

O 69: Poster: Solid-Liquid Interfaces

Time: Wednesday 18:00–20:00

Location: P2/EG

O 69.1 Wed 18:00 P2/EG

Understanding the mechanism of Li-mediated nitrogen reduction reaction — •YUANYUAN ZHOU and JENS K. NØRSKOV — Department of Physics, Technical University of Denmark, Kongens Lyngby, Denmark

Green ammonia production is a key environmental goal. As a crucial step towards this goal, a direct electrocatalytic N₂ reduction (eNRR) by protons and electrons emerges as a highly desirable alternative. However, all pragmatic attempts to develop such an electrochemical route have so far been hindered by invariably low selectivities and large overpotentials. The most reliable method presently is the lithium-mediated eNRR (LiNR) in non-aqueous electrolytes. [J. Choi *et al.* Nat. Commun. 11, 1-10 (2020)] Despite significant progress made to achieve high FE and current density [K. Li *et al.* Science 374, 1593-1597 (2021), S. Li *et al.* Joule, 6, 2083-2101 (2022)], the mechanism of LiNR is yet not fully understood due to so many intricate processes involved ranging from the atomic scale to the macroscopic scale. Moreover, most Li-NRR studies have the limitations of using a sacrificial solvent as proton donors and difficulties in scaling up production in batch reactors. The talk will, address the long-term stability and high activity of PtAu in the HOR process by suppressing the unwanted THF oxidation and improving the tolerance towards CO-poison. Furthermore, the crucial step for achieving an improved understanding the dynamic change of the solid-electrolyte interphase in different LiNR reaction conditions and the effect on the performance.

O 69.2 Wed 18:00 P2/EG

When qualitative do not imply quantitative differences: Analyzing the oxygen reduction reaction using first-principles kinetic Monte Carlo simulations. — •ELIA ZONTA¹, YOUNES HASSANI ABDOLLAHI^{1,2}, KARSTEN REUTER¹, and SEBASTIAN MATERA^{1,2} — ¹Fritz Haber Institute of the Max Planck Society, Berlin, Germany — ²Institute for Mathematics, Freie Universitaet Berlin, Germany, Germany

The oxygen reduction reaction (ORR) is one of the major bottlenecks for the efficiency of fuel cell devices. We implemented a first-principles kinetic Monte Carlo model for this reaction on Pt(111) using a mechanism from literature [1]. This model possesses two reaction pathways contributing to the electrochemical current density. Disabling one of these pathways results in an identical simulated Tafel plot for this reduced model, as compared to the original model with both pathways being active. One might conclude that the turned off pathway is effectively inactive also in the original model and, especially, has no impact on the qualitative kinetics. However, a detailed analysis reveals that both models lead to very different surface coverages and, particularly, exhibit different rate-determining steps. Thus, these qualitative microkinetic differences do not lead to any quantitative differences in the macrokinetic behavior.

[1] R.F. de Moraes, P. Sautet, D. Loffreda, and A.A. Franco, *Electrochim. Acta* 56, 10842 (2011).

O 69.3 Wed 18:00 P2/EG

Electric Double Layer effect on outer-sphere benzyl halides electro-reduction mechanism — •ALEKSANDR KRAMARENKO¹, FELIX STUDDT¹, and EVGENY PIDKO² — ¹Karlsruhe Institute of Technology, Karlsruhe, Germany — ²TU Delft, Delft, The Netherlands

Electrocatalytic CO₂ fixation is one of the most efficient methods of carbon dioxide conversion, which can be carried out at room temperature and pressure. Thus, the fixation of carbon dioxide with electrochemically activated benzyl halides is an environmentally friendly and ambitious method for the synthesis of the most important carboxylic acid derivatives, which are invaluable for pharmaceuticals and fuel production. For these types of processes, electrocatalysis is a key technology, where electrified interfaces are the main object of study and where the electrochemical potential determines the stability of adsorbed particles and the structure of the electric double layer (EDL) on the electrode surface. Therefore, it is important to gain insight into the electrode-electrolyte interface and the rate-determining reaction steps in order to improve electrode material selectivity and product yields. The combination of first principles and molecular dynamics simulations gives us a good understanding at the molecular level of charged interface phenomena and allows us to study elementary chemical pro-

cesses in detail, which sheds light on how to improve electrocatalytic reactivity.

