

O 73: Metal Substrates: Adsorption and Reaction of Small Molecules II

Time: Thursday 10:30–12:30

Location: CHE 91

O 73.1 Thu 10:30 CHE 91

Benchmarking machine-learned interatomic potentials for reactive surface dynamics at metal surfaces: accuracy vs speed — ●WOJCIECH STARK¹, JULIA WESTERMAYER¹, CAS VAN DER OORD², LINGJUN ZHU³, BIN JIANG³, GABOR CSANYI², and REINHARD MAURER¹ — ¹University of Warwick, UK — ²University of Cambridge, UK — ³University of Science and Technology of China, China

Machine-learned interatomic potentials (MLIP) have become widely used tools to accelerate *ab initio* molecular dynamics simulations in materials science. Many promising MLIPs emerged recently, ranging from simple linear models to deep neural networks (DNN), differing in stability, accuracy, and inference time. Reactive scattering dynamics are highly sensitive to potential corrugation and low reaction probabilities require extensive ensemble averaging. Therefore, MLIPs need to combine smooth and accurate landscapes with extremely efficient inference. In this study, we compare different families of MLIPs, from atomic cluster expansion (ACE), message-passing based Neural Network SchNet and embedded atom neural networks (EANN), to equivariant neural networks such as PaiNN and MACE on the example of reactive molecular hydrogen scattering on copper. We compare these diverse methods by measuring accuracy and inference performance directly on dynamical observables. This provides a detailed picture of MLIP accuracy, speed, and learning rate that goes beyond simple train/test error analysis.

O 73.2 Thu 10:45 CHE 91

Electrooxidation of 1-cyclohexyl ethanol on Pt single crystal electrodes — ●LUKÁŠ FUSEK^{1,2}, MARIA MINCHOVÁ³, VALENTÍN BRIEGA-MARTOS³, LUKAS FROMM¹, EVANIE FRANZ¹, JUNTAO YANG¹, ANDREAS GÖRLING¹, SERHIY CHEREVKO³, PETER WASSERCHIED^{1,3}, OLAF BRUMMEL¹, and JÖRG LIBUDA¹ — ¹Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany — ²Charles University, Prague, Czech Republic — ³Helmholtz-Institut Erlangen-Nürnberg, Germany

Isopropanol can be used as a liquid organic hydrogen carrier (LOHC), which is compatible with direct alcohol fuel cells. However, it has a limited hydrogen storage capacity. 1-Cyclohexyl-ethanol is a potential LOHC with an increased hydrogen storage capacity with two different functionalities, the alcohol (2 H+) and the cyclohexyl functionality (6 H+). In this study, we investigated the electrooxidation of 0.02 M 1-cyclohexyl ethanol on Pt(hkl) electrodes in 0.1 M HClO₄ using cyclic voltammetry and electrochemical infrared reflection absorption spectroscopy. We demonstrate that it is possible to oxidize electrochemically 1-cyclohexyl-ethanol to acetophenone. Additionally, we observed 1-cyclohexyl-ethanone and decomposition products. The latter poison the Pt surface, limiting the electrocatalytic activity. The possibility to dehydrogenate electrochemically not only the alcohol but also the cyclohexyl functionality may enable us to increase the hydrogen storage capacity of fuel cell compatible LOHCs substantially, reaching values that are comparable to conventional LOHCs.

1. Sievi, G. et al. *Energy Environ Sci* 12, 2305–2314 (2019).

O 73.3 Thu 11:00 CHE 91

Ab initio-based chemisorption and thermodynamic stability of atomic H and O on Pt-Ir alloy surfaces — ●TOBIAS WITTMANN, THORSTEN KLÜNER, and HALIL IBRAHIM SÖZEN — Institute of Chemistry, Carl-von-Ossietzky University of Oldenburg, 26129 Oldenburg, Germany

