ELECTROCHEMICAL SURFACE PHASE DIAGRAMS: SOLVATION EFFECTS AND SELECTIVITY

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Solid/liquid interfaces are at the heart of many problems of practical importance. Improving the life of battery materials, the efficiency of electro-catalysts or the protection against corrosion requires understanding of the processes occurring at the solid/liquid interface. Central to such an understanding is the identification of the structures forming at the surface of a solid immersed in an aqueous electrolyte. Unfortunately, our knowledge how the electrolyte influences their formation and thermodynamic stability is limited.

Ab initio modelling using density functional theory (DFT) has proven immensely successful in providing atomistic insight into various questions of materials science, but its application to electrochemical problems is challenging, due to the presence of the solvent. Utilising concepts from semiconductor physics has enabled us to overcome some of these obstacles [1], which opens, for example, the path to constructing electrochemical surface Pourbaix diagrams using *ab initio* calculations. These are phase diagrams, which depict the stability of surface structures as a function of the relevant environmental conditions of pH and electrode potential U. Constructing such an *ab initio* surface Pourbaix diagram for the (0001) surface of ZnO, we study the impact an aqueous electrolyte has on the thermodynamic stability of polar oxide surfaces. We find that solvation effects are highly selective. They have little impact on surfaces with metallic character, but favour the stabilisation of semiconducting surfaces experiencing a high electrostatic penalty in vacuum [2]. This high selectivity has direct consequences for the surface phase diagrams and explains why certain structures are preferentially observed in electrochemical environment.

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1. M. Todorova and J. Neugebauer, Phys. Rev. Applied **1**, 014001 (2014).
2. S. Yoo, M. Todorova and J. Neugebauer, Phys. Rev. Lett. **120**, 066101 (2018).