O 69.4 Wed 18:00 P2/EG

Atomistic electric double layer modeling of water/metal interfaces from AIMD and continuum approaches — •SUNG SAKONG and AXEL GROSS — Ulm University, Ulm, Germany

Electrochemical interfaces are typically associated with forming an electric double layer (EDL) whose theoretical modeling requires an appropriate description of the polarization of the electrode and the electrolyte. In principle, ab initio molecular dynamics (AIMD) simulations are the natural choice as they reliably treat the competing water-water and water-metal interactions and explicitly consider the electronic degrees of freedom [1]. However, this approach is computationally still very demanding and only allows simulations of relatively small canonical ensembles for limited simulation times. Thus, there is a need for computationally less demanding but still reliable approaches to model the EDL. By comparing EDL properties calculated from a continuum method based on a grand canonical scheme [2] with ab initio atomistic approaches [3], we will provide an outlook on possible future directions in the EDL modeling [4].

[1] A. Groß and S. Sakong, *Chem. Rev.* **122**, 10746 (2022).

[2] S. Sakong *et al.*, *Curr. Opinion Electrochem.* **33**, 100953 (2022).

[3] S. Sakong, A. Groß, *Phys. Chem. Chem. Phys.* **22**, 10431 (2020).

[4] A. Groß and S. Sakong, *Curr. Opinion Electrochem.* **14**, 1 (2019).

O 69.5 Wed 18:00 P2/EG

Water/InP(001) from Density Functional Theory — •ISAAC AZAHEL RUIZ ALVARADO and WOLF GERO SCHMIDT — Lehrstuhl für Theoretische Materialphysik, Universität Paderborn, Paderborn, Germany

Water adsorption on the In-rich and P-rich InP(001) surface is studied by density functional theory [1]. Single water molecules attach to three-fold coordinated surface In atoms on In-rich surfaces. Dissociative water adsorption is energetically favorable, but hindered by an energy barrier that decreases with increasing water coverage. The oxygen and hydrogen evolution reactions on InP are characterized by overpotentials of the order of 1.7-1.8 and 0.2-0.3 eV, respectively. The In-rich InP surface band edges lie above the redox potential for oxygen and favors hydrogen evolution. Water adsorption is less favorable on P-rich surfaces and characterized by weak physisorption due to charge accumulation between the water O atom and second-layer In surface atoms.

[1] IA Ruiz Alvarado, WG Schmidt, *ACS Omega* 7, 19355 (2022).

O 69.6 Wed 18:00 P2/EG

CO₂ Electroreduction Reactions at Gold and Copper Electrodes in Ionic Liquids — •BJÖRN RATSCHMEIER, GINA ROSS, and BJÖRN BRAUNSCHWEIG — University Münster, Institute of Physical Chemistry, Münster, Germany

Room-temperature ionic liquids (RTIL) can play a major role in CO₂ reduction reactions in mitigation of existing problems of aqueous electrolytes, such as high overpotentials and product selectivity. In this context, we have studied the influence of Au(111), Cu(111) single crystals, as well as Cu enriched Au(111) electrodes prepared by Cu underpotential deposition with Cu coverages of 1/3, 2/3 and 3/3, in 1-butyl-3-methylimidazolium trifluorosulfonylimide [BMIM][NTf₂] for CO₂RR. For Au and Cu enriched Au electrodes we observed high selectivity for H₂ and CO formation, with onset potentials at around -1.0 V vs SHE and a H₂/CO syngas ratio between 0.2-0.4, whereas for Cu only H₂ and traces of CO were detected until 1.5 V. By increasing the degrees of coverage of Cu on Au, we were able to modulate the syngas ratio to an optimum ratio of about 1.8 for a monolayer of Cu on Au(111), which approaches the ideal ratio of 2 for Fischer-Tropsch synthesis of hydrocarbons.

