O 32: Poster: Solid-Liquid Interfaces

Time: Tuesday 18:00–20:00 Location: Poster C

O 32.1 Tue 18:00 Poster C

Molecular dynamics simulations of dicalcium silicate - water interfaces by High-Dimensional Neural Network Potentials — •Bernadeta Prus[1,2] and Jörg Behler[1,2] — [1]Theoretische Chemie II, Ruhr-Universität Bochum, Germany — [2]Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, Germany

In recent years, there has been a growing utilization of High-Dimensional Neural Network Potentials (HDNNP) based on Density Functional Theory (DFT) calculations to enable high-quality molecular dynamics simulations of water interactions with a variety of solid minerals. This study explores the case of dicalcium silicate (Ca_2SiO_4), which is important in many fields. This chemical compound exhibits five polymorphic states, the low-temperature polymorph, denoted as γ, is naturally occurring in the Calcio-olivine mineral. The primary focus of this research is to compare the reactivity in contact with water of different terminations along the [010] surfaces of the γ polymorph of dicalcium silicate. The chosen computational approach allows the development of a single HDNNP suitable for molecular dynamics simulations for all distinct interfaces significantly reducing the computational time.

O 32.2 Tue 18:00 Poster C

Constructing High-Dimensional Neural Network Potentials for Oxide-Water Interfaces — •Jan Elsner and Jörg Behler — Theoretische Chemie II, Ruhr-Universität Bochum, Germany, and Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, Germany

Oxide-water interfaces are promising systems for catalytic water splitting, a process of significant interest due to its potential in sustainable hydrogen production. However, the complex nature of such interfaces and long time scales associated with dynamical processes presents a substantial theoretical challenge. High-Dimensional Neural Network Potentials (HDNNPs) provide a solution to these challenges by enabling atomistic simulations with DFT-level accuracy at only a fraction of the computational expense. We present the construction of a HDNNP suitable for studying oxide-water interfaces with the overarching goal to utilize these HDNNPs for atomistic simulations of these interfaces.

O 32.3 Tue 18:00 Poster C

Development of high-dimensional neural network potentials for solid-liquid interfaces — •Daniel Trzewik[1,2], Moritz R. Schäfer[1,2], Alexander L. Knoll[1,2], and Jörg Behler[1,2] — [1]Theoretische Chemie II, Ruhr-Universität Bochum, Germany — [2]Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, Germany

Solid-liquid interfaces play an essential role for chemical processes involving catalysis, electrochemistry and materials science. Modelling of these interfaces with first-principles methods remains computationally demanding due to the required system size. Machine learning potentials offer an efficient alternative at similar level of accuracy. The utilized high-dimensional neural network potentials (HDNNPs) in this project allow for a detailed investigation of solid-water interfaces. Molecular dynamics simulations reveal the structural arrangement and properties of the interface water as well as the interaction with the surface.

O 32.4 Tue 18:00 Poster C

Detection of surface intermediates for oxygen evolution on hematite using operando sum frequency spectroscopy — •Yuke Yang, Yujin Tong, and R. Kramer Campen — Faculty of Physics, University of Dusiburg-Essen, 47057 Duisburg, Germany

Hematite (α-Fe_2O_3) is a photoanode material that is widely studied for photoelectrochemical oxygen evolution (OER) due to its abundance, stability, non-toxicity, etc. However, the mechanism of OER on hematite that limits its performance is still undetermined. There is still controversy over single- and multi-hole mechanisms depending on the sample and electrolyte. Methods to probe the OER mechanism are indirect and thus possible control of the mechanism by the change in the sample is difficult to infer. Vibrational sum frequency spectroscopy (VSFS) is an interface-specific technique for systems containing bulk phases with inversion symmetry, which allows the direct observation of intermediates. Our VSFS results reveal the bias-dependent (dis)appearance of a succession of intermediates such as Fe-OH, Fe=O, and Fe-OOH. The results unambiguously show that the OER on our sample proceeds via a single-hole mechanism at pH 12.8. Additionally, we observe a bias-dependent surface phonon mode at around 650cm-1 due to lattice distortion, which may be related to the polaron formation and transport. Because of femtosecond pulses in the VSFS measurement, this work also suggests a path toward resolving chemical dynamics on ultrafast timescales.

