

## O 76: Focussed Session: Solid-liquid Interfaces II

Time: Thursday 16:00–19:00

Location: H31

**Topical Talk**

O 76.1 Thu 16:00 H31

**The origin of the high oxygen reduction activity on PtX (X = Sc, Y, La, Sm, Gd and ..) alloys and their activation mechanism.** — ●IB CHORKENDORFF — Technical University of Denmark, Kgs. Lyngby, Denmark

There is a strong demand for improving the anode material of the Proton Exchange Membrane Fuel Cell, either by increasing the activity and thereby being able to reduce the loading or by replacing Pt entirely. Recently we have found a new class of alloys, which are very active towards the Oxygen Reduction Reaction (ORR). The first catalyst were predicted in a DFT screening study which pointed for activity and stability towards Pt<sub>3</sub>Sc and Pt<sub>3</sub>Y and the latter proved particularly active by a factor 7-8 times as active as polycrystalline Pt. We have since expanded the number of catalyst to also include Zr, Hf, and La, but the most active and stable catalyst seems to be Pt<sub>5</sub>Ga. By comparison to our recent studies of PtCu catalyst it is possible to identify the surface composition more accurately. The Pt and Y, La, and Gd catalysts are among the most active and stable forming a rather thick skin consisting of several monolayers of Pt. This skin is found to be under compression (although the bulk alloy is expanded compared to pure Pt) leading to the necessary lower binding energy of oxygen explaining the enhanced ORR activity. The skin formation has been investigated by a broad range of surface science methods and the progress concerning the combination of ORR activity and structural investigation of polycrystalline, single crystal, and mass selected nanoparticles will be discussed.

O 76.2 Thu 16:30 H31

**Broadband SFG Spectroscopy of Specific Anion Adsorption at Pt(111)-Electrolyte Interfaces** — ●BJÖRN BRAUNSCHWEIG — University of Erlangen-Nuremberg, Institute of Particle Technology (LFG)

Vibrational broadband sum-frequency generation (SFG) synchronized with cyclic voltammetry (CV) was applied to study the electrochemical adsorption of (bi)sulfate and formate anions on ordered Pt(111) electrodes. SFG spectra of Pt(111) immersed in 0.1 M H<sub>2</sub>SO<sub>4</sub> reveal an intense vibrational band at 1270 cm<sup>-1</sup> for potentials >0.21 V vs. Ag/AgCl. A close comparison of SFG spectra with in-situ STM images and the CV reveals that this potential corresponds to a surface transformation from a disordered (bi)sulfate adlayer to an ordered layer with large domains of closed-packed ( $\sqrt{3} \times \sqrt{7}$ )R19.1° superstructures [1,2]. Changing the electrode potential results in significant Stark tuning of the (bi)sulfate band and to a second abrupt change in SFG amplitude, bandwidth and Stark tuning rate at 0.5 V that is indicative for a second surface transformation.

In addition to experiments in blank H<sub>2</sub>SO<sub>4</sub> dilutions, the adsorption of formate during the electrochemical oxidation of 0.5 M formic acid on Pt(111) has been studied with SFG. For potentials <0.3 V, CO is the dominant surface-adsorbed species, while potentials >0.3 V lead to co-adsorption of formate. Oxidative removal of CO at potentials >0.5 V leads to predominant adsorption of formate.

[1] Braunschweig, Dlott, Wieckowski et al.; JACS, **132**, 14036 (2010)[2] Braunschweig and Daum; Langmuir **25**, 11112 (2009)

O 76.3 Thu 16:45 H31

**Pt based PEMFC catalysts from colloidal particle suspensions - a toolbox for model studies** — ●JOZSEF SPEDER<sup>1</sup>, LENA ALTMANN<sup>2</sup>, MARCUS BÄUMER<sup>2</sup>, JACOB KIRKENS GAARD<sup>1</sup>, KELL MORTENSEN<sup>1</sup>, and MATTHIAS ARENZ<sup>1</sup> — <sup>1</sup>University of Copenhagen — <sup>2</sup>University of Bremen

Polymer membrane fuel cells (PEMFCs) represent a key technology for clean, efficient and sustainable energy conversion. One of the main problems in PEMFCs, however, is the sluggish oxygen reduction reaction (ORR). The objective of our work is to prepare and study model catalysts that can help to understand and thereby improve the existing commercially available electrocatalysts. A typical PEMFC catalyst consists of high surface area carbon supported Pt or Pt-alloy nanoparticles. Previous studies report sometimes with contradicting conclusions on the influence of the support, particle size and composition on the ORR activity. In general however, these studies do not selectively change only one of the variables, for example the Pt loading, while leaving the others constant, e.g. the particle size. In our work

we introduce a reliable, artefact-free method for studying these effects by synthesising carbon supported, Pt based catalysts from colloidal dispersions of well defined Pt NPs synthesized by an ethylene glycol method. We demonstrate that this preparation method enables a controlled synthesis of model catalysts where individual parameters such as support material and Pt loading can be tuned without changing other parameters. Thus for example the role of support material, Pt loading etc. can be investigated separated from each other.

