

Taking the electrochemical environment appropriately into account in the first-principles atomistic description of electrode/electrolyte interfaces

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Electrochemical processes occur at the interface between an electron conductor, the electrode, and an ion conductor, the electrolyte. Often liquid electrolytes are used whereas the electrodes consist of solid materials. A proper description of the liquid nature of the electrolyte requires to perform computationally expensive averages in order to take the statistical nature of the liquid into account. In this talk I will present how this can be achieved using ab initio molecular dynamics (AIMD) studies. Thus for example the potential of zero charge can be derived [1]. Still, these simulations are rather demanding. As an computational inexpensive alternative, the liquid electrolyte can be represented in an implicit solvent model [2]. This approach has been used to model the electro-oxidation of methanol on Pt(111) [3]. Employing the implicit solvent approach, the difference in the selectivity of the first methanol dehydrogenation step in heterogeneous and electro-catalysis can be reproduced [4]. Still, a more comprehensive validation of the implicit solvent model is required.

Furthermore, electrolytes typically contain solvated ions which often strongly interact with electrode surfaces. This can lead to a high ion coverage of the electrodes which significantly alters their properties. Using a grand-canonical approach within the concept of the computational hydrogen electrode, the competitive adsorption of hydrogen and halides on Pt(111) has been studied [5]. This approach also allows to derive trends in the electrode coverage as a function of the electrode potential which can be illustrated in Pourbaix diagrams (see Fig.1).

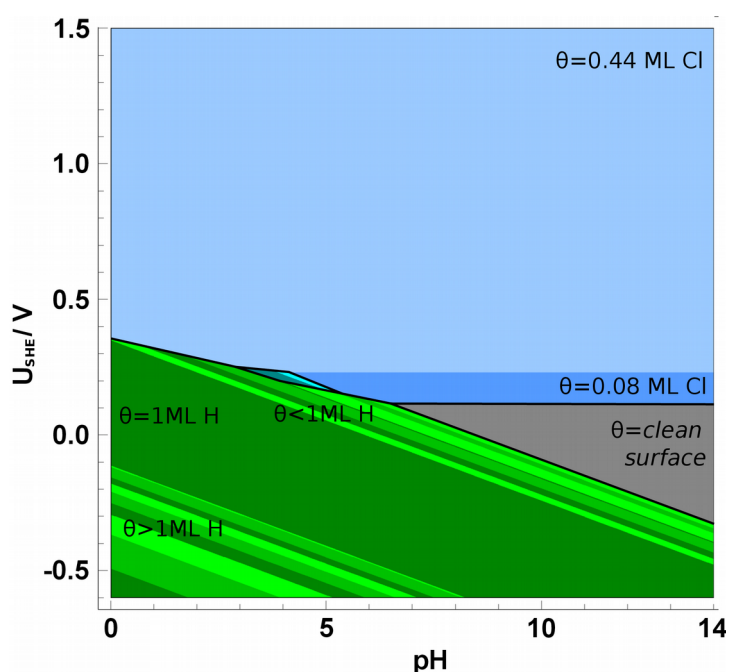


Fig1. Calculated Pourbaix diagram of the co-adsorption of chlorine and hydrogen on Pt(111) (from Ref. 5).

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3. S. Sakong and A. Groß, *ACS Catal.* **6**, 5575 (2016).
4. S. Sakong and A. Groß, *Electrocatal.* **8**, 577-586 (2017).
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