O 27: Solid-Liquid Interfaces: Reactions and Electrochemistry I

Time: Tuesday 10:30–13:00 Location: H4

O 27.1 Tue 10:30 H4

Combining electrochemical scanning tunneling microscopy with force microscopy — •Andrea Auer[1,2] and Franz J. Giessibl[2] — [1]Institute of Physical Chemistry, University of Innsbruck, Austria — [2]Institute of Experimental and Applied Physics, University of Regensburg, Germany

Atomic force microscopy (AFM), which can be performed simultaneously with scanning tunneling microscopy (STM) using metal tips attached to self-sensing quartz cantilevers (qPlus sensors) [1], has advanced the field of surface science by providing unprecedented spatial resolution under ultra-high vacuum conditions. The simultaneous performance of AFM and STM with atomic resolution in an electrochemical cell offers new possibilities for local imaging of electrode structures. Here, we present a combined AFM/STM instrument realized with a qPlus sensor and a custom-built potentiostat for electrochemical applications. Graphite was atomically resolved in both STM and AFM channels in acidic electrolytes [2]. The difference in contrast between AFM and STM images demonstrate the ability to measure conductance at the Fermi level (STM) but also the total charge density (AFM) in an electrochemical environment. This allows us to study important electrode processes that involve a change in charge density, such as adsorption, intercalation, or oxidation processes, and their atomic contrasts in more detail.

[1] F.J. Giessibl, Rev. Sci. Instrum. 90, 011101 (2019). [2] A. Auer, B. Eder and F.J. Giessibl, J. Chem. Phys. 159, 174201 (2023).

O 27.2 Tue 10:45 H4

Small change huge effect – Tuning CO2 reduction to Formaldehyde — •Michael Busch — Luleå University of Technology, Luleå, Sweden

CO_2 reduction is a central technology for energy conversion and as access route to basic feedstock for the chemical industry. Unfortunately, its potential is still hindered by high overpotentials and low selectivity towards post-CO products. So far, post-CO products can only be accessed reliably either through Cu catalysts or selected single atom catalysts like metal phthalocyanines. Recent experiments indicate, that Co phthalocyanine is even able to form formaldehyde in good yields.[1]

Building on these experiments, we will explore the underlying origin of this surprising finding using density functional theory (DFT) computations.[1,2] Our results indicate, that the pure Co phthalocyanine complex does not show any unexpected selectivity. However, upon adjusting potential and pH also the catalyst's protonation state is changed. This minor change in turn shifts the selectivity towards formaldehyde. These surprising insights provide an important puzzle piece for the rational design of improved CO_2 reduction catalysts.

[1] A. Singh, M. Busch, M. Robert et al. *J. Am. Chem. Soc.* **146** (2024) 22129.

[2] R. Khakpour, K. Farshadfar, M. Busch et al. *J. Phys. Chem. C.* **128** (2024) 5867.

O 27.3 Tue 11:00 H4

Quantitative Modeling of the Coordination and Solvation Dynamics of Electrically Charged Solvated Systems via Molecular Dynamics Simulations — •Zhenyu Wang, Mira Todorova, Christoph Freysoldt, and Jörg Neugebauer — Max Planck Institute for Sustainable Materials

Chemical and biological processes in water are influenced by the dynamics of the water solvation shell of ions. Despite progress in understanding ion solvation dynamics, the structural changes in the solvation shell with varying charge states remain underexplored. This study uses atomistic molecular dynamics calculations to investigate the solvation shell of a Na ion, as a prototype model, focusing on changes in water molecule arrangement due to charge variations. Gaussian process regression is used to analyze the reorientation of H_2O molecules as the Na-ion charge is changed from negative to positive. Results show significant effects of the ionic charge on the coordination to neighboring water molecules, which form distinct polyhedral structures, such as tetrahedra, triangles, pyramids, and octahedra. These formed patterns can be effectively characterized by using the H_2O-H_2O distance and H_2O-H_2O-H_2O angle. At the highest positive charge, H_2O molecules form an octahedral configuration, transitioning to pyramidal and triangular bipyramidal structures as the charge decreases. At a neutral charge, the solvation shell reveals maximum dispersion, which transitions into a single cluster at negative charges. This study provides valuable insights into ion solvation behavior and significantly enhances the understanding of ion solvation dynamics in aqueous environments.