O 32.5 Tue 18:00 Poster C

Influence of Cholic Acid and 1-Methylbenzimidazole on Cell Performance in Water-Based Dye-Sensitized Solar Cells — •Leon Rosenbecker, Daniel Holzhacker, and Derck Schlettwein — Institut für Angewandte Physik, Justus-Liebig-Universität Gießen

Dye-Sensitized Solar Cells (DSSCs) present an environmentally friendly low-cost photovoltaic concept, interesting under conditions of low light intensity and, in particular, for indoor applications. However, commonly used materials such as platinum at the counter electrode, acetonitrile as the solvent, and cobalt complexes as the redox mediator can be considered problematic. In this work, DSSCs with aqueous solutions of readily available 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as the redox mediator were prepared. To suppress undesired recombination, we studied cholic acid (CA) as a co-adsorbate, 1-methylbenzimidazole (MBI) as an electrolyte additive, or a combination of both. CA as a co-adsorbate improved both the short-circuit current density (jsc) and fill factor (FF) while not affecting the open-circuit voltage (Voc) up to a concentration of 7.5 mM in the dye bath. In case MBI was used as the additive in the electrolyte, also the Voc was improved, while jsc and FF were found to be higher than for CA. Increasing the MBI concentration from 0.1 M up to 0.4 M steadily increased the performance. A combination of both additives further increased the short-circuit current density while not sacrificing on the other cell characteristics.

O 32.6 Tue 18:00 Poster C

Comparison of PBE-, RPBE-, and RPBE-D3-approximation for diffusion energy barriers of S_{ad} and CH_3S_{ad} on clean and halogen-covered Cu(100) surfaces — •Falk Wendorff and Eckhard Pehlke — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

In density functional calculations often different approximations to the exchange-correlation energy functional are appropriate depending on the particular type of physical system. While the approximation by Perdew, Burke and Ernzerhof, PBE-GGA [1], is widely applied in surface calculations, water is known to be overstructured when using PBE-GGA and other functionals are preferable [2]. Thus, as a prerequisite for future studies of diffusion at electrochemical interfaces (motivated by [3]), we have investigated how much the diffusion energy barriers of S_{ad} and CH_3S_{ad} on clean and halogen-covered Cu(100) surfaces versus vacuum change, when using RPBE [4], without and with additional empirical correction for van der Waals interactions [5] instead of PBE. The calculations have been carried out with PWscf and PWneb from Quantum ESPRESSO [6].

[1] J.P. Perdew *et al.*, Phys. Rev. Lett. **77**, 3865 (1996).
[2] A. Groß, S. Sakong, Chem. Rev. **122**, 10746 (2022).
[3] Y.-C. Yang *et al.*, Langmuir **28**, 14143 (2012).
[4] B. Hammer *et al.*, Phys. Rev. B **59**, 7413 (1999).
[5] S. Grimme *et al.*, J. Chem. Phys. **132**, 154104 (2010).
[6] P. Giannozzi *et al.*, J. Phys. Condens. Matter **21**, 395502 (2009), *ibid.* **29**, 465901 (2017).

O 32.7 Tue 18:00 Poster C

DFT study of S subsurface diffusion on c(2×2)-Br covered Ag(100) — •Sönke Buttenschön, Jannik Thomas, and Eckhard Pehlke — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

In their video-STM study of the diffusion of sulfur adatoms on c(2×2)-Br covered Ag(100), Rahn and Magnussen [1] have observed an astounding subsurface diffusion mechanism different from the S_{ad} diffusion within the Br adlayer. They conclude that the S atoms can move within the top Ag layer underneath the c(2×2) halogen adsorbate layer. We have carried through density functional total-energy calculations with PWscf and PWneb from the Quantum ESPRESSO package [2] to examine the diffusion mechanism. The vacancy formation energy in the top Ag layer underneath the halogen away from, and close to the sulfur as well as energy barriers for various relevant elementary diffusion hops are presented.

Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), project 504552981.

[1] B. Rahn, O. M. Magnussen, J. Am. Chem. Soc. **140**, 9066 (2018).

[2] P. Giannozzi *et al.*, J. Phys. Condens. Matter **21**, 395502 (2009), *ibid.* **29**, 465901 (2017).