Electric vehicles powered by proton-exchange membrane (PEM) fuel cells are a CO₂ emission-free alternative to conventional fossil fuel vehicles. In this study, we report density functional theory (DFT) investigations of binary Pt-Ir surfaces, which are a promising candidate for bifunctional anode catalysts in PEM fuel cells that could enable higher long-term durability of the anode catalyst. The chemisorption behaviour of atomic H and O on bimetallic Pt₃Ir(111) and PtIr(111) surfaces was investigated for different coverages and compared with the monometallic Pt(111) and Ir(111) surfaces. We found that in both cases the chemisorption on the alloys becomes more stable with increasing number of Ir atoms at the adsorption site. Using the *ab initio* thermodynamics approach, we calculated phase diagrams for the chemisorption of atomic H and O species on these metal surfaces in

order to transfer our findings to finite temperature and pressure conditions prevailing in real PEMFCs. Our theoretical results can provide a fundamental understanding for subsequent studies of the hydrogen oxidation reaction (HOR) and oxygen evolution reaction (OER) on Pt-Ir alloy surfaces and are thus crucial for the rational development of new anode catalyst materials.

O 73.4 Thu 11:15 CHE 91

Approaching electrochemical interfaces by computational spectroscopy — ●HOLGER EUCHNER¹, JONGMIN KIM^{1,2}, MARGOT GUIDAT¹, MARIO LÖW², and MATTHIAS M. MAY^{1,2} — ¹Institute of Physical and Theoretical Chemistry, Universität Tübingen, 72076 Tübingen, Germany — ²Institute of Theoretical Chemistry, Universität Ulm, 89081 Ulm, Germany

Understanding interfacial processes on the atomistic scale is essential for improving and tailoring the performance of electrochemical devices. Unfortunately, due to limited experimental access to the electrochemical interface such understanding is difficult to obtain. Applying reflection anisotropy spectroscopy (RAS), an *operando* optical high resolution technique, to electrochemical interfaces can help to overcome this issue. However, the information contained in experimental RAS spectra needs to be interpreted by comparison with those of computational model systems. In this work, we present computationally determined spectra for different metal electrode surfaces and analyze the impact of adsorbants on the resulting RAS signal. For this purpose, the surface dielectric function is determined by applying the random phase approximation. Finally, the obtained spectra are compared to available experimental data, showing the potential power of this approach.

O 73.5 Thu 11:30 CHE 91

Atomistic Insights at Au(111) / Deep Eutectic Solvents Interface using in situ STM — ●YANNICK MATTAUSCH¹, AREEG ABDELRAHMAN¹, MAREN-KATHRIN HEUBACH¹, LUDWIG A. KIBLER¹, and TIMO JACOB^{1,2,3} — ¹Institute of Electrochemistry, Ulm University, Ulm, Germany. — ²Helmholtz-Institute-Ulm (HIU), Ulm, Germany. — ³Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany.

Deep eutectic solvents (DESs) have outstanding electrochemical characteristics such as high electrochemical stability and conductivity.[1][2] Nonetheless, the interactions between the metal electrode surface and DESs besides their electrochemical behavior, like the electrolyte / Au(111) interface structure are still poorly understood. Recently, the electrochemical behavior and adsorption structures of Au(111) in Ethylenglycole / Cholinchloride (2:1) have been studied, including an ordered chloride structure at 0.1 V *vs.* Pt and the potential induced surface reconstruction of Au(111).[3] Here, we go a step further by changing the electrolyte composition and studying its influence on the electrochemical behavior as well as the dynamics at the electrode-electrolyte interface at an atomistic level. To reach this aim, *in situ* scanning tunneling microscopy (STM) is employed to observe morphological changes at the electrode surface in real time and space.

[1] Smith, E. L., Abbott, A. P., Ryder, K. S., *Chem. Rev.* 114, 11060–11082 (2014). [2] Abbott, A. P., D'Agostino, C., Davis, S. J., Gladden, L. F., Mantle, M. D. *Chem. Chem. Phys.* 18, 25528–25537 (2016). [3] Tan, Z. et al., *ChemElectroChem* 7, 4601–4605 (2020).

