

O 106: Poster Session VIII: Poster to Mini-Symposium: Electrified solid-liquid interfaces III

Time: Thursday 13:30–15:30

Location: P

O 106.1 Thu 13:30 P

Gouy-Chapman and beyond: A new double layer model for Pt — ●KATHARINA DOBLHOFF-DIER — Leiden University, Leiden, The Netherlands

The Gouy-Chapman-Stern model and its various extensions (e.g., modified to include finite-size effects) are expected to represent the electric double layer structure in dilute electrolytes rather well. Consequently, these models form the basis of many constant-potential methods available in the various electronic structure codes. However, recent experimental results [1,2] show that the double layer capacitance of Pt(111) surfaces, and (to a lesser extent) of Au(111), does not follow the predictions made by these simplistic models. Consequently, we need to rethink the structure of the electric double layer. A reasonable match between theory and experiment can be attained when extending the standard Gouy-Chapman-Stern-like capacitance models by i) the hyperpolarizability caused by water adsorbing at the interface and ii) a weak attractive ion-surface interaction. These little effects strongly alter the potential vs. electric relation of the interface as well as the z-dependence of the near-surface electric field. Inclusion of these effects therefore does not only suggest a renewed picture of the double layer structure, the correct description of these properties is also relevant in order to obtain accurate adsorption energies of polar molecules and reaction barriers from first principle calculations.

[1] K. Ojha, N. Arulmozhi, D. Aranzales, and M.T. M. Koper; *Angew. Chem. Int. Ed.* 59, 711 (2020)

[2] K. Ojha, K. Doblhoff-Dier, M.T.M. Koper (unpublished)

O 106.2 Thu 13:30 P

Entropy changes during adsorption of pyridine on Au(111) in aqueous solutions — ●KATARINA JOSIFOVSKA, MARCO SCHÖNIG, and ROLF SCHUSTER — Karlsruhe Institute of Technology, Kaiserstraße 12, 76131 Karlsruhe

The adsorption of pyridine on gold surfaces has been often studied by applying various electrochemical, microscopic and spectroscopic techniques. Corresponding to reported data, pyridine adsorption occurs in anodic direction in two different structural orientations [1,2,3].

In attempt to describe the adsorption, we used different concentrations of pyridine in aqueous solutions over Au(111), on which we conducted electrochemical microcalorimetric measurements in our home-build calorimeter [4]. We measured the Peltier heat which provides direct information on the reaction entropy of the electrochemical processes, scanning the whole adsorption region.

Negative entropy was found for the anodic processes, with a strong minimum of ca. $-170 \text{ J/mol}\cdot\text{K}$ that was observed at about the same potential at which the reorientation occurs. This entropy reduction is in line with adsorption of weakly solvated neutral molecules from the solution, but also other processes, such as ion transport, entropy from double layer polarization, and/or accompanying solvent reorientation might contribute.

[1] L. Stolberg et al., *J. Electroanalytical Chem.* 1991, 241, 307. [2] J. Li et al., *J. Am. Chem. Soc.* 2015, 137, 2400. [3] S. Iqbal et al., *Electrochimica Acta* 2015, 186, 427. [4] R. Schuster, *Curr. Opin. Electrochem.* 2017, 1, 88.

O 106.3 Thu 13:30 P

Thermodynamic and kinetic data of the hydrogen evolution reaction (HER) from electrochemical microcalorimetry. — ●MARCO SCHÖNIG and ROLF SCHUSTER — Karlsruher Institut für Technologie, Deutschland

The hydrogen evolution reaction (HER) is an often investigated model electrocatalytic reaction. However, there are still open questions, like the influence of the alkaline metal cations in alkaline solution[1].

We measured the exchanged heat during the HER on Pt upon short potential or current pulses. The evolved heat is made up of reversible and irreversible contributions, which can be disentangled by measuring with different pulse polarities[2]. From the reversibly exchanged heat we derived the reaction entropy. The irreversible contribution to the exchanged heat corresponds to the overpotential. Thus, from the calorimetric data we can derive the overpotential as a function of current density, which allows for the determination of the exchange current density of the reaction and provides an alternative to the determination of kinetic parameters from Tafel plots.

The determined reaction entropies agree well with the standard reaction entropy of the HER in the respective solutions [3]. For the exchange current density, we found 1.3 mA/cm^2 for 0.1 M LiOH . For 0.1 M KOH and 0.1 M CsOH lower values were found, which is in accordance with trends observed in the literature[1].

[1] A.S. Bandarenka et al., *ChemElectroChem* 2018, 5, 2326.[2] R. Schuster, *Curr. Opin. Electrochem.* 2017, 1, 88.[3] B.E. Conway et al., *J.Chem. Soc., Faraday Trans.* 1 1978, 74,1373.

O 106.4 Thu 13:30 P

Ni(OH)₂ modified Cu(111): interfacial water structure and electrocatalysis — ●ANDREA AUER¹, FRANCISCO J. SARABIA², DANIEL WINKLER¹, VICTOR CLIMENT², JUAN FELIU², and JULIA KUNZE-LIEBHÄUSER¹ — ¹Institute of Physical Chemistry, University Innsbruck, Austria — ²Instituto Universitario de Electroquímica, Universidad de Alicante, Spain

The design of bimetallic electrodes is one key tactic to tune their activity and selectivity for electrocatalysis. Here, irreversible adsorption of Ni ions^[1] was used to prepare Ni(OH)₂ modified Cu(111) electrodes with different coverages and to study their effect on the hydrogen evolution reaction (HER) and CO reduction in alkaline media. To investigate the structure-activity relation, electrochemical scanning tunneling microscopy was performed and shows morphological changes upon modification consistent with adsorption of Ni(OH)₂ on the step edges. The presence of Ni(OH)₂ on Cu(111) leads to an enhancement in the rate of the HER, similar to Ni(OH)₂/Pt(111) electrodes^[1], but also changes the selectivity of the CO reduction. Intriguingly, laser induced temperature jump experiments reveal that the Ni(OH)₂ modification influences the charge distribution at the interface by a decrease of the electric field strength. This implies an easier reorganization of the interfacial water molecules facilitating charge transfer through the double layer, and thus enhancing the electrocatalytic reaction.