O 69.7 Wed 18:00 P2/EG

Exploring charge transfer at electrified interfaces via ab initio thermopotentiostat molecular dynamics — •FLORIAN DEISSENBECK¹, MIRA TODOROVA¹, CHRISTOPH FREYSOLDT¹, JÖRG NEUGEBAUER¹, and STEFAN WIPPERMANN^{1,2} — ¹Max-Planck-Institut für Eisenforschung, Düsseldorf — ²Philipps-Universität Marburg

Developing accurate simulation techniques to explore and predict structural properties and chemical reactions at electrified liquid/solid interfaces will be critical to surmount materials-related challenges in the context of energy conversion and storage. Exciting progress in recent years allows us now to realistically describe electric fields at charged surfaces from first principles. Building on these techniques, we recently introduced a “thermopotentiostat”: a novel approach to control the electrode potential in molecular dynamics (MD) simulations [1]. We demonstrate how to implement the thermopotentiostat into density-functional codes [2]. Using *ab initio* thermopotentiostat MD simulations, we explore the splitting of liquid water and charge transfer reactions at electrified Si and Ge surfaces.

[1] F. Deifßenbeck, C. Freysoldt, M. Todorova, J. Neugebauer, S. Wippermann, *Phys. Rev. Lett* **126**, 136803 (2021)

[2] F. Deifßenbeck, S. Wippermann, arXiv:2209.04363

O 69.8 Wed 18:00 P2/EG

Density functional calculations of diffusion paths of methyl thiolate on c(2x2)Cl- and Br-covered Cu(100) surfaces — ●FALK WENDORFF and ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

The surface dynamics of methyl thiolate on Cu(100) surfaces has been studied with video-STM in an electrochemical environment by Yang et al. [1]. Here we present density functional calculations for the diffusion paths and diffusion energy barriers using PWscf and PWneb from the Quantum ESPRESSO package [2]. The diffusion path of CH_3S_{ad} substitutionally adsorbed on the c(2x2)Cl- or Br-Cu(100) surface without further halogen vacancies has been inspired by the ‘rotation’ diffusion path of S_{ad} on these surfaces [3]. Additional vacancies in the halogen adlayer enable further diffusion paths of CH_3S_{ad} with significantly lower energy barriers. In case of the Cl coadsorbate the barrier decreases from 1.2 eV to 0.7 eV and in case of Br from 1.6 eV to 0.8 eV. The dipole moment change between the adsorption position and the transition state is negative, which is consistent with the experimental observations by Yang et al. that a more positive sample potential leads to a higher energy barrier [1,4].

[1] Y.-C. Yang *et al.*, *Langmuir* **28**, 40, 14143–14154 (2012).

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

[3] B. Rahn *et al.*, *Angew. Chem. Int. Ed.* **57**, 6065 (2018).

[4] M. Giesen *et al.*, *Surface Science* **595**, 127–137 (2005).

O 69.9 Wed 18:00 P2/EG

Growth and structure formation of [EMIm][OTf] on Au(111) — JONAS HAUNER¹, ●HANNA BÜHLMAYER¹, SIMON TRZECIAK², JULIEN STEFFEN³, DIRK ZAHN², ANDREAS GÖRLING³, and JÖRG LIBUDA¹ — ¹Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany — ²Computer Chemistry Center, Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Nägelsbachstraße 25, 91052 Erlangen, Germany — ³Chair of Theoretical Chemistry, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

The growth mechanisms of ultrathin ionic liquid (IL) films have recently received considerable attention. We report on *in situ* studies of 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 various sample temperatures and coverages, and identified three different surface structures. At low coverage, [EMIm][OTf] tends to exhibit a 2D-glass structure growing close to gold terraces and the elbows of the well-known herringbone structure of Au(111). Oblique and hexagonal structures of the IL are visible at higher coverage. With temperature-dependent measurements, possible phase transitions and melting points of [EMIm][OTf] were investigated. Small glass-like islands of IL melt at 190 - 200 K resulting in a mobile phase of 2D liquid/gas. Islands with highly ordered structures are stable up to 300 K.