O 73.6 Thu 11:45 CHE 91

2D chiral crystallization and thermally-induced on-surface polymerization of 2,3-dicarbonitrile-tetrahelixene on Ag(111) surface — ●ALEKSANDRA CEBRAT^{1,3}, CHRISTIAN WÄCKERLIN¹, KEVIN MARTIN², MANFRED PARSCHAU¹, NARCIS AVARVARI², and KARL-HEINZ ERNST^{1,3} — ¹Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland — ²Laboratoire Moltech-Anjou, CNRS-Université d'Angers, 49045 Angers, France — ³Department of Chemistry, University of Zurich, 8057 Zürich, Switzerland

The controlled on-surface polymerization using templates like metal surface and non-planar molecules can lead to synthesis of variable phthalocyanines and organic semiconducting polycyanine open-chains. Here, we report the initial results on the 2D chiral crystallization of racemic mixture of 2,3-dicarbonitrile-tetrahelixene on Ag(111) and its thermally-induced surface polymerization. Deposition of racemic

diCN[4]H up to 0.9ML coverage on Ag(111) kept at 300 K leads to formation of islands of honeycomb domains built of M- and P-enantiomers. Deposition of rac-diCN[4]H on 330K up to 0.9ML leads to aggregation of molecules into long molecular lines and denser phase of unbalanced domains with either enantiomers present in excess. Subsequent annealing to 420 K leads to partial desorption of molecular lines and formation of single tetramers built from different stereoisomeric subunits. The formation of polymerized species was confirmed ToF-SIMS. Finally, we performed LT-STM lateral manipulation of the tetramers units to affirm the nature of bonds as covalent.

O 73.7 Thu 12:00 CHE 91

Interaction of chlorine with lithium and magnesium anodes in Cl-ion batteries — •KANCHAN SARKAR¹ and AXEL GROSS^{1,2} — ¹Institute of Theoretical Chemistry, Ulm University, 89069 Ulm, Germany — ²Helmholtz Institute Ulm (HIU), Electrochemical Energy Storage, 89069 Ulm, Germany

We present the results of first-principles electronic structure calculations based on density functional theory addressing the adsorption of chlorine and the formation of a surface chloride on Li(001) and Mg(0001). This process is relevant for chloride-ion batteries in which lithium and magnesium are used as anode materials, but it is also of fundamental interest, as halide adsorption on metal electrodes is an important process in electrochemistry. We discuss the adsorption properties and determine the stable adsorption structures, both with respect to the free chlorine molecule but also as a function of the electrode potential. We will also address the process of chloride formation on the surface.

O 73.8 Thu 12:15 CHE 91

Bromine on Rh(111) - A combined XPS and LEED study — •EVA MARIE FREIBERGER¹, NATALIE J. WALESKA¹, ANTON HARRER¹, FELIX HEMAUER¹, VALENTIN SCHWAAB¹, HANS-PETER STEINRÜCK¹, and CHRISTIAN PAPP^{1,2} — ¹Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany — ²Freie Universität Berlin, Berlin, Germany

The adsorption of halogens on metals is a fundamental question in surface science. Detailed knowledge in this regard is of interest for any processes on surfaces, in which halogens are involved as a reactant or by-product. This plays a role, for example, in electrochemistry, when the electrolyte adsorbs at the electrodes, or in on-surface synthesis, which often relies on coupling reactions with halogens as the leaving group, leading to their accumulation on the surface.

We investigated the adsorption and thermal evolution of elemental bromine on the Rh(111) single-crystal surface by synchrotron radiation-based high-resolution X-ray photoelectron spectroscopy (XPS), temperature-programmed XPS, and low energy electron diffraction (LEED). The adsorption of bromine on Rh(111) held at 170 K was followed in situ by XPS, revealing a coverage-dependent shift in the Br 3d spectra. Using LEED as a complementary method, we propose that the observed shift is caused by different bromine superstructures on Rh(111): a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure for lower coverages and a compression structure for saturation coverage. Subsequent heating shows a quite high temperature stability of bromine on Rh(111) up to 925 K, indicating covalent bonding.