O 32.8 Tue 18:00 Poster C

Electrochemical Setup for High-Resolution Hydration Layer Mapping under Potential Control — •Antonia Köhler, Ralf Bechstein, and Angelika Kühnle — Physical Chemistry I, Bielefeld University, Germany

Electrochemical processes are of importance in a wide range of fields such as energy storage, sensors and electrocatalysis. However, many fundamental processes at the electrode-electrolyte interface are still poorly understood. It is widely known that the presence of an applied electric field has a significant influence on the structure at the interface, including the hydration structure. An ideal method for investigating the hydration structure at the molecular level is three-dimensional atomic force microscopy (3D-AFM). Here, we present 3D-AFM data unravelling the hydration structure at the Au(111) surface in the absence of an applied electric field. Furthermore, an electrochemical setup that allows for high-resolution hydration layer mapping under potential control is described. It is based on the 3D-AFM setup, additionally equipped with a three-electrode arrangement connected to a potentiostat. In future, this setup should be capable to map the electrode-electrolyte interface under potential control.

O 32.9 Tue 18:00 Poster C

In-liquid plasma modified Ni expanded metals as hydrogen evolution reaction and oxygen evolution reaction catalyst — •Justus Leist, Lukas Forschner, Timo Jacob, and Albert K. Engstfeld — Ulm University, Institute of Electrochemistry, Ulm, Germany

Applying a sufficiently high voltage to a gas-evolving electrode in an aqueous electrolyte can lead to the formation of a water vapor sheath around the electrode, in which a plasma can be ignited. With this so-called Contact Glow Discharge Electrolysis (CGDE), it is possible to modify the surface structure of an electrode. [1] This in turn can be used to tune the catalytic activity of an electrode, as shown recently for the oxygen evolution reaction (OER) on CGDE modified Ni foams.[2]

In this work, we show the effect of CGDE treated Ni expanded metals on the hydrogen and oxygen evolution reaction. These kinds of electrodes are less prone to bubble inclusion compared to foams. The structural properties of the electrodes are studied by scanning electron microscopy (SEM) and electrochemical methods, such as cyclic voltammetry (CV). The catalytic activity for the OER and HER is investigated using alkaline flow electrolysis cells to mimic industrial operating conditions at different temperatures. The observed trends in reactivity are discussed with respect to the structural changes obtained due to the CGDE and their relationship with oxidation states before and the temperature during HER and OER.

[1] Artmann et al. *ChemPhysChem* **22** (2021) 242. [2] Hausmann et al. *Advanced Energy Materials* **12** (2022) 38.

O 32.10 Tue 18:00 Poster C

Classical and ab initio simulations of the gold - water interface including instantaneous polarisation effects — •Elspeth Smith and Marialore Sulpizi — Ruhr Universität Bochum, Bochum, Germany

Electronic polarisation plays a huge role in the structure and dynamics of many systems, including metal-electrolyte interfaces, and its inclusion requires careful consideration in the setup of any molecular simulation. Typically, classical force fields are not designed to include polarisation effects, however recent advancements in their design have began to accurately simulate instantaneous polarisation effects. In this work, I study gold-water interfaces, employing a recently developed classical model which includes polarisation effects by means of a harmonically coupled core-shell pair for every gold atom. I compare results obtained from this potential with those from ab initio density functional theory simulations to clarify the extent and applicability of the classical polarizable force field. In particular molecular distribution and orientation at the gold/liquid interface is addressed. These techniques are applied to a number of systems, including pure water and water-electrolyte solutions, as well as different geometries of the gold surface, including the (111) and (100) surfaces.

O 32.11 Tue 18:00 Poster C

Benchmarking various ab initio and empirical models to describe electrified water-metal interfaces — •Samuel Mattoso, Mira Todorova, Stefan Wippermann, and Jörg Neugebauer — Max-Planck-Institut für Eisenforschung , Max-Planck-Straße 1, 40237 Düsseldorf

Modeling of electrified water-metal interfaces provides valuable insights into processes at solid/liquid interfaces and suggests routes towards improving clean energy storage and production, corrosion protection and sustainable electrocatalysis. Density functional theory (DFT) is often the tool of choice. A faithful description of metal-water interfaces requires an equally accurate description of both the solid and the liquid phase, in addition to the interface between them. To this end, we explore the impact of different exchange-correlation functionals on relevant bulk properties, such as the water radial distribution function and metal lattice constant. We then use H adsorption to probe our accuracy in describing the Au(111) surface, before employing DFT-based molecular dynamics (MD) simulations to explore the behavior of H at the Au(111)/water interface. In addition, we discuss the employed workflows, encompassing both classical and quantum mechanical, static and dynamic calculations, also under applied bias.

