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CA18234
$2H_2O \rightarrow 2H_2 + O_2$

Multiscale approaches for modeling water splitting with nanocrystals

COST Online Workshop on Tuesday, February 16th, 2021
Location: Zoom Meeting

https://tuwien.zoom.us/j/98996087423?pwd=Ynl1dU40QUtQZk9WSEZ2MWMva0xjQT09
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PROGRAM

9:30–9:35	**OPENING**	
9:35–10:10	Experimental Modelling of Electrode / Electrolyte Interfaces	Gareth Parkinson
10:10–10:45	Merging Multiscale Theory and Data Sciences to Tackle Operando Energy Conversion Systems	Karsten Reuter
10:45–11:00	**BREAK**	
11:00–11:35	Understanding the Effect of Surface States in Photo-Electrochemical Water Oxidation by Multiscale Modeling	Anja Bieberle-Hütter
11:35–12:10	Unraveling the nature and the identity of the active sites in heterogeneous catalysis via structure-dependent microkinetic modeling	Matteo Maestri
12:10–13:30	**LUNCHBREAK**	
13:30–14:05	Structure of Electrode / Electrolyte Interfaces from First Principles	Axel Gross
14:05–14:40	Photocatalytical Hydrogen Evolution by Molecular Catalysts – Challenges Arising from Multiple Timescales – an Experimentalist’s Perspective.	Benjamin Dietzek
14:40–15:00	**BREAK**	
15:00–15:35	Modeling Photo and Electro Nanocatalysts for Water Splitting in Water	Cristiana Di Valentin
15:35–16:10	Predicting Gas-Particle Partitioning Coefficients of Atmospheric Molecules with Machine Learning	Patrick Rinke
16:10-16:15	**CLOSING REMARKS**	

ZOOM MEETING

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Experimental Modelling of Electrode / Electrolyte Interfaces

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Electrochemical water splitting is an environmentally friendly technology to store renewable energy in the form of chemical fuels. Among the earth-abundant first-row transition metal-based catalysts, mixed Ni-Fe oxides have shown promising performance for effective and low-cost catalysis of the oxygen evolution reaction (OER) in alkaline media, but the synergistic roles of Fe and Ni cations in the OER mechanism remain unclear. In this talk, I will discuss how the presence of Ni changes the reactivity of a model $Fe_3 O_4$ (001) single crystal using a combination of surface science techniques in ultra-high-vacuum (LEED, XPS, LEIS, STM), AFM in air, as well as cyclic voltammetry in alkaline media.

A significant improvement in the OER activity is observed when the top surface presents an Fe:Ni composition ratio in the range 20-40%, which is in good agreement with what has been observed for powder catalysts. A decrease in the OER overpotential is observed following surface aging in electrolyte for three days. At higher Ni load, AFM shows the growth of a new phase consistent with (oxy)-hydroxide phase which, according to CV measurements, but this does not seem to correlate with the surface activity towards OER. EIS suggests that the OER precursor species observed on the clean and Ni-modified surfaces are similar and Fe-centered, but form at lower overpotentials when the surface Fe:Ni ratio is optimized. As such, the well-defined $Fe_3 O_4$ (001) surface can serve as a model system for understanding the OER mechanism and establishing the structure-reactivity relation on mixed Fe/Ni oxides.

Merging Multiscale Theory and Data Sciences to Tackle Operando Energy Conversion Systems