O 69.10 Wed 18:00 P2/EG

In situ surface X-ray diffraction studies of Pt(110) — ●FINN SCHRÖTER¹, JAN OLE FEHR¹, TIMO FUCHS¹, JAKUB DRNEC², MARTA MIROLO², DAVID HARRINGTON³, and OLAF MAGNUSSEN¹ — ¹Christian-Albrechts Universität zu Kiel — ²European Synchrotron Radiation Facility — ³University of Victoria

The surface oxidation of platinum is an important process in the degradation of platinum electrocatalysts in PEM fuel cells, limiting their lifetime. Its atomic-scale mechanism has been addressed in extensive studies by structure-sensitive *in situ* techniques. However, these studies up to now have been restricted to room temperature, whereas real fuel cells operate at elevated temperatures of 60°C or higher. We here present first temperature-dependent of the surface oxidation of Pt(111) electrodes in perchlorate solution by *in situ* high-energy surface X-ray diffraction (HESXRD) The measurements were performed at the ID31 beamline of the European Synchrotron Radiation Facility using photon energies of 70 keV. The kinetics of oxidation-induced extraction of Pt atoms out of the surface was quantitatively determined and correlated with the electrochemical charge transfer measured simultaneously in the experiments. The work was funded by the Deutsche Forschungsgemeinschaft via grant 418603497 and the BMBF via project 05K19FK3.

O 69.11 Wed 18:00 P2/EG

The self-assembly process of helical molecules — THI N. HA NGUYEN¹, F. GÜNTHER², K. PREIS¹, ●J. KELLING¹, C. TEGENKAMP¹, and S. GEMMING¹ — ¹Institut für Physik, TU Chemnitz, Chemnitz — ²Instituto de Fisica de Sao Carlos, Universidade de S\~{a}o Paulo, Sao Carlos, Brazil; Instituto de Geociencias e Ciencias Exatas, Universidade Estadual Paulista, Rio Claro, Brazil

Helical polyalanine (PA) molecules gathered a lot of interest as the propagation of electrons along the helical backbone structure comes along with spin polarization. Via liquid and solid scanning tunneling microscopy (STM) we studied the ordering of physisorbed and chemisorbed PA molecules on HOPG and Au surfaces. While enantiopure PA molecules adsorb in a hexagonally close-packed structure, we found heterochiral dimers with a rectangular unit cell for DL-PA. Despite the steric hindrance, the packing density of the DL-PA heterophase is increased by 25% compared to the enantiopure PA structure. Apparently, this is achieved by shifting D- and L-PA along their helical axis. Moreover, the alpha-helix structure of the PA molecules seems to be preserved; thus, electrostatic forces indeed play an important role for the formation and stabilization of the helical structure. In parallel, the interactions between PA homo- and heterochiral pairs were analyzed by van-der-Waals-corrected DFT-based tight binding calculations. Denser packing geometries can be reached by heterochiral PA pairs. Second, coarse-grained classical potentials were derived from the DFTB data, and the different PA phases seen in STM were also successfully obtained from Monte-Carlo simulations.

