

O 20: Solid / liquid interfaces II

Time: Monday 17:15–19:15

Location: WIL B321

O 20.1 Mon 17:15 WIL B321

dynamic electromechanical response during cyclic voltammetry: measurement strategies — ●QIBO DENG^{1,2}, MAXIM SMETANIN^{1,2}, and JÖRG WEISSMÜLLER^{1,3} — ¹Institute of Materials Physics, Hamburg University of Technology, Hamburg, Germany — ²Institute of Nanotechnology, Karlsruhe Institute of Technology, Karlsruhe, Germany — ³Institute of Materials Mechanics, Helmholtz Zentrum Geesthacht, Geesthacht, Germany

We explore experimental strategies for measuring the impact of elastic strain on the electrode potential, E , of Au in weakly adsorbing aqueous electrolytes. More precisely, our experiment aims at measuring the potential-strain response $dE/d\epsilon|_q$ at different states of the electrode. The symbols q and ϵ denote superficial charge density and tangential (elastic) strain, respectively. Emphasis is on measuring the variation of response with E during cyclic voltammetry in extended potential intervals, including dominantly capacitive regions of the voltammogram as well as electroadsorption processes. By means of validation, we explore three independent strategies for separating the cyclic variation of potential of current from the voltammogram proper. The results are in close quantitative agreement. We describe the setup and report results for 111-textured gold electrodes in aqueous H₂SO₄ and HClO₄. We find that the response is generally negative-valued. Furthermore, the magnitude of response peaks at a potential which is close to the pzc and which is displaced relative to the potential of largest AC-capacitance.

O 20.2 Mon 17:30 WIL B321

Influence of the substrate on the chemical state of adsorbed organic molecules: A XPS-study — ●STEPHAN BREUER¹, THANH-HAI PHAN¹, MAYER THOMAS², BROEKMANN PETER³, and WANDELT KLAUS^{1,4,5} — ¹University of Bonn, Institute of Physical and Theoretical Chemistry, Wegelerstr. 12, D-53115 Bonn — ²Technical University of Darmstadt, Department of Material Science — ³University of Berne, Department of Chemistry and Biochemistry — ⁴University of Wrocław, Institute of Experimental Physics, Poland — ⁵University of Rome "Tor Vergata", Department of Physics, Italy

The template effect of an ordered surface and the self assembly of organic molecules due to their intermolecular interactions allow the formation of nano-structures in a bottom-up approach. We work in an aqueous solution which allows the deposition of thermolabile molecules. An electrochemical environment allows applying an electrical potential in order to change the redox state of organic adsorbates which in turn influences their intermolecular interactions. We have studied the adsorption of redox active organic molecules (e.g. viologens and porphyrins) on copper surfaces which are precovered with specifically adsorbed anions. The organic molecules are adsorbed as cationic moieties which bind electrostatically to the anion layer. Changes in the redox state influence their self-assembly behaviour. In this study we will show our characterization of the chemical and redox state of viologens on Cu(111) precovered with sulphide compared to former results on chloride precovered Cu(100) [1].

[1] St. Breuer et al., N. J. Phys, 10, 2008, 125033 (24pp).

O 20.3 Mon 17:45 WIL B321

Dynamic Electromechanical Response during Cyclic Voltammetry: Interfacial Processes — ●MAXIM SMETANIN¹, QIBO DENG¹, and JÖRG WEISSMÜLLER^{1,2} — ¹Institute of Materials Physics, Hamburg University of Technology, Hamburg, Germany — ²Institute of Materials Mechanics, Helmholtz Zentrum Geesthacht, Geesthacht, Germany

An interest in the impact of elastic strain on the electrochemical behavior of metal electrodes was rapidly increasing over the past decade. Research scope in that context includes the impact of strain on the electrode potential at constant charge density as well as the repercussions of mechanical deformation for electroadsorption phenomena and electrocatalytic reaction rates. Here, we show experimental data for the potential-dependence in typical potential regimes of cyclic voltammetry. The response of potential to the strain was measured using a lock-in technique. Aqueous H₂SO₄ and HClO₄ electrolytes were used. We found that the electrode potential, E , linearly depends from the strain, at least within the potential range from -0.8 V up to 1.6 V vs Ag/AgCl - the range accessible in aqueous electrolytes. However, the amplitude of the potential-strain response depends significantly on

E within the double layer - possibly due to the two factors specific ionic adsorption or double layer capacitance. According to our model the response parameter provides access for quantifying the amount of the charge transferred - the measure typically not accessible by over techniques.