O 27.4 Tue 11:15 H4

Field-induced water autoionization in two- and three-dimensions — •Yair Litman and Angelos Michaelides — University of Cambridge, Cambridge, U. K.

The behaviour of water under an electric field critically influences the performance of numerous energy conversion and storage devices and remains a subject of active investigation. Recent experiments have shown that at electric field strengths exceeding 10^8V/Å, the water dissociation reaction ($2H_2O \rightleftharpoons H_3O^+ + OH^-$) is significantly accelerated, a phenomenon known as the (secondary) Wien effect [1].

In this work, we employ the modern theory of polarization to perform (periodic) *ab initio* molecular dynamics simulations of water under external electric fields, both in bulk and under nanoconfinement. Our simulations reveal that electric fields facilitate the water dissociation reaction by not only reducing the enthalpy of the reaction but also by increasing the corresponding entropic contribution. Furthermore, we demonstrate that geometric constraints imposed by a 2D confinement can amplify the field-induced reaction rates. These findings highlight the importance of entropy changes in field-induced aqueous reactions and propose nanoconfinement as a promising avenue for enhancing the efficiency of electrocatalytic reactions.

[1] J. Cai. *et al.*, Nat. Commun **13**, 5776 (2022)

O 27.5 Tue 11:30 H4

Predicting Electrocatalytic Urea Synthesis Using a Two-dimensional Descriptor — •Amy Wuttke and Alexander Bagger — Department of Physics, Technical University of Denmark

Electrochemical synthesis routes offer a sustainable alternative to conventional fossil-based processes for producing chemical commodities. An example is the crucial fertiliser urea ($CO\,(NH_2)_2$), that can be synthesised by co-reducing CO_2 and nitrite (NO_2^-) on transition metal surfaces [1]. This reaction also serves as a model system for studying electrochemical CN-coupling. However, achieving high selectivity toward urea remains a significant challenge due to the complexity of competing reaction pathways.

In this talk, a predictive framework for urea selectivity is presented based on adsorption energies as descriptors without referring to a full reaction mechanism [2]. Using Density Functional Theory, we calculated 10 adsorption energies as potential descriptors on 19 transition metal surfaces. Through Principal Component Analysis, this high-dimensional dataset is reduced to two key descriptors: *H and *O adsorption energies. Our findings demonstrate that these descriptors effectively explain urea selectivity on transition metals, offering a simplified approach to guide catalyst design.

[1] M. Shibata et al., J. Electrochem. Soc., 145(2), 595-600 (1998), doi: [10.1149/1.1838309].

[2] A. Wuttke and A. Bagger, Predicting Electrocatalytic Urea Synthesis Using a Two-Dimensional Descriptor, in review. Research Square Preprint, Jul. 17, 2024, doi: [10.21203/rs.3.rs-4749942/v1].

O 27.6 Tue 11:45 H4

Effect of water on the diffusion barriers of S_{ad} on Cu(100) and Ag(100): DFT-calculations — •Falk Wendorff, Sönke Buttenschön, and Eckhard Pehlke — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel, Germany

Diffusion of adatoms at the electrochemical interface is affected by the electrolyte in various ways. Here we focus on the effect of pure water at the pzc on the diffusion barriers within Transition State Theory. Due to the dynamics of the H_2O molecules in liquid water the process is complicated to simulate. We have investigated the diffusion of a sulfur adatom on Cu(100) and Ag(100) surfaces in the presence of water using explicit water molecules in DFT simulations. The calculations have been carried out with PWscf and PWneb from Quantum ESPRESSO [1]. We have started from initial water layers generated by the Water Structure Creator by Dávila López *et al.* [2] and performed subsequent MD simulations of the water molecules at fixed sulfur and substrate positions. The results show that water lowers the diffusion barriers of sulfur on the metal surfaces compared to the interface versus vacuum.

Funded by the Deutsche Forschungsgemeinschaft project 504552981.

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

[2] A. C. Dávila López *et al.*, J. Chem. Phys. **155**, 194702 (2021).