O 32.12 Tue 18:00 Poster C

Temperature-dependent structure formation in the wetting layer of the ionic liquid $[C_2C_1Im][OTf]$ on Au(111) — •Jonas Hauner[1], Hanna Bühlmeyer[1], Simon Trzeciak[2], Julien Steffen[3], Andreas Görling[3], Dirk Zahn[2], and Jörg Libuda[1] — [1]Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany — [2]Computer Chemistry Center, Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Nägelsbachstraße 25, 91052 Erlangen, Germany — [3]Chair of Theoretical Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

We report on in-situ studies on the structure of ultrathin films of the ionic liquid (IL) 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIm][OTf]) on Au(111). The IL thin films were prepared by physical vapor deposition and investigated by scanning tunneling microscopy (STM). We carried out measurements at sample temperatures between 100 K and 350 K on submonolayers and monolayers of [EMIm][OTf]. In this temperature range, we identified three different surface structures. At a submonolayer coverage, [EMIm][OTf] tends to exhibit a 2D-glass structure growing close to gold terraces and the elbows of the herringbone structure of Au(111). Oblique and hexagonal structures of the IL are visible at higher coverage. We investigated the phase transitions and the melting behavior of these wetting layers by temperature dependent STM measurements. Ordered domains are visible above the bulk melting temperature up to 350 K.

O 32.13 Tue 18:00 Poster C

In Situ Study of Ferrocenylundecanethiol Conformations — •Nelli Kremer, Tim Lämmerzahl, and Eckart Hasselbrink — Universität Duisburg-Essen, Essen, Deutschland

Self-assembled monolayers (SAMs) of alkanethiols have been extensively studied as model systems. Many research groups have investigated the structures of the monolayer under ambient conditions. However, structural changes of monolayers on electrode surfaces in electrolyte solutions in comparison to those in air are expected, because of the interaction between the adsorbed molecules and the species in solution. Therefore SAMs with ferrocene-terminated alkanethiols are of great interest since the orientation of the monolayer can be controlled by the redox-active functional group. By applying a potential, the ferrocene group in the monolayer on a gold surface readily exchanges an electron with gold. Previous studies have shown that the angle between the alkyl chain and the normal to the electrode surface changes upon oxidation, while structural reorientation associated with the rotation of the ferrocene group occurs.

Our vibrational sum frequency spectroscopy setup, which provides a resonant narrowband infrared laser pulse for pumping and a broadband femtosecond IR visible pulse pair, enables us to suppress the nonresonant background, which arises due to the metallic surface, and study the intramolecular vibrational energy redistribution (IVR) of 11-Ferrocenylundecanethiol (FcC11) on gold as well as the change of IVR due to the potential-dependent reorientation.

O 32.14 Tue 18:00 Poster C

Tip Classification of High Resolution AFM Imaging in Liquids — •Farzin Irandoost[1], Fillippo Federici Canova[2], Takeshi Fukuma[3], Tobias Dickbreder[4], Franziska Sabath[4], Ralf Bechstein[4], Angelika Kühnle[4], and Adam S. Foster[1,3] — [1]Department of Applied Physics, Aalto University; Helsinki, Finland — [2]Nanolayers Research Computing Ltd., London, England — [3]Nano Life Science Institute (WPI-NanoLSI), Kanazawa University; Kanazawa, Japan — [4]Physical Chemistry I, Bielefeld University, Germany

AFM imaging in liquids is profoundly influenced by scanning height and tip, leading to different 2D maps for the same crystal surface. This study introduces a workflow to discern diverse contrast patterns arising from AFM scanning height and tip dependency. Our workflow, firstly, clusters images in large experimental datasets based on contrast pattern similarities, then links the clusters to relevant free energy simulations based on the tip characteristics.

