From semiconductor defect chemistry to electrochemistry: Insights into corrosion mechanisms from ab initio concepts

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Understanding the mechanisms leading to corrosion will aid the development of strategies for protection against corrosion. Gaining insight into the microscopic processes occurring at a solid/liquid interface, however, is hard for both experimental measurements and theoretical modelling. In particular the involvement of different classes of materials (metal, semiconductor/insulator, liquid) with dissimilar characteristics is challenging for theoretical modelling, since this imposes different requirements on investigational approaches. The liquid phase is probably most challenging regarding its dynamics and rich configurational space, requiring long sampling times. The correct alignment between the solid's band structure and the redox potentials is arguably the most important prerequisite for the occurrence of a reaction. Yet density functional theory, in particular with conventional functionals, has known deficiencies in describing band gaps and/or alignment correctly. While remedies for such failures may exist, they are often computationally prohibitively expensive and not tractable.
Point defects, a common attribute of each phase within a corroding system, are an attractive descriptor from a modelling point of view. They enabled us to develop an approach that naturally links ab initio calculations to experimental observables, such as pH and the electrode potential U, which define and govern the state of an electrochemical system [1]. Using the example of Zn corrosion it will be discussed how point defects can be used to gain insight into fundamental corrosion mechanisms by the construction of defect stability diagrams [2] and suggest routes to counteract corrosion [3].

[1] M. Todorova and J. Neugebauer, Phys. Rev. Appl. **1** (2014) 014001.
[2] M. Todorova and J. Neugebauer, Surf. Sci. **631** (2015) 190-195.
[3] M. Todorova and J. Neugebauer, Farad. Discussions **180** (2015) 97-112.