**15 min. break****Topical Talk**

O 76.4 Thu 17:15 H31

**Coupling electrochemistry to an ICP-MS - online-investigation of electrode material dissolution** — ●KARL MAYRHOFER, SERHIY CHEREVKO, ANGEL TOPALOV, ANNA SCHUPPERT, JOSEF MEIER, ALEKSANDAR ZERADJANIN, and IOANNIS KATSOUNAROS — Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

Continuous electrochemical flow reactors for efficient conversion of electrical energy into chemicals and vice versa, i.e. fuel cells and electrolyzers, become increasingly important for our energy sustainability and environmental concerns. The search for improved electrocatalyst materials, which constitute the core of electrochemical energy conversion devices, has been typically dominated by the optimization of kinetic activity of catalysts and efficiency of whole cells. However, also the stability of the materials is highly important for a potential commercialization, if not even more important, and should at least always be considered in parallel. In this presentation I will demonstrate how such investigations are done on a fundamental level, and what can be learned from these studies for large scale applications. The focus will be on the recent methodological developments from our group, in particular the scanning flow cell (SFC) coupled to an ICP-MS for studying noble metal catalysts as used in low-temperature fuel cell electrochemical reactors.

O 76.5 Thu 17:45 H31

**Quantitative void detection in thin platinum films by electrochemical means** — ●MICHAEL SCHEELE, DAMIAN BÜRSTEL, and DETLEF DIESING — Universität Duisburg - Essen, Fakultät für Chemie, Universitätsstrasse 2, D - 45141 Essen, Germany

In modern catalysis and energy conversion technologies thin metal films (10-100 nm) deposited on different substrates are widely used. The wetting of the substrate by the metal during the deposition is crucial for the formation of voids and islands in the thin metal film. Due to a different catalytic behavior of small metal islands (nanoparticles) and different chemical behavior of the substrate (corrosion) the absence of voids and islands is desirable in most cases. A 10 nm thin platinum film is prepared on a substrate consisting of tantalum covered with an ultrathin tantalum oxide film (5 nm). Cyclic voltammetric experiments on the thin platinum film are carried out in sulfuric acid. Although platinum films show a quite good wetting behavior on the oxide, small fractions of uncovered substrate area can show up during preparation or in the electrochemical experiments. The high capacitance of the liquid-oxide-tantalum interface in the voids of the platinum film can be used to measure the charging current of the interface. Hereby the fraction of the substrate which is in contact with the electrolyte and not with the platinum can be estimated. The result indicates that this method is a good way for in-situ detection of uncovered area fractions down to 10<sup>-3</sup> of an 10 nm thick platinum film during surface reactions in liquid media.

O 76.6 Thu 18:00 H31

**Electrochemical activity of Ru(0001) electrodes modified by monolayer Au islands** — ●TAMARA HUSCH, OTAVIO BRANDAO ALVES, ALBERT K. ENGSTFELD, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany

Bimetallic surfaces where a second metal covers part of a substrate bulk metal, exhibit unique catalytic properties which differ from those of the individual components and possibly also from those of a surface fully covered by a monolayer film of the second metal. The latter was demonstrated for PtML/Ru(0001) [1], where Pt islands act as catalyst

for OH and H adsorption on the Ru(0001) substrate.

In this work we investigated whether similar effects can take place also on partly Au monolayer island covered Ru(0001) surfaces, or whether Au monolayers simply leads to blocking of the Ru(0001) surface. Submonolayer Au covered Ru(0001) surfaces were prepared by evaporation at room temperature under ultra high vacuum (UHV) conditions. After determination of the Au coverage by scanning tunneling microscopy (STM), the electrochemical properties of the Au/Ru bimetallic surface were characterized in an electrochemical flow cell attached to the UHV system. Surprisingly, the data show that the charge in the respective adsorption peaks is independent of the Au coverage, and is always equivalent to a 0.2 ML Au coverage. Possible reasons leading to this unusual behavior are discussed.

