

## CPP 19: Solid-liquid interfaces: Reactions and electrochemistry II (joint session O/CPP)

Time: Monday 16:45–18:15

Location: MA 144

CPP 19.1 Mon 16:45 MA 144

**Pt modified Ru(0001) electrodes: structure-activity relationship for the CO and MeOH electrooxidation** — ●ALBERT K. ENGSTFELD, JENS KLEIN, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

Bimetallic PtRu catalysts are the most prominent catalyst material in polymer electrolyte membrane fuel cells for the electrooxidation of methanol (MeOH) since it enables the oxidation of the strong binding reaction intermediate CO from the surface at much lower overpotentials compared to a bare Pt catalyst. The underlying process is attributed to a so-called Langmuir Hinshelwood bifunctional mechanism, where the CO oxidation from Pt and Ru sites is promoted by the preferential adsorption of oxygen on neighboring Ru sites. In this work, we will show in comparison the electrocatalytic CO and MeOH oxidation on well defined Pt-modified Ru(0001) electrodes (surface alloys and Pt sub-/multilayer structures), prepared under UHV conditions and characterized on an atomic scale level with scanning tunneling microscopy (STM). For the surface alloys as well as submonolayer Pt-modified Ru(0001) we will show that the formation of bifunctional sites is indeed beneficial for the CO electrooxidation but is surprisingly inactive for the MeOH electrooxidation. On Pt multilayer structures, thus a surface without bifunctional sites, the MeOH electrooxidation is significantly more active compared to the mixed surfaces. Based on these results we will discuss the rate-limiting steps for the MeOH electrooxidation on these surfaces and discuss the influence of related electronic and geometric effects on both the CO and MeOH oxidation.

CPP 19.2 Mon 17:00 MA 144

**Influence of Pt step sites on the electro-oxidation of CO** — ●JENS KLEIN, VALERIA CHESNYAK, EVELYN ARTMANN, JULIAN BÖSKING, ALBERT K. ENGSTFELD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm

The performance of the CO electro-oxidation on Platinum (Pt) catalysts strongly depends on the surface structure of the catalyst. It has been reported that Pt electrodes with a large number of low coordinated step sites show an enhanced activity for the electro-oxidation of an adsorbed monolayer of CO, which was ascribed to active sites on the step edges.<sup>[1]</sup>

In this work we investigated the role of Pt steps in the electro-oxidation of CO on Pt electrodes under continuous CO supply (bulk CO oxidation). We prepared Pt(111) single crystal electrodes and varied the Pt step edge density by physical vapor deposition of Pt on the crystal under UHV conditions. The structural properties were characterized by scanning tunneling microscopy (STM). To identify the actual role of Pt step edges we blocked the respective sites, by decorating the Pt steps with a narrow Au film, since Au supported on Pt(111) was reported to be inert for the CO oxidation.<sup>[2]</sup> The electrocatalytic measurements, which were performed in an electrochemical flow cell, provide information on the role of the Pt steps in the CO oxidation and consequences of these findings will be discussed.

[1] G. García et al., *ChemPhysChem*. 12 (2011) 2064.

[2] D. C. Skelton et al., *J. Phys. Chem. B*, 103 (1999) 964.

CPP 19.3 Mon 17:15 MA 144

**Comparing solvation effects on adsorbates at water/Pt(111) interface with implicit and explicit solvents** — ●SUNG SAKONG and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

For a realistic description of the elementary electrocatalytic processes at electrode/electrolyte interfaces, an adequate method to treat the solvated molecules at the interface is necessary. Since the solvation in liquid solvent requires thermodynamic sampling which is computationally demanding within ab initio molecular dynamics (AIMD) approach, numerically efficient implicit solvent methods which address solvation effects through a polarization potential and a corresponding electrostatic energy are becoming increasingly popular.

The structure of liquid water in the bulk and near electrode surfaces differs. Therefore we consider an implicit solvent method that

determines cavitation on the fly using the charge density evaluated by quantum chemical methods. We will compare solvated reaction intermediates in the methanol electro-oxidation at the Pt(111)/water interface using an implicit solvent method and using explicit solvating water layer at the interface in order to assess the reliability of the implicit solvent approach.