Invited Talk O 27.7 Tue 12:00 H4

Ultrafast electrochemistry beyond the RC time constant — •Yujin Tong — Universität Duisburg-Essen, Duisburg

Electrochemistry relies on charge transfer, which can occur on time scales from femtoseconds to seconds or longer. Traditional electrochemical detection methods are limited in their ability to study ultrafast processes such as solvent reorganization and electron tunneling. This presentation focuses on the advancements and challenges in ultrafast electrochemistry, specifically exploring processes occurring on timescales shorter than the RC time constant. Traditional electrochemical processes have typically been studied over longer timescales, often constrained by limitations in mass diffusion and hardware capabilities. However, recent developments in ultrafast laser technology and femtochemistry have enabled the observation of rapid processes with femto /pico second time resolution at electrochemical interfaces, such as ultrafast potential relaxation in electric double layers and the dynamics of solvated electrons [1-3]. [1] G. Zwaschka, F. Lapointe, R. K. Campen, Y. Tong, Curr. Opin. Electrochem. 29, 100813 (2021) [2] F. Lapointe, M. Wolf, R. K. Campen, Y. Tong, J. Am. Chem. Soc. 142, 18619-18627 (2020) [3] Z. Huang, M. Bridger, O. A. Naranjo-Montoya, A. Tarasevitch, U. Bovensiepen, Y. Tong, R. K. Campen, arXiv preprint, doi: 10.48550/arXiv.2304.06684 (2023)

O 27.8 Tue 12:30 H4

Deciphering the Capacitance of the Pt(111)/Water Interface: A Micro- to Mesoscopic Investigation by AIMD and Implicit Solvation — •Lang Li, Karsten Reuter, and Nicolas Hörmann — Fritz-Haber-Institut der MPG, Berlin

We use *ab initio* molecular dynamics simulations based on density-functional theory to revisit the enigmatic capacitance peak of the electrified Pt(111)/water interface around the potential of zero charge. We demonstrate that counterbalancing the electronic excess charges with partially charged hydrogen atoms constitutes a computationally efficient approach to converged interfacial water structures. The thus enabled detailed analysis of the interfacial water response clarifies that the peak in the capacitance is predominantly due to structural reorientation, although its magnitude is significantly increased by strong internal electronic polarization, also known as charge transfer (CT). We find that CT is more complex than previously thought, resulting from the interplay between chemisorbed water and depolarization effects from surrounding water. Finally, we demonstrate that quantitative agreement with the experimental peak can be achieved through inclusion of the interfacial response into an implicit solvent model for the extended part of the double layer. This suggests that such models can accurately reproduce screened interfacial fields as a function of potential, despite their notoriously small native capacitance. [1] L. Li, K. Reuter, N. G. Hörmann, accepted by ACS Electrochem.

O 27.9 Tue 12:45 H4

Efficient periodic density functional theory calculations of charged molecules and surfaces using Coulomb kernel truncation — •Sudarshan Vijay[1], Martin Schlipf[1], Henrique Miranda[1], Ferenc Karsai[1], Martijn Marsman[1], and Georg Kresse[1,2] — [1]VASP Software GmbH, Berggasse 21, 1090 Vienna, Austria — [2]Faculty of Physics and Center for Computational Materials Science, University of Vienna, Kolingasse 14-16, A-1090 Vienna, Austria

Density functional theory (DFT) calculations of charged molecules and surfaces are critical to applications in electro-catalysis. Periodic DFT implementations such as the Vienna ab-initio Simulation Package (VASP) compute the electrostatic potential under 3D periodic boundary conditions, which necessitates charge neutrality. In this work, I will discuss our recent implementation of 0D and 2D periodic boundary conditions. Unlike 3D boundary conditions, our implementation allows for calculations of charged molecules and surfaces. We implement these boundary conditions using the Coulomb kernel truncation method. We compute the electrostatic potential under 0D and 2D boundary conditions by selectively subtracting unwanted long range interactions from the potential under 3D boundary conditions, removing the need for performing any Fourier transforms in padded supercells. To illustrate the computational efficiency of our method, we perform large supercell calculations of the formation energy of a charged chlorine defect on an NaCl(001) surface and perform long time-scale molecular dynamics simulations on an Au(211) | water electrode-electrolyte interface.