O 69.12 Wed 18:00 P2/EG

DFT calculation of the S_{ad} diffusion energy barriers on Ag(100) in the presence of Br coadsorbates — ●SÖNKE BUTTENSCHÖN and ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

Coadsorbed halides are known to affect the adatom diffusion on metal surfaces [1]. As a prerequisite for theoretical modelling of the S_{ad} diffusion on Ag(100) as a function of Br coverage, we have calculated the effect of single and multiple Br coadsorbates on the S_{ad} adsorption energy as well as on the energy at the transition geometry along the S_{ad} diffusion path for various Br coadsorbate configurations with Br coverages up to 0.25. The density functional total-energy calculations have been carried through with PWscf and PWneb from the Quantum ESPRESSO package [2]. The dipole moment of S_{ad} is negative. It is larger in magnitude at the transition state (TS) than at the adsorption position. Averaged over the considered S-Br configurations the absolute value of the S_{ad} dipole moment has a tendency to decrease with Br coverage in qualitative agreement with a depolarization model. After similar averaging, for the TS configurations the superposition of individual S_{TS} -Br pair interaction energies tends to overestimate the actual S_{TS} -Br interaction. Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation), project 504552981.

[1] B. Rahn, O. M. Magnussen, *ChemElectroChem* **5**, 3073 (2018).

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

O 69.13 Wed 18:00 P2/EG

Correlation between electrostatic and hydration forces on silica and gibbsite surfaces: An Atomic Force Microscopy Study — ●IGOR SIRETANU, ARAM KLAASSEN, and FRIEDER MUGELE — Physics of Complex Fluids Group, MESA+ Institute, Faculty of Science and Technology, University of Twente, PO Box 217, 7500 AE Enschede, The Netherlands

The balance between hydration and Derjaguin Landau Verwey Overbeek forces at solid-liquid interfaces controls many processes, such as colloidal stability, electrochemistry and ion adsorption. Yet, the hydration forces origin and their relation to the surface charge density controlling the continuum scale electrostatic forces are poorly understood. We argue that these two types of forces are largely independent of each other. Here we performed AFM using intermediate-sized tips that enable the simultaneous detection of DLVO and oscillatory hydration forces at the interface between gibbsite:silica-aqueous electrolyte interfaces. We extract surface charge densities from forces using DLVO theory in combination with a charge regulation boundary conditions for variable pHs and salt concentrations. We simultaneously observe both DLVO and oscillatory hydration forces for an individual crystalline gibbsite particle and the amorphous silica for all fluid compositions. While the diffuse layer charge varies with pH as expected, the oscillatory hydration forces are largely independent of pH and salt concentration, supporting our hypothesis that both forces indeed have a very different origin. We rationalize this based on the distribution of OH groups available for H-bonding on the two distinct surfaces.

O 69.14 Wed 18:00 P2/EG

The interfacial (electronic) structure of InP(001) in contact with electrolytes studied via computational Reflection Anisotropy Spectroscopy — •VIBHAV YADAV¹, MARGOT GUIDAT^{1,2}, MARIO LÖW², JONGMIN KIM^{1,2}, HOLGER EUCHNER¹, and MATTHIAS M. MAY^{1,2} — ¹Institute of Physical and Theoretical Chemistry, University of Tübingen — ²Institute of Theoretical Chemistry, University of Ulm, Germany

Controlling the electrochemical interface of III-V semiconductors is of great relevance for hydrogen production in Photoelectrochemical water splitting devices. Under operating conditions InP surfaces in contact with the electrolyte can undergo polymerization or dissolution, with the possible formation of In-O-In as charge recombination centers [1,2]. In this work, we vary the oxygen adatom coverage on In-rich and P-rich InP(001) surfaces using Density-functional Theory. Furthermore, we show that combining computational and experimental Reflection Anisotropy Spectroscopy has the potential to provide a better understanding of InP surfaces and their (electronic) structure under applied potentials. [1] May MM, Lewerenz HJ, Lackner D, Dimroth F, Hannappel T. Nat Commun 15, 2015, 9 (15), 8286. [2] Löw M, Guidat M, Kim J, May MM, RSC Adv. 2022, 12 (50), 32756.