O 80: Poster Session VI: Poster to Mini-Symposium: Electrified solid-liquid interfaces I

Time: Wednesday 13:30–15:30 Location: P

O 80.1 Wed 13:30 P

Vibrational Sum Frequency Generation Studies of Carbon Dioxide Reduction on Gold: Effects of Electric Fields and Electrolyte Cations. — •Spencer Wallentine[1], Quansong Zhu[1], Savini Bandaranyake[1], Somnath Biswas[2], and Robert Baker[1] — [1]Ohio State University, Columbus Ohio, USA. — [2]Princeton University, Princeton New Jersey, USA

The electrochemical interface is complex in function yet elegant in its ability perform redox processes. These processes are sensitive to the electrolyte cation during carbon dioxide reduction, however the reason for this remains the subject of debate. Using vibrational sum frequency generation we measure in-situ spectra of adsorbed carbon monoxide on polycrystalline gold during carbon dioxide reduction. The surface bound carbon monoxide redshifts with applied potential due to the Stark effect. From this Stark shift we measure the interfacial electric field, which reaches a maximum of 35 MV/cm. We find that the interfacial electric field begins to saturate at -0.9 V vs SHE, and is indicative of the formation of a dense cation layer in the interfacial region. Interestingly, -0.9 V is coincident with the onset of high efficiency carbon monoxide production, which suggest that interfacial cations or the associated electric field enhance this faradaic process. These results are further corroborated by an increase in the Tafel slope, which is predicted to occur as the active site density decreases due to site blocking by ions. Taken together we obtain a atomistic picture of the electrode electrolyte interface where ions block some of the active sites, but the remaining sites are more active due to electric field stabilization.

O 80.2 Wed 13:30 P

Dodecanethiol on gold nanoparticles promotes catalytic performance by preventing trace ion deposition — •Hongyu Shang[1], Spencer Wallentine[1], Daniel Hofmann[2], Quansong Zhu[1], Catherine Murphy[2], and Robert Baker[1] — [1]The Ohio State University, Columbus, Ohio, USA — [2]University of Illinois: Urbana, IL, US

Nanoparticles are very efficient heterogeneous catalysts due to their inherent surface to volume ratio and tunability. Small organic molecules are usually used as capping agents to stabilize and control the size of the nanoparticles, which significantly affect the catalytic performance. To study the influence of capping agents in catalyzing carbon dioxide (CO2) to carbon monoxide (CO), we have performed carbon dioxide reduction (CDR) reaction on ultra-small (d=2nm) gold nanoparticles capped with different capping agents. We find that dodecanethiol on gold nanoparticles promotes catalytic selectivity and stability by inhibiting trace ion deposition that are responsible for rapid deactivation. Both the geometric structure and the microscopic ordering of the stabilization agent are found to influence the inhibition ability of the catalyst toward ion deposition. In addition, dodecanethiol capped gold nanoparticles exhibit a CO yield that is 100 times greater than polycrystalline gold when using ambient water source to prepare electrolyte. These findings give a better understanding in improving catalytic performance and provide a good opportunity to address the overlooked challenge of electrolyte purity.

O 80.3 Wed 13:30 P

Turn on the power - a theoretical adsorption study of electrified low- and high-index platinum/electrolyte interfaces — •Simeon D. Beinlich[1,2], Nicolas G. Hörmann[1,2], and Karsten Reuter[1,2] — [1]Technical University of Munich, Munich, Germany — [2]Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Simulating properties of electrified solid-liquid interfaces critically depends on the ability of modeling the energetics of such a system in a sensitive way. For over a decade now, the computational hydrogen electrode (CHE) was very successful in approximating the energetic influence of an applied electrode potential. By construction, however, it lacks the ability to model important electric-field and double-layer induced effects such as electrode potential or pH-dependent shifts in the relative stability of adsorption sites.

By describing the solid-liquid interface in a more detailed, grand canonical (GC) manner [1], that explicitly accounts for capacitive charging, we are able to simulate such shifts for various adsorption sites and adsorbate species on a high- and a low-index platinum surface. We compare classical CHE simulations with the GC approach and with a second-order approximation of it – the latter, in essence, consisting of the classical CHE expression and additional double-layer contributions (CHE+DL, [1]). It turns out that the CHE+DL approach – at computational costs comparable to the classical CHE approach – very accurately reproduces the GC results, offering a powerful tool for modeling electrified solid-liquid interfaces.

[1] N.G. Hörmann *et al.*, npj Comp. Mat. **6**, 136 (2020).

O 80.4 Wed 13:30 P

***Ab initio* Study of NiOOH (0001) Surfaces: Deprotonation and Alkali Metal Cation Adsorption** — •Mohammad J. Eslamibidgoli[1], Piotr Kowalski[1], Axel Gross[2], and Michael H. Eikerling[1] — [1]Institute of Energy and Climate Research, Modeling and Simulation of Materials for Energy Technology (IEK-13), Forschungszentrum Jülich, 52425 Jülich, Germany — [2]Institute of Theoretical Chemistry, Ulm University, Albert-Einstein-Allee 11, D-89069 Ulm, Germany