Success relies on selecting a sensitive latent vector and implementing a robust clustering benchmark. While statistical analysis of Fourier transforms peaks as image descriptors, aided by tSNE and K-means clustering shows promise in qualitative evaluation, developing a quantitative method for large dataset evaluation remains a priority. To this end, we are developing a method for lattice vector extraction out of experimental data, which makes quantitative benchmarks available for periodic crystal images. Also, the latter can be used as an alternative way of describing images containing periodic patterns.

O 32.15 Tue 18:00 Poster C

Development of Novel Substrates for In Situ Time-resolved Infrared Spectroscopy of Catalytically Active Interfaces — •Moritz Thun[1,2], Johannes Dittloff[1,2], and Ian D. Sharp[1,2] — [1]Walter Schottky Institute, Technische Universität München, Germany — [2]Physics Department, TUM School of Natural Sciences, Technische Universität München, Germany

Electrocatalytic reduction of CO_2 to carbon-based fuels can help to reduce atmospheric greenhouse gas concentrations and provide chemical storage capacities for renewable energies. Copper-based electrocatalysts uniquely offer a tunable range of diverse products. However, understanding and controlling the underlying reaction mechanisms requires in situ probes of the catalyst interface under working conditions. To this end, surface enhanced infrared reflection absorption spectroscopy (SEIRAS) can be used to detect the absorption and desorption of molecules on catalytic interfaces in real time.

Here, we demonstrate a stable substrate with SEIRAS-active surface morphology comprising evaporated Ti/Au metal film on nanostructured black silicon, as confirmed by monitoring the monolayer adsorption of 4-methoxypyridine. Next, Ti/Cu on black silicon, stabilized against surface reconstruction by a thin Nafion layer, allowed us to detect adsorbed CO during CO_2 reduction. We aim to detect additional products of the CO_2 reduction on copper by improving material design, enabling its extension to time-resolved SEIRAS measurements. Furthermore, we are exploring the replacement of Au layers with sputtered metal nitrides on black silicon to achieve versatile SEIRAS activity.

O 32.16 Tue 18:00 Poster C

Interfacial behavior of Perchlorate and Sodium Perchlorate in Air/Water Interface at varying concentrations — •Christina Susan Abraham and Marialore Sulpizi — Department of Physics, Ruhr Universität Bochum, 44780 Bochum, Germany

The presence of polarizable anions at aqueous interfaces has important implications that are relevant to both technological and environmental processes. Consequently, there has been a growing interest in understanding the propensity of anions at the air/water interface. While the behavior of the anions at interfaces has been studied, the effect of increased anionic concentrations at the air/water interface is still not very clear. This becomes important particularly in the field of aqueous based electrolytes where higher concentrations would directly affect the voltage window. In this study we have investigated the interfacial behavior of HClO4 and NaClO4 salt solutions employing AIMD simulations. The concentrations explored in this investigation span a spectrum from low (1M) to high (12M). As the salt concentration increases, the ion*water interactions show significant changes, not only in comparison with the lower concentrations but also with respect to the bulk HClO4/NaClO4-water systems.

O 32.17 Tue 18:00 Poster C

Fourth-Generation High-Dimensional Neural Network Potentials for Molecular Chemistry in Solution. — •Djamil Abdelkader Adel Maouene[1,2], Moritz Richard Schäffer[1,2], Moritz Gubler[3], Stefan Goedecker[3], and Jörg Behler[1,2] — [1]Theoretische Chemie II, Ruhr-Universität Bochum, Germany — [2]Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, Germany — [3]Department Physik, Universität Basel, Switzerland

Machine learning has found many applications in the fields of chemistry and materials science, and high-dimensional neural network potentials (HDNNPs) have become an accurate tool to represent the multi-dimensional potential energy surface in atomistic simulations.

Here, we compare the performance of two types of HDNNPs, i.e., 2G-HDNNPs and 4G-HDNNPs, in the description of organic molecules in aqueous solution. While it has been shown for many systems that 2G-HDNNPs are well suited to represent local bonding as a function of the atomic environments, they are not applicable to systems in which long-range charge transfer is important. Such systems can be addressed by 4G-HDNNPs, in which the atomic charges depend on structural or electronic changes even very far away in the system. Using typical organic molecules, the performance of both approaches is illustrated.