[1] F. J. Sarabia, P. Sebastián-Pascual, M. T. M. Koper, V. Climent, J. M. Feliu, *ACS Appl. Mater. Interfaces* 2019, 11, 1, 613-623.

O 106.5 Thu 13:30 P

Amino acids adsorption at electrified gold/aqueous interface — ●DENYS BIRIUKOV^{1,2} and ZDENEK FUTERA² — ¹Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo nám. 2, 16610 Prague 6, Czech Republic — ²Institute of Physics, Faculty of Science, University of South Bohemia, Branišovská 1760, 370 05 České Budějovice 2, Czech Republic

Molecular detailization of gold/aqueous interfaces in an external electric field stimulates various applications in electrochemistry. In this contribution, we investigate the adsorption of several, particularly charged amino acids, since they represent principal components of proteins and other molecular junctions. Using all-atom molecular dynamics simulations and free energy calculations, we show that positively charged amino acids exhibit larger interfacial changes than negatively charged when an external electric field is applied. The reason is the ability of the side-chain of positively charged amines to replace water molecules in the first adsorption layer at Au (111) surface. Charge-neutral amino acids are also capable to penetrate into the interfacial water structure, so their response to an applied electric field reflects that of positively charged amino acids. However, it is overall less significant due to charge-neutrality of the molecule. Contrary, negatively charged carboxylates adsorb with their carboxyl group further from the surface, i.e., an applied electric field acting on the side-chain is screened by the solvent. This leads to reduced electric field effects and weaker adsorption in general. Current results provide a useful information, which may help to interpret complex electrokinetic phenomena.

O 106.6 Thu 13:30 P

In-situ optical detection of charge distributions at electrified solid-liquid interfaces — ●CHRISTOPH COBET, SAUL VAZQUEZ-MIRANDA, LUIS ROSILLO-OROZCO, and KURT HINGERL — Johannes Kepler University, Altenbergerstr 69, 4040, Linz, Austria

Polarization optical methods like Spectroscopic Ellipsometry are used by us to determine the distribution of charges, i.e. electrons and ions, and their potential dependent variation in the uppermost atomic layers of a working electrode as well as in the inner Helmholtz plane above. Our focus laid initially on planar surfaces with regular atomic structure

to discriminate the different contributions to the optical response. On the one hand, the aforementioned optical probes are extremely sensitive to electronic surface/interface changes even in the presence of sub-monolayer changes. On the other hand, exactly this advantage often makes it problematic to extract quantitative information. But we will show that valuable additional information is accessible which is in parts complimentary to results of conventional methods such as impedance spectroscopy, EC-STM or novel XPS approaches. This will be demonstrated for single crystalline metal (Cu) as well as metal-oxide (ZnO) surfaces; both drosophila-like examples of catalytic surfaces where the optical resonances of Drude electrons, of electrons in surface states and of electronic states in the electrostatic as well as strain field at electrified solid-liquid interfaces contribute to the measured signal. [1] S. Vazquez-Miranda, et.al.: J. Phys. Chem. C 124, 5204 and 25403 (2020); [2] M.-H. Chien, et.al.: J. Phys. Chem. C 122, 8984 (2018), [3] G. Barati, et.al.: Langmuir 30, 14486 (2014)

O 106.7 Thu 13:30 P

Electrochemical properties of Ru(0001) - pH effects, anions effects and anodic H₂ formation — ●ALBERT K. ENGSTFELD¹, SIMON WEIZENEGGER², ZENONAS JUSYS², JOACHIM BANSMANN²,

JAKUB DRNEC³, and R.JÜRGEN BEHM² — ¹Institute of Electrochemistry, Ulm University, Ulm — ²Institute of Surface Chemistry and Catalysis, Ulm University, Ulm — ³ESRF, Grenoble, France

The electrochemical properties of Ru electrodes in aqueous electrolyte are very complex since it interacts strongly with anion species and shows overlapping surface redox processes. Furthermore, it has recently been shown in HClO₄ electrolyte that hydrogen adsorbed in the hydrogen evolution region, is desorbed in the positive-going scan by hydroxyl displacement from the surface, to form H₂ at potentials more positive than the equilibrium potential of $E(\frac{1}{2}\text{H}_2/\text{H}^+) = 0 \text{ V}$, instead of forming H⁺. [1] Here we present the electrochemical properties of Ru(0001) in acid and alkaline electrolytes. The electrodes were prepared under UHV conditions and investigated in an electrochemical flow cell combined with differential electrochemical mass spectrometry (DEMS). With the DEMS data, we provide direct evidence for hydrogen adsorption in H₂SO₄ electrolyte, which was so far not considered. Additional surface X-Ray diffraction (SXRD) measurements in H₂SO₄ reveal a strong hysteresis in the potential dependent structural properties and adlayer composition. The herein reported processes are suggested to be characteristic for other strongly interacting metals in general. [1] Scott & Engstfeld, et al, CatSciTechnol, 10 (2020) 6870