O 20.4 Mon 18:00 WIL B321

Light-induced electron transfer and charge transport in mesoporous ZnO/D149 hybrid films — ●MELANIE RUDOLPH¹, HIDETOSHI MIURA², and DERCK SCHLETTWEIN¹ — ¹Institute of Applied Physics, Justus-Liebig-University Giessen, Germany. email:schlettwein@uni-giessen.de — ²Chemiecrea Co., Ltd., 2-1-6 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Dye-sensitized solar cells (DSC) consist of a nanostructured semiconductor/dye hybrid layer as light absorbing and electron conducting phase, permeated by a liquid phase ensuring transfer of positive charges to a counter electrode. In this study, nanostructured ZnO was electrodeposited on fluorine-doped tin oxide (FTO) and loaded with the fully organic dye D149. The ZnO/D149 electrodes were analyzed in contact with a liquid iodide/triiodide electrolyte. Steady-state photocurrent and photovoltage measurements were performed to derive basic photovoltaic parameters like short-circuit photocurrent, open-circuit photovoltage and external quantum efficiency (IPCE). Open-circuit photovoltage decay measurements (OCVD) as well as intensity-modulated photovoltage spectroscopy (IMVS) were utilized to obtain information about the extent and mechanisms of recombination, i.e. unwanted back transfer of electrons from ZnO to D149 or to the liquid contact phase. Intensity-modulated photocurrent spectroscopy (IMPS) served to gain an insight into electron transport within the porous zinc oxide films. The interplay between light-induced charge transfer from D149 to ZnO, electron transport within the porous ZnO matrix and recombination of photoinjected electrons is discussed.

O 20.5 Mon 18:15 WIL B321

In situ Diffraction Studies of Homoepitaxial Growth of Cu(001) from Aqueous Electrolyte — ●FREDERIK GOLKS^{1,2}, YVONNE GRÜNDER², JOCHIM STETTNER², KLAUS KRUG², JÖRG ZEGENHAGEN¹, and OLAF M. MAGNUSSEN² — ¹European Synchrotron Radiation Facility, Grenoble, France — ²Universität Kiel, Institut für Experimentelle und Angewandte Physik, Kiel, Germany

Motivated by the pivotal role of copper electroplating in the production of interconnects for ULSI microelectronics, we have studied the homoepitaxial growth of Cu(001) in aqueous electrolytes containing 1 mM chloride and 1 or 5 mM Cu²⁺ by in-situ surface x-ray diffraction with high time resolution. Although diffusion-limited layer-by-layer growth is observed over a wide potential regime, a pronounced mutual interdependence of the interface structure and the growth behavior is found. Thus, the tendency towards surface roughening is increased in the presence of a complete c(2x2) Cl⁻ adlayer [1] while the ordering of the Cl⁻ adlayer is slowed down during Cu deposition. Furthermore, the presence of polyethylene glycol (PEG), a commonly used inhibitor in industry, results in significantly lower microscopic growth rates and an increased tendency towards 3D growth.

[1] Y. Gründer, D. Kaminski, F. Golks, K. Krug, J. Stettner, O. M. Magnussen, A. Franke, J. Stremme, E. Pehlke, Phys. Rev. B **81**, 17 (2010)

O 20.6 Mon 18:30 WIL B321

Electrochemical studies of excited charge carriers with thin platinum film electronic devices in sulfuric and hydrochloric solution — ●DAMIAN BÜRSTEL, MICHAEL SCHEELE, ANDREAS BARMSCHIED, KEVIN STELLA, and DETLEF DIESING — Fakultät für Chemie, Universität Duisburg-Essen, D-45117 Essen, Germany

