

O 73: Solid/liquid interfaces II (focused session)

Time: Thursday 15:00–17:45

Location: H33

Invited Talk

O 73.1 Thu 15:00 H33

Theoretical studies on the electrocatalytic Oxygen reduction reaction on Pt — ●TIMO JACOB — Universität Ulm, Albert-Einstein-Allee 47, D-89069 Ulm

The oxygen reduction reaction (ORR) is one of the most important reactions in basic electrochemistry and for various applications such as fuel cells. However, due to the high complexity of this reaction the exact mechanisms is still unknown.

Using density functional theory, we investigated different mechanisms of the ORR on Pt electrodes [1]. Among the three main mechanisms (i.e., O_2^{ad} -Dissociation, OOH^{ad} -Formation, and $HOOH^{ad}$ -Formation) we found that $HOOH^{ad}$ -Formation is the preferred process in gas phase. When including water solvation as an environmental effect, the reaction paths were modified, leading to drastic changes in the energetics and a nearly identical preference for the O_2^{ad} -Dissociation and the OOH^{ad} -Formation mechanisms. Interestingly, inclusion of solvent as well as electrode potential effects resulted in a picture showing that both Langmuir–Hinshelwood and Eley–Rideal mechanisms could be at play, making the ORR a rather complex reaction, where rigorous evaluation of the kinetics of all paths coupled together under certain environmental parameters was required to further elucidate the complicated nature of the overall reaction process.

[1] S. Venkatchalam, T. Jacob, *Handbook of Fuel Cells Vol. 5&6*, W. Vielstich, H. A. Gasteiger, H. Yokokawa (Eds.), John Wiley & Sons Ltd., Chichester, UK (2009)

Invited Talk

O 73.2 Thu 15:30 H33

Investigations on Pt based catalysts for PEM fuel cells: from model systems to high surface area catalysts — ●MATTHIAS ARENZ — Technische Universität München, Physikalische Chemie, Lichtenbergstr. 4, D-85748 München

The long term stability as well as the slow rate of the oxygen reduction reaction (ORR) are the main fundamental problems in the catalysis concerning polymer electrolyte membrane fuel cells. On Pt based model electrodes (single crystals and polycrystalline samples), it has recently been demonstrated how by fine-tuning the electronic structure of the surface, the specific activity for the oxygen reduction can be drastically enhanced. However, there is still a great challenge to create catalyst particles with the electronic and structural properties of the most active bulk crystal surfaces. For this task, the testing of high surface area catalysts, especially establishing the true specific activity of nanoparticle catalysts, is of highest importance. In the presentation the testing of high surface area catalysts by the so-called thin film rotating disc electrode method is critically discussed. It will be shown how reproducible activity measurements can be performed. In this respect it is demonstrated how the treatment of catalysts affects their surface composition and structure. Furthermore, a new TEM methodology for testing the stability of catalysts in accelerated ageing tests is introduced as well as new results on size selected Pt particles are shown.

Invited Talk

O 73.3 Thu 16:00 H33

Computer Simulation of Electrolyte / Solid Interfaces — ●ECKHARD SPOHR — Lehrstuhl fuer Theoretische Chemie, Universitaet Duisburg-Essen, D-45141 Essen, Germany

This talk will review the state of the art and recent advances of atomistic computer simulations of interfaces between electrolytes and electrolyte solutions and solid interfaces. I will focus on the simulation of charged interfaces and systems of electrochemical importance. Simulation methodology and several examples from various research groups including our own will be discussed in some detail. The examples will cover structural aspects, interfacial dynamics, and prototypical electrochemical reactions such as proton discharge on metal electrodes.

O 73.4 Thu 16:30 H33

Multilayer passivated AlGaIn/GaN-sensors for stable pH-measurements — ●STEFANIE LINKOHR, VOLKER CIMALLA, CHRISTOPH NEBEL, and OLIVER AMBACHER — Fraunhofer Institute for Applied Solid State Physics Tullastraße 72, 79108 Freiburg, Germany

Due to its high chemical stability in physiological fluid and the large spontaneous polarization AlGaIn/GaN-sensors are of particular impor-

tance for pharmaceutical and medical sensors. They are advantageous for the fabrication of very sensitive and robust biosensors to detect ions, bio-molecules and the bioactivity of cells in solutions, gases and polar liquids. The ion-sensitive field effect transistor (ISFET) is realized by an open gate surface placed in a measuring solution and controlled by a reference electrode. Based on the sensing principle of an AlGaIn/GaN-heterostructure ions cause a change of the two-dimensional electron gas (2DEG) near the surface. Negative charge depletes and positive charge accumulates the 2DEG. With an achievable sensitivity of 57 mV/pH these sensors are able to measure the pH-value close to Nernst limit. The sensors have to be appropriately protected. The passivation has to protect the inactive areas and the contacts but should be biocompatible and chemical stable in acidic and alkaline liquids. In this work, we investigate various passivations such as SiNx, DLC (diamond like carbon), SiO₂-SiNx-doublelayer (up to 500 nm) and various SiO₂-SiNx-SiO₂-SiNx-multilayers (up to 700nm). The multilayer passivations show the best chemical stability, no memory effects, no ionic diffusion and a minimal drift less than 0.01 pH/h.

