

O 8: Solid-Liquid Interfaces 1: Reactions and Electrochemistry

Time: Monday 10:30–12:45

Location: S054

Topical Talk

O 8.1 Mon 10:30 S054

Dynamic structure changes of bare and modified Cu(111) during CO and water activation — ●ANDREA AUER¹, NICOLAS HÖRMANN², MIE ANDERSEN³, KARSTEN REUTER², and JULIA KUNZE-LIEBHÄUSER¹ — ¹Institute of Physical Chemistry, University of Innsbruck, Austria — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ³Aarhus Institute of Advanced Studies, Denmark

CO is a key intermediate in the electro-oxidation of energy carrying fuels. Single-crystal Cu(111) model catalysts efficiently electro-oxidize CO in alkaline media, under strong and continuous surface structural changes that lead to simultaneous strengthening of the CO and weakening of the OH binding, which makes the observed high activity possible.

Cu(111) modified with Ni(OH)₂ and Co(OH)₂ reveals strong morphological changes upon adatom deposition, which lead to a significant enhancement in the rate of the alkaline hydrogen evolution reaction (HER), one of the most important processes in the development of hydrogen-based energy conversion devices. Adatom modification influences the charge distribution at the solid/liquid interface by a decrease of the electric field strength negative of the potential of zero charge. This implies an easier reorganization of the interfacial water molecules facilitating charge transfer through the double layer. The tendency of Cu(111) to restructure is found to dominate its electrochemical properties. The structural changes of the electrode surface are intimately related to the electric field at the solid/liquid interface and to its electrocatalytic activity, in general.

O 8.2 Mon 11:00 S054

Cu(111) reconstruction and oxidation imaged in oxygen free alkaline media with electrochemical scanning tunneling microscopy — ●TONI MOSER, ANDREA AUER, and JULIA KUNZE-LIEBHÄUSER — Department of Physical Chemistry, University of Innsbruck, Innrain 52c, Innsbruck, Austria

Cu has recently gained attention due to its capability to efficiently oxidize CO at low overpotentials^[1]. However, the structural evolution of the surface at anodic potentials causing initiation of oxide formation under complete exclusion of oxygen has yet to be fully understood. While Cu(111) oxidation has previously been studied with electrochemical scanning tunneling microscopy (EC-STM), investigations without atmospheric oxygen and without contamination from dissolved glassware in alkaline media are sparse. Recent results indicate a significant delay in the anodic formation of Cu₂O in completely deaerated alkaline electrolyte, which indicates a significant impact of dissolved O₂ on the oxidation of copper surfaces. In this work, we focus on the in-situ investigation of hydroxide adsorption on and oxidation of Cu(111) via EC-STM, eliminating atmospheric oxygen by conducting the experiments inside an Ar-filled glove box. The delayed formation of an amorphous oxide layer at anodic potentials and subsequent reduction processes at cathodic potentials, where a smoothening of the surface can be observed, as well as new insights into the hydroxide adsorption structure are presented.

[1] A. Auer, M. Andersen, E.-M. Wernig, N. G. Hörmann, N. Buller, K. Reuter & J. Kunze-Liebhäuser, *Nat Catal* 3, 797-803 (2020).

O 8.3 Mon 11:15 S054

Enhanced Field Effects at Protruding Defect Sites in Electrochemistry? – A Theoretical Evaluation — ●SIMEON D. BEINLICH^{1,2}, NICOLAS G. HÖRMANN¹, and KARSTEN REUTER¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ²Technical University of Munich, Munich, Germany

Does electrochemistry at protruding surface sites differ significantly from that at ideal low-index surfaces? Intuitively, classical electrostatics suggest a local field enhancement at protruding sites. In this case, a dipole-field-like picture would suggest a pronounced potential-dependence of adsorption energies at such sites.

Here, we evaluate these dependencies for various adsorbates on vicinal Pt(111) surfaces using first-principles calculations in combination with a fully grand canonical approach [1]. Our results show an enhancement of the local electric field at pristine surfaces. However, it is lifted upon adsorption and hence does not cause the anticipated stronger field-effects. Nevertheless, we observe dramatic variations in the potential-dependence which can be rationalized from the differ-

ences in surface dipoles that form upon adsorption. These correlate with site coordination showing a consistent trend across adsorbates and adsorption sites.

We rationalize these findings and discuss how the adsorption behavior changes on defect-rich, undercoordinated surfaces in an electrochemical environment.

[1] S.D. Beinlich *et al.*, *ACS Catal.* **12** 6143–6148 (2022)

O 8.4 Mon 11:30 S054

Vapor adsorption on carbon nanomembranes (CNMs) — ●EN-NEITA KHAYYA, PETR DEMENTYEV, and ARMIN GÖLZHÄUSER — Faculty of Physics, Bielefeld University, 33615 Bielefeld, Germany

Intrinsically porous carbon nanomembranes (CNMs) demonstrate promising mass transfer properties with respect to separation of liquids and gases. To complement the permeation studies with CNMs, we introduce a spectroscopic experiment for probing adsorption of vaporous substances on their surface under ambient conditions. Polarization-modulation infrared reflection absorption spectroscopy (PM IRAS) is used to quantify the number of adsorbed species with the help of innovative calibration approaches, including azeotropic mixtures and immobilization in a polymer matrix. Water and alcohols are found to readily condense on supported CNMs yielding liquid-like interfaces. The results are consistent with the vapor permeation rates measured in free-standing CNMs.