Excited charge carriers induced by chemical processes like the adsorption or desorption of atomic hydrogen at metal surfaces have already been investigated under UHV conditions. These carriers can be detected by systems with an internal electric barrier, like MIM-(metal-insulator-metal), MIS-(metal-insulator-semiconductor) or MS-(metal-semiconductor) sensors. The internal barrier inside the sensors separates ground state carriers from excited carriers. It is an open question, whether electrochemical reactions on metal sur-

faces also evoke hot charge carriers. We study the electrochemical deposition of hydrogen (via H_{upd}) on platinum and the oxidation of platinum in sulfuric and hydrochloric solution. As sensors Pt-TaOx-Ta, Pt-SiOx-Si and Pt-Si-sensors were used with 10-30 nm thick Pt films. By electrochemical cyclic voltammetry and simultaneous recording of the current at the tantalum or silicon back electrode it is possible to detect voids (down to a fraction of 10^{-3}) in the thin platinum film. 30 nm thick platinum films were found to cover the underlying layer completely. In this case the devices can be used to monitor deviations from the electronic equilibrium since excited carriers cause a device current through the internal barrier. Deviations from the electronic ground state were found in the case of the H_{upd} formation.

O 20.7 Mon 18:45 WIL B321

Dealloying studies of Cu₃Pd single crystal surfaces — ●SHILAN MEIMANDI and FRANK UWE RENNER — Max Planck Institute for Iron Research, Max Planck Strasse 1, 40237 Düsseldorf

Binary noble metal alloys serve as model cases for dealloying in the context of corrosion studies [1]. Dealloying is a common corrosion process during which the more active element of an alloy is selectively dissolved into the electrolyte. Several aspects of formation of porous surface during dealloying has not completely been understood. The nano-porous metals formed by dealloying methods have application potential in a variety of fields such as catalysts, actuators, and biomedical sensors. The Cu-Pd system is interesting as a model system for corrosion as well as a potential catalyst material. The initial dealloying and selective dissolution of single-crystals Cu₃Pd (111) and Cu₃Pd (100) in 0.1 M H₂SO₄ have been studied. With in-situ X-ray diffraction, we observed the epitaxial Pd layer peak by increasing the potential close to the critical potential. Also with Ex-Situ atomic force microscopy (AFM), the formation of nanoscale islands of Pd (5-25 nm) as nobler metal have been revealed. Our aim is to study the initial steps of dealloy-

ing of well-defined Cu-Pd surfaces on the atomic scale and to compare the results to the Cu-Au system [2]. [1] R.Newman, K.Sieradzki, Science 263 (1994), 1708. [2] Renner et al., Physical Review B 77 (2008), 235433

O 20.8 Mon 19:00 WIL B321

Stability and electrocatalytic activity of Pt nanoclusters supported on graphene monolayers on Ru(0001) — ●OTAVIO B. ALVES¹, CHRISTOPH LORENZ¹, HARRY E. HOSTER^{1,2}, and R. JÜRGEN BEHM¹ — ¹Ulm University, Institute of Surface Chemistry and Catalysis, 89069 Ulm, Germany — ²Present Address: Technische Universität München, Centre for Electromobility, 50 Nanyang Drive, Singapore 637553

We have investigated the electrochemical properties and the electrocatalytic activity of model electrodes consisting of nanosized Pt clusters (10 - 50 atoms) on a graphene monolayer film deposited on a Ru(0001) substrate. The graphene films are attractive supports since they provide a structurally well-defined nanostructured template for the formation of ordered arrays of metal nanoparticles or clusters [1]. Inasmuch as the graphene covered surface is electrochemically inert, these model systems allow us to determine the electrochemical characteristics and the electrocatalytic activity of the Pt clusters. Activity and stability of these systems are measured in a wall-jet type flow cell located in an electrochemical pre-chamber attached to the main UHV system. Cluster arrays with different total Pt coverages and cluster size distributions, as determined by scanning tunnelling microscopy (STM), were investigated, concentrating on the O₂ reduction reaction as model reaction. The general electrochemical behaviour of the Pt cluster arrays will be discussed and compared to that of bulk Pt.

[1] A. T. N'Diaye *et al.*; Phys. Rev. Lett. 1997, 97, 215501.