O 73.5 Thu 16:45 H33

Electrochemical experiments in sulphuric acid with electronic devices — ●ANDREAS BARMSCHIED, DAMIAN BÜRSTEL, ECKART HASSELBRINK, and DETLEF DIESING — Institut für Physikalische Chemie, Universität Duisburg Essen

With chemical experiments on the surfaces of thin film devices one can monitor for example adsorbate induced changes in the film resistivity or the existence of excited charge carriers in the course of a reaction. We show that thin platinum films on Si-SiO_x-substrates show a well defined surface chemistry in 0.1 M sulphuric acid. Parts of the electrochemical charge transfer at the Pt-acid interface can be monitored as a device current flowing from the Pt to the silicon. This transfer ratio depends on the inner potential difference of the device across the SiO_x layer as well as on the outer electrode potential across the platinum-sulphuric acid interface. The transfer of charge carriers generated at the platinum-acid interface within the adsorption and desorption reaction of hydrogen is found to have a dependence on the inner device potential which is very similar to that one of photo excited carriers. On the other hand, charge carriers generated during the sulphate adsorption or platinum oxidation reaction do not exhibit similarities in the transfer through the internal interfaces of the device with photo excited carriers.

O 73.6 Thu 17:00 H33

Investigations on Pt based catalysts for PEM fuel cells: The stability of Pt-Co alloys — ●KATRIN HARTL and MATTHIAS ARENZ — Technische Universität München, Physikalische Chemie, Lichtenbergstr. 4, D-85748 München

The long term stability as well as the slow rate of the oxygen reduction reaction (ORR) are the main fundamental problems in the catalysis concerning polymer electrolyte membrane fuel cells. On Pt based model electrodes (single crystals and polycrystalline samples), it has recently been demonstrated how by fine-tuning the electronic structure of the surface, the specific activity for the oxygen reduction can be drastically enhanced. However, there is still a great challenge to create catalyst particles with the electronic and structural properties of the most active bulk crystal surfaces. For this task, the testing of high surface area catalysts, especially establishing the true specific activity of nanoparticle catalysts, is of highest importance. In the presentation the testing of high surface area catalysts by the so-called thin film rotating disc electrode method is critically discussed. It will be shown how reproducible activity measurements can be performed. In this respect it is demonstrated how the treatment of catalysts affects their surface composition and structure. Furthermore, a new TEM methodology for testing the stability of catalysts in accelerated ageing tests is introduced as well as new results on size selected Pt particles are shown.

O 73.7 Thu 17:15 H33

Electrokinetics and Charge Inversion as studied by Single Colloid Electrophoresis — ILYA SEMENOV, ●GUNTHER STOBER, PERIKLIS PAPADOPOULOS, and FRIEDRICH KREMER — Institute for Experimental Physics I (MOP), University of Leipzig, Linnestrasse 5, 04103 Leipzig, Germany

Single Colloid Electrophoresis (SCE) is employed to measure in a specifically designed microfluidic cell the electrophoretic and electroosmotic mobility for the identical colloid. Charge inversion in dependence on concentration, valency and acidity is observed and is proved to be fully reversible. The results are discussed with in terms of overcharging as caused by ion-ion correlations.

The determination and prediction of the surface charge density of the particle's surface are thus of prime importance. This requires an accurate model for the electric double layer at the solid/liquid interface. The standard electrokinetic model is not accurate in strongly coupled systems. That is, for systems containing multivalent ions, high ionic concentration and/or strong surface charge.

A phenomenon known as charge inversion may be seen in electrokinetic measurements such as electrophoresis in presence of multivalent ions, where the sign of the electrokinetic potential appears to be opposite to the expected one. The interpretation of such a result is still controversial. Often it is explained by specific chemical adsorption of multivalent counter-ions. However, the pure electrostatic interactions, i.e. the ion-ion correlations, can cause overcharging by the strong accumulation of counter-ions in contact with a charged surface.

O 73.8 Thu 17:30 H33

Step bunching instability of Au(11n) vicinal surfaces in elec-

trolyte — ●MOHAMMAD AL-SHAKRAN¹, GUILLERMO BELTRAMO¹, HARALD IBACH², and MARGRET GIESEN¹ — ¹Institute of Bio-and Nanosystems ,IBN4, Jülich Forschungszentrum GmbH — ²Institute of Bio-and Nanosystems ,IBN3, Jülich Forschungszentrum GmbH

Flame annealed vicinal Au(11n) electrodes, n=5, 7, 9 11, 17, were studied by means of electrochemical scanning tunneling microscopy (STM), cyclic voltametry (CV) and capacitance curves in sulfuric and perchloric acid solution. STM results show that Au(11n) is unstable against step bunching. The surfaces arrange into alternating stripes of reconstructed surface (almost free of steps) and steep, unreconstructed step bunches. Though very stable, the step bunches still show a high mobility of individual steps within the bunch, indicating that the step bunches formed after flame annealing represent an equilibrium structure even at higher electrode potentials. Analyzing the step-step distance distribution shows that the relative amount of reconstructed area shifts with potential. As a consequence, the CVs of Au(11n) show a distinct change in the peak structure as well as in the minimum of the capacitance curves representing the potential of zero charge (pzc) which surprisingly is still well defined. We could show that a well-defined minimum in the capacitance curves exists below a maximum structure size of reconstructed and unreconstructed areas. Our results offers for the first time a comprehensive interpretation of the complex structure of CVs and capacitance curves on vicinal Au(11n) surfaces.