[1] H. Hoster, B. Richter, and R.J. Behm, *J. Phys. Chem B* 108 (2004) 14780.

O 76.7 Thu 18:15 H31

**Aligning electronic energy levels in electrochemical systems**

— ●MIRA TODOROVA and JÖRG NEUGEBAUER — Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf

The relative position of a solid's band structure or an ion transition level with respect to the water energy levels is crucial for the understanding and quantification of electrochemical reactions at solid/liquid interfaces. In terms of electronic structure water has been shown to exhibit features similar to an amorphous semiconductor [1]. As such, it does not have well defined band edges, which makes the technique of aligning defect levels with respect to the band-edges, commonly used in semiconductor physics, not very practicable. Other alignment possibilities, which exploit the reduced sensitivity of an electrostatic potential or some deep level within the band-gap of a material with respect to the band-edge positions and their possible shift, upon changing the used exchange-correlations functional, have been discussed in the semiconductor literature. We explore the applicability of such techniques to electrochemical problems, by discussing the alignment of the electronic levels of ions in water. Utilising our findings and our recently developed method to identify the electrode potential and pH-value within an electrochemical system we explore the stability of ZnO surfaces as a function of environmental conditions.

[1] F. Williams, S.P. Varma, and S. Hillenius, *J. Chem. Phys.* 64, 1549 (1976).

O 76.8 Thu 18:30 H31

**Structural Control of ZnO Thin Films Electrochemically Grown on Microstructured Electrodes**

— ●MARTINA STUMPP, CHRISTIAN LUPO, and DERCK SCHLETTWEIN — Justus-Liebig-Universität Gießen, Institut für Angewandte Physik, Heinrich-Buff-

Ring 16, D-35392 Gießen

Zinc oxide (*ZnO*) can be used as electrode material in dye sensitized solar cells and in microelectronic devices. Electrochemical deposition is an energy-efficient and economic processing method to obtain compact or porous crystalline thin films of *ZnO*. Microelectrodes were used as substrates for the electrodeposition of *ZnO* under pulsed galvanostatic conditions from aqueous zinc nitrate solutions. The *ZnO* growth was characterized by scanning electron microscopy and confocal laser microscopy. For current densities below the limiting current density, homogenous films were obtained, whereas for current densities greater than those limited by the diffusion of  $Zn^{2+}$  and  $NO_3^-$ , strongly dendritic structures were formed. The geometric distribution of the transport of the precursors from solution relative to the electrode surface and the subsequent formation of *ZnO* was discussed based on a model of a duplex diffusion layer. When polarizing only one of two sets of interdigitated microstructured electrode bands a peculiar sequence of deposition either on the polarized electrode band and/or on the non-polarized electrode band was observed. An influence of convective diffusion was found to be the reason for such sequence.

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**Electroless deposition of porous zinc oxide films on aluminium**

— ●STEPHANIE KÜNZE and DERCK SCHLETTWEIN — Institute of Applied Physics, Justus-Liebig-University Giessen, Germany.

Porous zinc oxide is discussed as an active semiconductor in dye-sensitized solar cells. Metal substrates are of interest to provide excellent conductivity and mechanical flexibility of cells. Metal substrates that are protected by an oxide layer in contact to air (passivated metal) can lead to cells containing even an iodide-containing electrolyte without the danger of corrosion. Aluminium can serve as such a metal substrate. Sheets of aluminium were pre-treated in highly-concentrated hydrochloric acid and subsequently in an alkaline zinc hydroxide solution (zincate stain). A coat of zincate was left on the aluminium surface. Porous zinc oxide films were prepared by electroless deposition on such pretreated planar aluminium substrates in the presence of the xanthene dye *EosinY* by two methods. Either a zinc-chloride solution saturated with oxygen or an aqueous solution of 0.1 M  $Zn(NO_3)_2$  was used. The growth of zinc oxide was characterized by optical microscopy, scanning electron microscopy (SEM) and a stylus method to determine the layer thickness. The difference between the two forms of deposition is reported and a mechanism for this electroless deposition on aluminium is proposed and will be discussed. The influence of the amount of deposited zincate from the pre-treatment on the film thickness of the porous zinc oxide and the coverage of the metal surface is shown. In this context also results of an electroless deposition of porous zinc oxide on etched sheets of zinc was analyzed.