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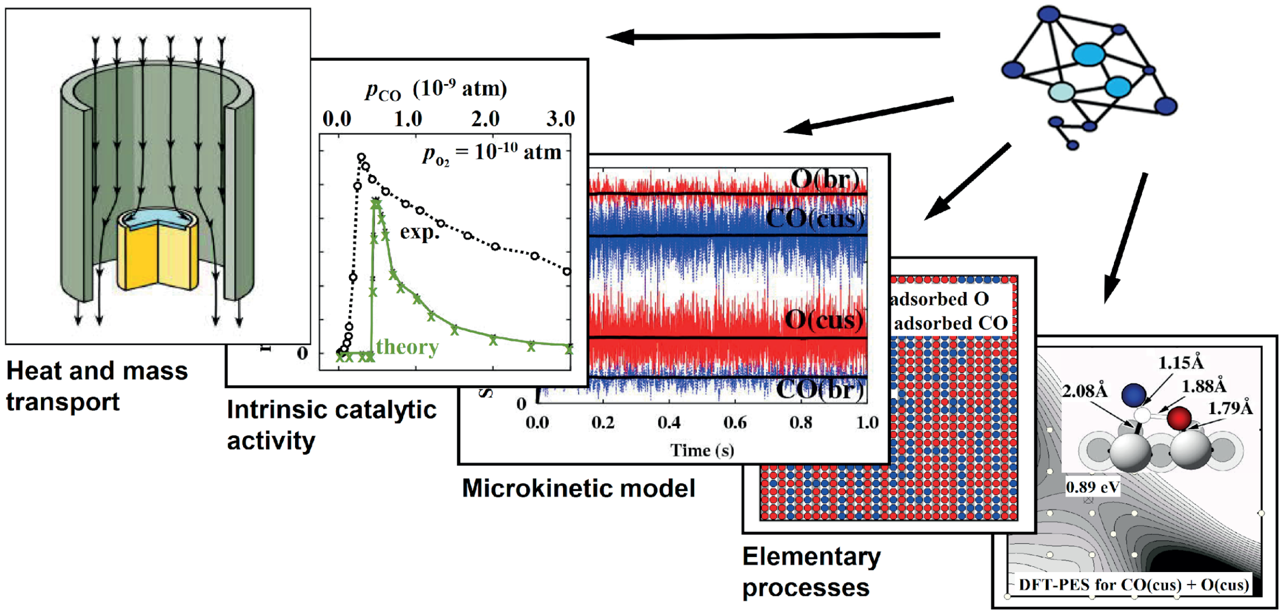
Emerging operando spectroscopies and microscopies reveal a highly dynamic behavior of interfaces in energy conversion systems. Insufficient insight and the concomitant inability to control or exploit the corresponding strong structural and compositional modifications centrally limits the development of performance catalysts, electrolyzers or batteries required for a sustainable energy supply for our society. Predictive-quality modeling and simulation has become a major contributor to accelerated design all across the materials sciences, not least through powerful computational screening approaches. Current first-principles based methodology is nevertheless essentially unable to address the substantial, complex and continuous morphological transitions at working interfaces. I will review this context from the perspective of first-principles based multiscale modeling [1], highlighting that the fusion with modern machine learning approaches is likely key to tackle the true complexity of working systems. Approaches pursued by our group thereby aim at maximum data efficiency by exploiting physical models wherever possible or through active learning that only queries data on demand. Illustrative examples will be drawn from thermal methanation catalysis [2] and electrocatalytic oxygen evolution [3].



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Understanding the Effect of Surface States in Photo-Electrochemical Water Oxidation by Multiscale Modeling

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Oxygen evolution reaction (OER) has been identified as one of the performance-limiting processes in photoelectrochemical (PEC) water splitting. One of the reasons for the low OER performance is related to the existence of different types of surface states at the semiconductor-electrolyte interface: recombining surface states (r-SS) and surface states due to intermediate species (i-SS). In this study, we investigate how different types of surface states affect PEC water oxidation and how they impact experimental measurements. In the first part of the talk, we present our new computational approach in which we combine a microkinetic model of the OER on the semiconductor surface with the energetics at the electrochemical interface and the charge carrier dynamics within the semiconductor [1,2]. In the second part of the talk, we use the model to simulate the impact of r-SS and i-SS on the current-voltage curves, hole flux, surface state capacitance, Mott-Schottky plots, and chopped light measurements. We compare the impact of the different surface states on the characteristic values of the electrochemical interfaces, such as capacitances, onset potential, maximum current density, Fermi level pinning. Our approach in combination with experimental comparison allows distinguishing the impact of r-SS and i-SS in PEC experiments.

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Unraveling the nature and the identity of the active sites in heterogeneous catalysis via structure-dependent microkinetic modeling

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There is no doubt that the rational interpretation of the structure-activity relation in catalysis is a crucial task in the quest of engineering the chemical transformation at the molecular. In this respect, multiscale analysis based on structure-dependent microkinetic modelling is acknowledged to be the essential key-tool to achieve a detailed mechanistic understanding of the catalyst functionality. However, the effect of the structure of the catalyst on reactivity and selectivity is at present neglected in state-of-the-art microkinetic analysis. In this talk, I will present the development of a methodology for the analysis of the structure-activity relation in heterogeneous catalysis. This includes the development of both novel experimental tools and first-principles analysis. Selected examples in the context of CH4 activation, WGS and r-WGS and NO oxidation will be presented [1–4].

