Stability and reactivity of solid/liquid interfaces from ab initio calculations

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Solid-liquid interfaces are at the heart of many problems of practical importance. Understanding the processes occurring at such interfaces is crucial, for example, for the improvement of battery materials, electro-catalysis or corrosion. Central to such an understanding is the knowledge of the surface structures that form when a solid is immersed in an aqueous electrolyte, how their formation and stability is influenced by the presence of the electrolyte or how the interface evolves under applied bias. To address these questions, we focus on two materials relevant to the field of corrosion.

Constructing an electrochemical surface Pourbaix diagram, which depicts the stability of the polar (0001) surface of ZnO as a function of *p*H and electrode potential *U*, we find that solvation effects are highly selective. They have little impact on surfaces with metallic character, but largely stabilize semiconducting structures, particularly ones that have a high electrostatic penalty in vacuum [1].

Moving beyond the thermodynamic treatment requires the ability to apply an external bias. This is not straight forward to do when using a standard density functional theory code with periodic boundary conditions, because of the requirement of a constant Fermi level throughout the supercell. Our development of an approach enabling such a fully ab initio description of a solid/liquid interface, allowed us to study the anomalous H_2 evolution at the Mg surface at anodic conditions [2]. We find that this phenomenon, which has puzzled the corrosion community for more than a century, is due to an unusual adsorption, which triggers a reaction resembling a Heyrovsky reaction.

References:

[1] S. Yoo, M. Todorova und J. Neugebauer, Phys. Rev. Lett. **120**, 066101 (2018).

[2] S. Surendralal, M. Todorova und J. Neugebauer, Phys. Rev. Lett. (under review).