[1] *J. Chem. Phys.* **142**, 234107 (2015).

[2] *ACS Catal.* **6**, 5575 (2016).

[3] *Electrocatalysis* **8**, 577 (2017).

CPP 19.4 Mon 17:30 MA 144

**Microcalorimetric measurement of double layer charging in ionic liquids** — ●JEANNETTE LINDNER<sup>1</sup>, FABIAN WEICK<sup>1</sup>, STEFAN FRITTMANN<sup>1</sup>, FRANK ENDRES<sup>2</sup>, and ROLF SCHUSTER<sup>1</sup> — <sup>1</sup>Institute of Physical Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany — <sup>2</sup>Institute of Electrochemistry, TU Clausthal, Clausthal, Germany

The reversible molar heats, i.e., the Peltier heats of processes in the electrified double layer at an IL/Au(111) interface were measured via electrochemical microcalorimetry. The Peltier heat corresponds to the entropy change during electrochemical double layer charging. 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide was used as ionic liquid. We found a decrease of  $\Delta RS$  by 143 J/(K\*mol) between E vs. Pt = -0,9 V and +1,0 V and  $\Delta RS = 0$  for E vs. Pt = -0,25 V.  $\Delta RS = 0$  corresponds to the maximum of the double layer formation entropy SMax. We interpret SMax as the maximum of mixing entropy of cations and anions within a lattice gas model with negligible ionic interactions. As a consequence, SMax corresponds to the pzc (point of zero charge) of the system. In order to quantitatively explain the found magnitude of the S variations, one has to include entropy contributions from multiple layers.

CPP 19.5 Mon 17:45 MA 144

**A thermodynamic approach on specific anion adsorption via electrochemical Microcalorimetry** — ●MARCO SCHÖNIG and ROLF SCHUSTER — Karlsruhe Institute of Technology, Karlsruhe, Germany

The understanding of specific adsorption is of fundamental importance for the description of the electrochemical double-layer. With electrochemical microcalorimetry we measured the reversibly exchanged heat during the anion adsorption/desorption process, which is directly correlated with the reaction entropy of the electrochemical process (1). Using this method we investigated the adsorption of halides (Cl-, Br-, I-) and oxoanions (SO<sub>4</sub><sup>2-</sup>/HSO<sub>4</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>) on Au(111) as a function of the surface polarization. For all systems the exchanged heat increased in the adsorption region of the respective anion. A possible explanation may be the configuration entropy of an anion lattice gas.

(1) J. M. Gottfried und R. Schuster. *Surface Microcalorimetry*. In: *Surface and Interface Science*. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2016, S. 73-126

CPP 19.6 Mon 18:00 MA 144

**Enhanced Photoanode Activity with Co-Fe Prussian blue as genuine Water Oxidation Catalyst** — ●FRANZISKA HEGNER<sup>1</sup>, NÚRIA LÓPEZ<sup>1</sup>, JOSÉ-RAMÓN GALÁN MASCARÓS<sup>1</sup>, and SIXTO GIMENEZ<sup>2</sup> — <sup>1</sup>ICIQ Tarragona — <sup>2</sup>INAM, Castellón

Catalysts based on Prussian blue analogues have shown high water-oxidation efficiencies with exceeding long-term stabilities. Moreover, their application as co-catalysts on well-known photoanode materials, such as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and BiVO<sub>4</sub>, has shown success. We studied the electrochemical behaviour, catalytic efficiency and impedance under light and electrical field conditions. Also transient absorption spectroscopy (TAS) is used to gain more information about the behaviour of the system. In addition, we employed various theoretical simulations based on hybrid Density Functional Theory, DFT, and evaluated their applicability. With a combination of theoretical, as well as experimental studies, the true catalytic function of cobalt-iron Prussian blue as a co-catalyst on light-absorbing semiconductors can be evaluated.