O 8.5 Mon 11:45 S054

Investigating Zirconium Nitride Cathodes for the Electrochemical Nitrogen Reduction Reaction — ●TEODOR APETREI, SASWATI SANTRA, VERENA STREIBEL, and IAN D. SHARP — Walter Schottky Institut, Technische Universität München, Garching, Germany

The electrochemical nitrogen reduction reaction (NRR) can convert nitrogen to ammonia at ambient conditions. The most critical factor to activate N₂ is to cleave the N-N triple bond. Transition metal nitrides have been proposed as electrocatalysts for the NRR, with computational studies predicting that N-N bond cleavage can be facilitated via a Mars-van-Krevelen mechanism. Herein, we experimentally test this prediction by investigating sputter-deposited ZrN thin films for the NRR. Our investigations indicate that small amounts of ammonia are indeed produced when pristine ZrN thin films are used as NRR cathodes. However, we also observe nitrogen loss and electrochemical instabilities, which could indicate a sacrificial rather than catalytic role of ZrN. Hence, to accelerate the rate-limiting N-N bond splitting step and facilitate nitrogen replenishment, we anchor Fe SACs onto ZrN. Our preliminary results indicate that high-temperature attachment of Fe SACs leads to overall smaller current densities. However, electrochemical measurements and comparative XPS and XRD studies of the pre- and post-NRR samples suggest an increased nitrogen stability within the Fe-modified ZrN films and improved electrochemical stability. Whether this Fe-modification also facilitates N-N bond dissociation and boosts the NRR activity is currently investigated.

O 8.6 Mon 12:00 S054

Towards Understanding Platinum Degradation: Modelling the Growth of Nanoislands — ●FRANCESCO VALLS MASCARO¹, MARC T.M. KOPER¹, and MARCEL J. ROST² — ¹Leiden Institute of Chemistry, Leiden University — ²Huygens-Kamerlingh Onnes Laboratory, Leiden Institute of Physics, Leiden University

Platinum is the catalyst of choice in many electrochemical energy conversion systems like fuel cells due to its superior activity. However, the stability of platinum catalysts is limited under fuel cell operation conditions. This degradation process has been extensively studied by cyclic voltammetry and inductively coupled plasma mass spectrometry (ICP-MS) [1, 2]. The origin of this degradation is most likely linked to the roughening of the surface due to the nucleation and growth of platinum nanoislands [3, 4, 5, 6]. In this work, we model, fully analytically and with the support from electrochemical data, the growth of these nanoislands on Pt(111) in perchloric acid. The model here presented successfully describes the surface growth taking place during the oxidation-reduction cycling. Different parameters such as the flux of adatoms and vacancies were obtained from the fittings between the model and the experimental data.

References: [1] Topalov, A. et al., *Chem. Sci.*, 5, 631 (2014) [2] Sandbeck D.J.S. et al., *ACS Appl. Mater. Interfaces*, 12, 25718 (2020) [3] Jacobse, L. et al., *Nat. Mater.* 17, 277 (2018) [4] Jacobse, L. et al., *ACS Cent. Sci.* 5 (12), 1920 (2019) [5] Rost, M.J. et al., *Nat. Commun.* 10, 5233 (2019) [6] Ruge, M. et al., *J. Am. Chem. Soc.*, 139, 4532 (2017)

O 8.7 Mon 12:15 S054

Exploring the Limits of Mean-Field Theory in Modeling Thermodynamic Cyclic Voltammograms — •NICOLAS BERGMANN, NICOLAS G. HÖRMANN, and KARSTEN REUTER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Deutschland

Mean-field theory (MFT) is at the heart of many approaches to simulate materials. Recently, MFT has been used to model thermodynamic cyclic voltammograms (CVs) [1], a standard electrochemical experiment. However, its accuracy limitations in this context remain unclear.

Here, we outline our general ansatz to derive mean field models for thermodynamic CVs based on *ab initio* DFT calculations of a wide variety of adsorbate configurations [1]. To derive continuous MFT expressions, we use nonparametric Gaussian process regression. We apply our method to assess the fingerprint CV of Cu(100) in iodine-containing, alkaline solutions. The simulations offer new insights into the competitive adsorption between I and OH. Additionally, we benchmark our method by comparing a mean-field model to grand canonical lattice Monte Carlo simulations for the well-studied system Ag(100) in Br-containing electrolyte [2,3].

We analyze in detail the respective (dis-)advantages of both methods.

[1] N.G. Hörmann *et al.*, *J. Chem. Theory Comput.* **2021**, 17, 1782
[2] M.T.M. Koper, *J. Electroanal. Chem.* **1998**, 450, 189-201
[3] M. Nakamura *et al.*, *Phys. Rev. B* **2011**, 84, 165433

O 8.8 Mon 12:30 S054

Neural network surrogates for kinetic Monte Carlo models of electrocatalytic surfaces — •YOUNES HASSANI ABDOLLAHI^{1,2}, JÜRGEN FUHRMANN³, and SEBASTIAN MATERA^{1,2} — ¹Institut f. Mathematik, Freie Universität Berlin, Arnimallee 6, 14195 Berlin, Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ³Weierstraß-Institut f. Angewandte Analysis u. Stochastik, Mohrenstr. 39 10117 Berlin, Germany

The kinetic Monte Carlo method (kMC) is the physically most sound approach for addressing the kinetic interplay of elementary processes at electrocatalytic surfaces but also comes at high computational costs. Therefore, computationally efficient surrogate models are highly desirable which allow the utilization of kMC simulation results in coarser scale simulations.

Using the oxygen reduction reaction on Pt(111) as a prototypical example, we investigate regression neural networks as surrogates to reproduce the stationary TOF as a function of all reaction conditions, i.e. electrostatic potential, concentrations, and temperature. We found that a relatively shallow perceptron with 2 layers of 32 and 32 neurons, respectively, and SiLU activation functions serve as an appropriate choice. We demonstrate the performance of this model with a varying number of kMC data points. Finally, we discuss how this model can be incorporated into a multiscale modeling approach, which addresses the interaction of transport and kinetics.