

O 96: Solid-Liquid Interfaces IV: Reactions and Electrochemistry

Time: Thursday 15:00–18:00

Location: TC 006

O 96.1 Thu 15:00 TC 006

How to exploit the electrochemical driving forces to understand electrochemical CO(2) reduction — ●GEORG KASTLUNGER¹, HENDRIK HEENEN², and NITISH GOVINDARAJAN³ — ¹Technical University of Denmark, Fysikvej, Kongens Lyngby, Denmark — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — ³Materials Science Division, Lawrence Livermore National Laboratory, Livermore, California, USA

The first-principles understanding of complex reaction mechanisms in electrocatalysis aids not only the discovery of improved catalytic materials but also the choice the ideal reaction environment for tailored products. For the latter, an appropriate understanding of the influence of the electrochemical driving forces, such as potential and pH, is key.

In my talk, I will present density functional theory-based studies on electrocatalytic reaction mechanisms with a special focus on electrochemical CO(2) reduction (eCO(2)R). I will describe how the combination of constant-potential DFT approaches^I and transition state theory-based considerations allow us to explicitly study the potential and pH dependence of multistep reaction networks.^{II} I will further discuss the kinetic characteristics of the competing elementary reactions within eCO(2)R and their consequences on the potential and pH response of the product selectivity.^{III}

I. Kastlunger et al., *J. Phys. Chem. C* 122, 12771-12781 (2018).

II. Kastlunger et al., *ACS Catal.* 12, 4344-4357 (2022).

III. Kastlunger et al., *ACS Catal.*, 13, 7, 5062-5072 (2023)

O 96.2 Thu 15:15 TC 006

Multiscale modeling reveals mass transport-controlled product selectivity in electrochemical CO₂ reduction on Cu — ●ADITH RAMAKRISHNAN VELMURUGAN¹, YOUNGRAN JUNG², DAEHYUN NAM³, and STEFAN RINGE¹ — ¹Korea University, Seoul, Republic of Korea — ²Seoul National University, Seoul, Republic of Korea — ³DGIST, Daegu, Republic of Korea

Electrochemical CO₂ reduction, one of the most promising processes for a sustainable closure of the artificial carbon cycle, is severely limited by the lack of a catalyst that can reduce CO₂ to higher-reduced chemicals actively and selectively. Cu is the only catalyst found to produce considerable amounts of C₂ products, albeit at high overpotentials. The conversion mechanism is unclear, with different active sites and rate-determining steps being proposed. In addition, the mass transport of CO₂ has been suggested to significantly impact the product selectivity. Gas-diffusion-layer (GDL)-based electrolyzers have become a state-of-the-art solution to circumvent these mass transport limitations. In this work, we present a new multi-scale model based on first-principles kinetics, and a modification of a recently reported gas diffusion electrode model. From this model, we show that even in GDL systems, mass transport is the limiting factor governing all experimentally observed trends in product selectivity, irrespective of the reaction mechanism or product pathway. We further find indications of C₂/C₁ product selectivity being dependent on the pore size and depth. This work provides strong evidence for the importance of mass transport in designing CO₂ electrolyzers.

O 96.3 Thu 15:30 TC 006

The mechanism of electrochemical CO₂ reduction to post CO and C₂₊ products over single atom catalysts — REZA KHAKPOUR¹, KAVEH FARSHADFAR¹, KARI LAASONEN¹, and ●MICHAEL BUSCH^{2,3} — ¹Aalto University, Esbo, Finland — ²Luleå University of Technology, Luleå, Sweden — ³Wallenberg Initiative Materials Science for Sustainability (WISE), Luleå, Sweden

Electrochemical reduction of CO₂ to CO or post CO products is of central importance for energy storage and conversion. A promising class of catalysts for CO₂ reduction are single atom catalysts (SACs) which consist of a single metal atom embedded into graphene. These materials are generally believed to only form C₁ compounds. However, recent experiments indicate, that methane together with minor amounts of products with 2 or more carbon atoms are formed over Fe phthalocyanine complexes, which are structurally similar to classical SACs.^[1]

In this contributions we will explore the reaction routes from CO₂ to methane and C₂₊ compounds using density functional theory (DFT) computations [2]. Our results indicate, that the selectivity between dif-

ferent products mainly depends on activation barriers and is strongly influenced by the CO and proton concentration close to the electrode.

[1] S.-T. Dong, C. Xu, B. Lassalle-Kaiser *Chem. Sci.* 14 (2023) 550.

[2] R. Khakpour, K. Farshadfar, M. Busch et al. *submitted*.

