O 34: Poster Solid-Liquid Interfaces: Reactions and Electrochemistry

Time: Tuesday 13:30–15:30 Location: P3

O 34.1 Tue 13:30 P3

Free Energy Calculations of Electrolyte Decomposition Reactions on Lithium Battery Electrodes — •Azad Kirsan and Bernd Meyer — Interdisciplinary Center for Molecular Materials and Computer Chemistry Center, FAU Erlangen-Nürnberg

For the development of lithium metal batteries (LMBs) it is essential to understand how a stable solid electrolyte interphase (SEI) is formed. Ethylene carbonate (EC), a commonly used electrolyte, plays a critical role in SEI formation through its electrochemical decomposition at the electrode surface. Thus, insights into the mechanism of the decomposition reaction are of crucial importance for understanding the processes that govern SEI composition, structure and stability.

In this work, *ab initio* molecular dynamics simulations using state-of-the-art enhanced sampling methods (metadynamics, umbrella sampling, well-sliced metadynamics [1]) including explicitly the liquid electrolyte were performed in order to unravel the reaction mechanisms of the first steps of the EC dissociation on a Li_2O surface. The trajectories, encompassing more than 1 ns of sampling time, were used to reconstruct the free energy surfaces and obtain activation barriers for the decomposition reaction.

[1] S. Awasthi, V. Kapil, N.N. Nair, J. Comput. Chem. **37** (2016) 1413

O 34.2 Tue 13:30 P3

Optimizing Parameters in Metadynamics Simulations for Free Energy Calculations — •Marlene Sell, Azad Kirsan, and Bernd Meyer — Interdisciplinary Center for Molecular Materials and Computer Chemistry Center, FAU Erlangen-Nürnberg

The calculation of free energy surfaces (FES) is essential for understanding chemical reactions. Especially the free energy differences between educts, products and possible transition states, as well as the structure of the latter, allow insight into the nature of the reactions. Well-sliced metadynamics (WS-MTD) [1] is a novel method to calculate FES. It combines umbrella sampling and metadynamics in order to speed up the simulations. However, it employs several fine-tuning parameters whose exact influence on the efficiency and accuracy of the results is not yet well understood.

In this study, the FES of the reaction of 1,3-butadiene and ethylene to cyclohexene, the simplest Diels-Alder reaction, was calculated by WS-MTD. This reaction is well studied, both experimentally and theoretically, and could thus be used to compare the influence of the studied parameters. Using FES calculated with different values of the relevant parameters, the free energy differences between the educts, transition state and products were determined in the form of the activation barrier and reaction energy. These were compared to literature values from experimental and other theoretical studies.

[1] S. Awasthi, V. Kapil, N.N. Nair, J. Comput. Chem. **37** (2016) 1413

O 34.3 Tue 13:30 P3

Exploration of the Pt(111)-water interface by high-dimensional neural network potentials — •Daniel Trzewik[1,2], Moritz R. Schäfer[1,2], Alexander L. Knoll[1,2], and Jörg Behler[1,2] — [1]Theoretische Chemie II, Ruhr-Universität Bochum, Germany — [2]Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, Germany

Detailed insights into solid-liquid interfaces are crucial for understanding many processes in catalysis and electrochemistry. Accurately modeling these interfaces using first-principles methods is computationally very demanding, which strongly restricts the complexity of the systems that can be studied. Machine learning potentials now can provide an efficient alternative with almost no loss in accuracy. In this study, high-dimensional neural network potentials (HDNNPs) are employed to investigate the Pt(111)-water interface in detail. After training to DFT reference data, molecular dynamics simulations are utilized to uncover the structural and dynamical properties of the interfacial water molecules.

O 34.4 Tue 13:30 P3

Studying Tricalcium Silicate-Water Interfaces Using High-Dimensional Neural Network Potentials — •Henry Wang[1,2], Bernadeta Prus[1,2], and Jörg Behler[1,2] — [1]Theoretische Chemie II, Ruhr-Universität Bochum, Germany — [2]Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, Germany

The advent of machine learning potentials (MLP) trained to energies and forces from electronic structure calculations has revolutionized the simulation of solid-liquid interfaces by molecular dynamics (MD). For instance, High-Dimensional Neural Network Potentials (HDNNP) have shown excellent accuracy for describing the interaction of water with numerous solid minerals. In this study, we investigate interfaces of liquid water with alite (Ca_3SiO_5), an important cement mineral exhibiting various polymorphic states. Using large-scale MD simulations, an analysis of the structural and dynamical properties of interfacial water is presented.

O 34.5 Tue 13:30 P3

Electrocatalytic CO_2 Reduction in Ionic Liquid/Nitrile Electrolytes — •Björn Ratschmeier, Arik Geringswald, Alisa Kamaric, and Björn Braunschweig — University Münster, Institute of Physical Chemistry, Münster, Germany

Room-temperature ionic liquids (RTILs) play an important role in CO_2 reduction reactions (CO_2RR), providing a viable alternative to aqueous electrolytes, but face challenges such as high overpotentials and product selectivity. As we have previously shown for 1-butyl-3-methylimidazolium trifluorosulfonylimide ([BMIM][NTf_2]) electrolytes [1], the accessibility of water as a co-reactant at the interface is a limiting factor for CO formation potentials. To modulate the interfacial structure, different concentrations of acetonitrile and benzonitrile were introduced into [BMIM][NTf_2] electrolytes in the presence of 1.5 M H_2O. The resulting mixtures were investigated in terms of CO_2RR at polycrystalline Au electrodes. The presence of 7.5 M benzonitrile resulted in a 20-fold increase in CO formation, and in even higher CO concentrations with acetonitrile compared to the pure ionic liquid. Consequently, we propose that nitrile additives tune the interfacial structure in such a way that the access of water molecules is improved. In order to validate this hypothesis, we aim for an in-depth investigation of the bulk electrolyte as well as of the interfacial structure using *in situ* IR and SFG spectroscopy. [1] Ratschmeier et al. Electrochem. Sci. Adv. 2023, 3, e2100173.

O 34.6 Tue 13:30 P3

Investigating Zinc Oxide-Water Interfaces with High-Dimensional Neural Network Potentials — •Jan Elsner and Jörg Behler — Theoretische Chemie II, Ruhr-Universität Bochum, Germany, and ResearchCenter Chemical Sciences and Sustainability, Research Alliance Ruhr,Germany

Zinc oxide (ZnO) is a promising material for sustainable hydrogen production via catalytic water splitting. The interface of ZnO with water exhibits complex dynamical behavior, including water dissociation and recombination, as well as long-range proton transport. Traditionally, density functional theory (DFT)-based molecular dynamics has been the primary theoretical tool for probing such mechanisms at the atomistic scale. However, the complexity of the interface, requiring large simulation boxes, and the long time scales associated with dynamical processes pose substantial theoretical challenges for any method relying on explicit electronic structure calculations. High-Dimensional Neural Network Potentials (HDNNPs) offer a solution to these challenges, enabling atomistic simulations with DFT-level accuracy at only a fraction of the computational expense. Here, we present HDNNP-based simulations of ZnO-water interfaces, providing insights into their structure and dynamics.