in operando, we directly correlate, for the first time, the evolution of the hydrogen adsorption peaks on Pt(111) to the observed roughening of the surface. In the later stages, we find a strong correlation between the evolution of the roughness and the absorption peaks clearly indicating that each created step contributes equally strong to the adsorption signal as well as to the roughness. However, and fully surprising, in the early stage step edges are created that seem to be chemically "dead".

CPP 15.5 Mon 16:00 MA 144

Driving hydrodgen evolution and oxidation on Pt with femtosecond laser pulses — ●GREGOR ZWASCHKA, YUJIN TONG, MARTIN WOLF, and R. KRAMER CAMPEN — Fritz Haber Institute of the Max Planck Society, Berlin, Germany

The Hydrogen Evolution and Oxidation Reactions (HER/HOR) on Pt have been studied for decades due to their fundamental interest and importance in applications such as electrolyzers and fuel cells. Despite much effort there is no clear view of the mechanism of these reactions that can explain the large dependence of their rates on surface structure, pH and electrolyte. Because the HER/HOR on Pt are fast, one possible explanation for the challenge in obtaining such mechanistic insight is that intermediates exist on the Pt electrode surface at very low concentrations under steady state reactive conditions. In principle such a limit can be overcome by rapidly and transiently increasing the amount of reactants present and characterizing their effect. Here we present our efforts to trigger the HER/HOR on Pt using femtosecond laser pulses. The resulting, laser-induced voltammogram clearly shows that the femtosecond pulse train induces HER/HOR and that the magnitude of this effect depends on crystal face in a manner rationalizable by the surface electronic structure. Control experiments varying pulse lengths, energies and the frequencies of the incident field suggest that we induce the HER/HOR by creating a population of hot electrons. These results offer a novel experimental window on the HER/HOR and are a first step in experimentally characterizing the mechanisms of these important reactions.

CPP 15.6 Mon 16:15 MA 144

On-surface synthesis of covalent architectures for energy conversion chemistry — ●PATRICK ALEXA¹, DORIS GRUMELLI², DIANA HÖTGER¹, VJAY VIAS³, BETTINA LOTSCH^{1,4}, RICO GUTZLER¹, and KLAUS KERN^{1,5} — ¹Max Planck Institute for Solid State Research, 70569 Stuttgart, Germany — ²Universidad Nacional de La Plata, 1900 La Plata, Argentina — ³Marquette University, Milwaukee, WI 53233, USA — ⁴University of Munich (LMU), 81377 Munich, Germany — ⁵Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

Creating nanostructures in a bottom-up approach by using molecular precursors allows for the fabrication of tailored nanomaterials for specific applications such as energy conversion. In particular (metal)organic networks synthesized in UHV on crystalline surfaces can be used as efficient electrocatalysts. Inspired by the photocatalytic hydrogen evolution properties of triazine-containing bulk covalent organic frameworks, we investigate structurally similar 2D networks for their propensity for the hydrogen evolution reaction. In

this work we synthesize two-dimensional covalent polymers from 2,4,6-tri-(4-bromophenyl)-1,3,5-triazine on Au(111) and visualize their topography by scanning tunneling microscopy. The polymer-decorated surface shows a promising improvement for the hydrogen evolution re-

action compared to bare Au(111) in electrocatalytic experiments. The influence of electrolyte exposure and electrocatalytic conditions on the polymer structure is discussed. These results highlight the capability of single-layer functional 2D polymers for electrocatalysis.