Topical Talk

O 96.4 Thu 15:45 TC 006

Importance of charge transfer descriptor for the computational screening of electrocatalysts — ●STEFAN RINGE — Korea University, Seoul, Rep. of Korea

Electrochemistry has become a key player in establishing a global sustainable energy landscape. Unfortunately, most electrochemical processes are limited in their efficiency and selectivity which has prevented them from replacing carbon-intensive industrial processes. Computational simulations have the potential to conquer the vast chemical space and reveal so far unconsidered new electrocatalysts and boost the performance of these devices. This, however, requires the knowledge of computationally accessible activity and selectivity descriptors. In this work, and by the example of electrochemical CO₂ reduction, it is shown that the conventionally considered adsorption energy descriptor is not enough to distinguish product selectivity among catalysts. Including specifically the electrochemical environment in the quantum chemical calculations, we find that a charge-transfer descriptor is separately required, such as the work function or the potential of zero charge. With this, experimental trends in product selectivity can be well described, thus providing a new set of descriptors for high-throughput screening of electrocatalysts.

O 96.5 Thu 16:15 TC 006

Potentially Uncontrolled Barrier Calculations for Electrocatalysis — ●SIMEON D. BEINLICH^{1,2}, GEORG KASTLUNGER³, KARSTEN REUTER^{1,2}, and NICOLAS G. HÖRMANN¹ — ¹Fritz-Haber-Institut der MPG, Berlin — ²Technische Universität München — ³Technical University of Denmark, Kongens Lyngby, Denmark

Does computing electrochemical barriers necessarily require the use of a potentiostat? Here, we present a novel set of potentiostat-free methods for computing grand canonical activation barriers at constant potential from common canonical DFT calculations [1]. Making most efficient use of the underlying DFT data, these methods can, by construction, re-create potentiostat-based results. Moreover, they offer several systematic approximations that cover the potential-induced electronic and geometric responses, while only requiring a single transition state search at the point of zero charge, i.e. at zero excess charge.

Besides offering new pathways for efficiently calculating electrochemical activation barriers, our analysis highlights the importance of including geometric effects and more generally sheds light on the similarities and dissimilarities between a canonical and a grand canonical treatment of electrochemical interfaces. [1] S.D. Beinlich *et al.*, *J. Chem. Theory Comput.*, <https://doi.org/10.1021/acs.jctc.3c00836>

O 96.6 Thu 16:30 TC 006

Relation between Electrocatalyst Morphology and Product Selectivity from Multi-Scale Reaction Models — ●HEMANTH S. PILLAI, HENDRIK H. HEENEN, KARSTEN REUTER, and VANESSA J. BUKAS — Fritz-Haber-Institut der MPG, Berlin

Electrocatalytic selectivity has shown a puzzling dependence on experimental parameters related to catalyst morphology. We argue that such effects can often be rationalized on the basis of mesoscopic mass transport. Basis for the underlying mechanism is the competition that arises from exchanging surface-bound, yet volatile, reaction intermediates between the electrode and the bulk electrolyte. The catalyst morphology can be decisive in driving this competition since its surface area directly affects the probability that a diffusing species will return to the surface for continued conversion, rather than escape as an early intermediate product. It remains unclear, however, exactly how catalyst morphology is predicted to affect the resulting selectivity and neither is the level of detail that needs to be considered. In this study, we specifically demonstrate this competition for the electrochemical CO₂ reduction on Cu. For this purpose, we develop a simple multi-scale model that couples diffusion to the electrochemical surface kinetics. This allows to predict selectivity towards the early CO product, while systematically improving the representation of catalyst morphology within our model: from an effective one-dimensional

descriptor of surface roughness, to an explicit two-dimensional consideration of surface corrugation.

O 96.7 Thu 16:45 TC 006

Converging Divergent Paths: Constant Charge vs. Constant Potential Energetics in Computational Electrochemistry —

•NICOLAS G. HÖRMANN, SIMEON D. BEINLICH, and KARSTEN REUTER — Fritz-Haber-Institut der MPG, Berlin

Using the example of a proton adsorption process, we analyze and compare two prominent modelling approaches in computational electrochemistry at metallic electrodes – electronically canonical, constant-charge and electronically grand-canonical, constant-potential calculations. We first confirm that both methodologies yield consistent numerical results for the differential free energy change in the infinite cell size limit. This validation emphasizes that, fundamentally, both methods are equally valid and precise. In practice, the grand-canonical, constant-potential approach shows superior interpretability and size convergence as it aligns closer to experimental ensembles and exhibits smaller finite-size effects. On the other hand, constant-charge calculations exhibit greater resilience against discrepancies, such as deviations in interfacial capacitance and absolute potential alignment, as their results inherently only depend on the surface charge, and not on the modeled charge vs. potential relation. The present analysis thus offers valuable insights and guidance for selecting the most appropriate ensemble when addressing diverse electrochemical challenges.