Nickel-based oxides are highly active, cost effective materials for the oxygen evolution reaction (OER) in alkaline conditions. Recent experimental studies have revealed the importance of surface deprotonation and alkali metal cation adsorption on the OER activity of Ni oxide surfaces, in contact with aqueous alkaline electrolyte [1,2]. In this study, we employ the DFT+U method within the grand-canonical scheme based on the computational hydrogen electrode [3,4] to determine the stable interface structure of β-NiOOH (0001) under varying electrochemical conditions (pH and electrode potential). We will discuss the effect of surface water layer and the potential-dependent shift in Gibbs free energy of adsorption arising from the interaction of surface dipoles with the interfacial electric field on the computed surface Pourbaix diagrams. [1] Diaz-Morales, O. et al. Chem. Sci. **2016**, 7, 2639-2645. [2] Garcia, A. C. et al. Angew. Chem. Int. Ed., **2019**, 58, 12999-13003. [3] Nørskov, J. K. et al. J. Phys. Chem. B, **2004**, 108, 17886-17892. [4] Groß, A. **2021**, Curr. Opin. Electrochem., accepted for publication.

O 80.5 Wed 13:30 P

Parameterization of ESM-RISM for the Pt(111)-Electrolyte Interface — •Rebekka Tesch[1,2,3], Michael H. Eikerling[1,2,3], and Piotr M. Kowalski[1,2] — [1]Theory and Computation of Energy Materials (IEK-13), Forschungszentrum Jülich, 52425 Jülich, Germany — [2]Jülich Aachen Research Alliance, JARA-CSD and JARA-ENERGY, 52425 Jülich, Germany — [3]Chair of Theory and Computation of Energy Materials, Faculty of Georesources and Materials Engineering, RWTH Aachen University, 52062 Aachen, Germany

Modeling of electrode/electrolyte interfaces at the atomic scale under applied potential is essential for understanding electrocatalytic reactions. A promising approach to treat the coupled interface phenomena is the Effective Screening Medium Reference Interaction Site Method (ESM-RISM) [1] that combines Density Functional Theory with the integral theory of liquids. However, ESM-RISM implements Lennard-Jones (LJ) interaction potentials for electrolyte-electrolyte and electrode-electrolyte interactions. The choice of LJ parameters is thus crucial for obtaining a realistic description, but these parameters are rarely transferable. To address this issue we fit the LJ parameters to reproduce ab initio electrolyte density profiles for the Pt(111)-aqueous electrolyte interface. We also scrutinize the choices of further input parameters in the ESM-RISM implementation [2]. These steps yield a more accurate description of the Pt(111)-electrolyte interface.

[1] Nishihara and Otani, Phys. Rev. B 96, 115429, 2017.

[2] Fernandez-Alvarez and Eikerling, ACS Appl. Mater. Interfaces 11, 46, 43774, 2019.

O 80.6 Wed 13:30 P

Recent advancements in the development of screening approaches and descriptors for electrocatalytic processes — •Kai Exner — University Duisburg-Essen, Faculty of Chemistry, Theoretical Chemistry, Universitätsstraße 5, 45141 Essen, Germany — Cluster of Excellence RESOLV, Bochum, Germany

For the identification of electrocatalysts from databases, heuristic screening approaches have been established to categorize materials into active and inactive [1]. Most of these studies rely on the initial idea of Nørskov, Rossmeisl, and co-workers in that only the binding energies (thermodynamics) of potential reaction intermediates (RIs) within the electrocatalytic cycle are assessed. Recently, this thermodynamic picture was challenged, reporting that the optimum binding energy shifts from thermoneutral to weak bonding with increasing driving force [2]. This result, explained by an extension of the Sabatier principle for electrocatalytic reactions [3], has direct implications on the energetics of multiple-electron processes, such as the four-electron oxygen evolution reaction. There, the thermodynamic overpotential, commonly used as activity descriptor, has been replaced by a universal descriptor, Gmax(η), factoring overpotential and kinetic effects into the analysis [4]. The present contribution aims to provide an overview of the recent advancements in the application of heuristic screening approaches and descriptors for the hydrogen and oxygen evolution reactions.

[1] KSE, Adv. Funct. Mater. 2020, 30, 2005060. [2] KSE, Angew. Chem. Int. Ed. 2020, 59, 10236. [3] K.S. Exner, Curr. Opin. Electrochem. 2021, 26, 100673. [4] KSE, ACS Catal. 2020, 10, 12607.

O 80.7 Wed 13:30 P

We hold these truths to be self-evident, that all halide CVs are created equal. — •Nicolas G. Hörmann[1,2] and Karsten Reuter[2] — [1]Technische Universität München, Garching, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Consistent with chemical intuition, the cyclic voltammograms (CVs) of Ag(111) in halide containing solutions are essentially identical for Cl, Br, and I, when simulated based on DFT calculations and the computational hydrogen electrode (CHE) approximation. Quite in contrast, experiments reveal significant differences in CV peak heights and shapes.

Here we show that the DFT results can be reconciled with experiment, when using a fully grand canonical description in an implicit solvent model that allows for capacitive charging [1]. It is thus only the latter and not the adsorption energetics at the potential of zero charge, that leads to the experimental variation in the CVs across the halide series. This finding is supported by a general analysis of the relation between grand canonical and CHE energetics, which in addition provides new insights into non-Nernstian behavior and the relevance of classical electrochemical concepts such as the electrosorption valency[2].

[1] N.G. Hörmann *et al.*, J. Chem. Phys. **150**, 041730 (2019). [2] N.G. Hörmann *et al.*, npj Comput. Mater. **6**, 136 (2020).