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Structure of electrode/electrolyte interfaces from first principles

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In principle, it is clear how we should appropriately model electrode/electrolyte interfaces atomistically: Reliable quantum chemistry calculations of these interfaces should be performed under potential control with an appropriate number of electrolyte molecules considered and their statistical nature taken into account through averaging over sufficiently long ab initio molecular dynamics (AIMD) simulations. However, unfortunately such an approach is currently not possible and will probably not be possible for a long time due to technical and numerical obstacles. Here I will present a two-step approach to approximately address the structure of electrode/electrolyte from first principles [1]. First, the coverage of electrode surfaces with ions from the electrolyte will be determined using grand-canonical approaches [2, 3, 4].

Here, the presence of electrolyte might even be neglected in the adsorption of small ions such as protons or halides. On the other hand, I will present results of extensive AIMD simulations for specific electrode/electrolyte interfaces [5, 6] which allow detailed atomistic insights into structures and processes at these interfaces including the electric double layer.

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Photocatalytical Hydrogen Evolution by Molecular Catalysts – Challenges Arising from Multiple Timescales – an Experimentalist’s Perspective.

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Hydrogen evolution by moelcular photocatalysts requires the light-driven accumulation of multiple electrons on the catalytically active center to yield the metal catalyst in a sufficiently low oxidation state. While the first photodriven charge transfer from a photoactive center of the molecular catalysts to the catalytically active center, is typically well studied. This electron transfer creates a molecular intermediate, which needs to absorb light (again) to transfer a second electron to the catalyst, which – only then – can reduce protons to hydrogen. In this contribution I will present our recent experimental advances to gain spectroscopic insights into the complex electron transfer cascade, deciphering the elementary reaction steps on a range of timescales underlying the photocatalytic mechanisms.

Modeling Photo and Electro Nanocatalysts for Water Splitting in Water

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In this talk I will present an overview on the activity of my group devoted to the design of 0D (TiO2) and 2D (h-BN or graphene based) nanocatalysts for the photo- and the electro-catalysis of water in water, through the combination of quantum mechanics with molecular mechanics or by means of continuum models.

Predicting Gas-Particle Partitioning Coefficients of Atmospheric Molecules with Machine Learning

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The formation, properties and lifetime of secondary organic aerosols in the atmosphere are largely determined by gas-particle partitioning coefficients of the participating organic vapours. Since these coefficients are difficult to measure or to compute, we developed a machine learning model to predict them given molecular structure as input. Our data-driven approach is based on the dataset by Wang et al. [1], who computed the partitioning coefficients and saturation vapour pressures of 3414 atmospheric oxidation products from the master chemical mechanism using the COSMOtherm program. We train a kernel ridge regression (KRR) machine learning model [2] on the saturation vapour pressure (P_{vap}), and on two equilibrium partitioning coefficients: between a water-insoluble organic matter phase and the gas phase ($K_{WIOM/G}$), and between an infinitely dilute solution with pure water and the gas phase ($K_{W/G}$). For the input representation of the atomic structure of each organic molecule to the machine, we test different descriptors such as the Coulomb matrix [3] and the many-body tensor [4]. Our best machine learning model predicts P_{vap} and $K_{WIOM/G}$ to within 0.3 logarithmic units and $K_{W/G}$ to within 0.43 logarithmic units compared to the original COSMOTherm calculations [5]. This is equal or better than the typical accuracy of COSMOtherm predictions compared to experimental data (where available). We then apply our machine learning model to a dataset of 35,383 molecules that we generated based on a carbon 10 (C10) backbone and functionalized with 0 to 6 carboxyl (-COOH), carbonyl (=O) or hydroxyl (-OH) functional groups. Our C10 model is representative of the Wang et al. data set and allows us to efficiently identify organic molecules with a low saturation vapour pressure P_{vap} [5].

This work was done in collaboration with Emma Lumiaro and Milica Todorović at Aalto University and Theo Kurten and Hanna Vehkamäki at Helsinki University.

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