O 96.8 Thu 17:00 TC 006

Approximating Grand-Canonical Energetics of Electrified Semiconductor-Electrolyte Interfaces – A Benchmark Study —

•HEDDA OSCHINSKI^{1,2}, KARSTEN REUTER^{1,2}, and NICOLAS G. HÖRMANN¹ — ¹Fritz-Haber-Institut der MPG, Berlin — ²Technische Universität München

Computational studies of the electroadsorption of adsorbates centrally target the grand canonical (GC) energetics $\mathcal{G}^s(\phi_E)$ with respect to an applied potential ϕ_E . For metal electrodes, $\mathcal{G}^s(\phi_E)$ can be well described by a parabolic form that incorporates the interfacial capacitance C at the potential of zero charge. Unfortunately, for semiconductors (SC), this appealing approximation breaks down due to the existence of the band gap. Here, we propose a simple extension that explicitly incorporates the electrode density of states (DOS) and thus allows to describe C for both metals and SCs. For SCs, C is thereby partitioned into a DOS capacitance and a solution capacitance using a straightforward DOS shift picture that combines the filling of electronic states with the shift of the electrostatic potential drop across the electrode-electrolyte interface. Using density-functional theory calculations in an implicit solvation environment, we benchmark the model for a set of conducting and semiconducting/insulating 2D materials. The GC energetics is reliably reproduced across the entire materials space, with only minor deviations but at a fraction of the computational cost. The analysis underlines the importance of the position of the band gap and the response of the solution, in line with classical macroscopic ideas of semiconductor electrochemistry.

O 96.9 Thu 17:15 TC 006

Thermodynamic Cyclic Voltammograms from First Principles —

•NICOLAS BERGMANN, NICOLAS G. HÖRMANN, and KARSTEN REUTER — Fritz-Haber-Institut der MPG, Berlin

Computationally, the predictive-quality modeling of cyclic voltammograms (CVs) is complicated by the need to accurately account for the interactions and reactive chemistry at the liquid electrolyte/solid electrode interface, as well as for the electrostatic interactions of the diffuse double layer at applied potential conditions [1]. For sufficiently small scan rates, *ab initio* thermodynamics approaches help to meet these challenges.

Here, we compare different approximations commonly employed in

such approaches [1]. Using the well-studied model system of Ag(100) in a Br-containing electrolyte as a show case, we analyze the influence of statistical sampling of the adlayer, how implicit solvent models affect the surface energetics, and the benefits of augmenting traditional zero-field calculations - aka the computational hydrogen electrode (CHE) - with capacitive double layer energetics (CHE+DL) [2]. Finally, we illustrate the possibility to expand our methodology to more complex systems by examining the CVs of Cu(100) electrodes in alkaline, I-containing electrolytes.

[1] N. Bergmann, N.G. Hörmann, and K. Reuter, *J. Chem. Theory Comput.* (in press) DOI:10.1021/acs.jctc.3c00957.

[2] N.G. Hörmann and K. Reuter, *J. Chem. Theory Comput.* **17**, 1782 (2021).

O 96.10 Thu 17:30 TC 006

On the Origin of Electrocatalytic Selectivity during the Oxygen Reduction Reaction on Au(111) —

•ELIAS DIESEN, KARSTEN REUTER, and VANESSA J. BUKAS — Fritz-Haber-Institut der MPG, Berlin

A puzzling observation during the oxygen reduction reaction (ORR) on Au electrodes is the preference to form hydrogen peroxide (H_2O_2), instead of the thermodynamically favored water product. This selectivity cannot be explained on the basis of thermodynamic reaction models that simply assume a series of proton-coupled electron transfers (PCETs). Here, we use *ab initio* molecular dynamics along with umbrella sampling to obtain free energy profiles for competing key ORR steps on Au(111). Our comparison includes not only PCETs, but also “chemical” reaction steps that do not include a Faradaic charge transfer, such as desorption or surface dissociation. This allows us to explore favorable reaction paths, while varying the capacitive charging to represent realistic ORR potentials. Our results show that all reaction steps competing with H_2O_2 formation have sizeable kinetic barriers and are thus prohibited, even though they may be thermodynamically favored. We find that this situation does not change under more reducing conditions and specifically determine the “nobleness” of Au as playing a decisive role in preventing O-O bond scission. It is thus not the applied potential, but the underlying chemistry that drives the ORR selectivity. In general, our study thus highlights the kinetic competition between PCET and non-PCET steps that cannot be resolved via simple Brønsted-Evans-Polanyi (BEP) scaling relations.

O 96.11 Thu 17:45 TC 006

Computational chemistry analysis of passive layer formation and breakdown mechanisms in ferritic stainless steels —

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Despite extensive research on passive layer formation and breakdown, several questions still remain unanswered. These include the reasons behind the bilayer nature of the passive layer, the decrease in hydrogen and oxygen diffusivity upon entering the passive layer, the underlying mechanisms of passive layer formation and breakdown, and the influence of microstructure on passive layer formation and function in stainless steels. In this study, we employed ReaxFF molecular dynamics to investigate passivation and depassivation of stainless steel in a polycrystalline structure. Through static and dynamic calculations, we elucidated the mechanisms of passive layer formation, which were primarily governed by clustering. Our analysis also highlighted the significant role of hydrogen diffusion and its reaction with metallic compounds in depassivation. We have identified several physical phenomena involved in the processes of passivation and depassivation, which can provide explanations for the aforementioned unresolved points.