Fundamental Atomic Insight in Electrocatalysis

Electrochemical energy conversion reactions depend on the atomic structure of the interface between the electrode and the electrolyte. In order to make advances in technology, atomic-scale simulations are needed to provide insight and fundamental understanding of the electrocatalytic reactions. Thus electronic structure calculations relevant for electrocatalysis have attracted a lot of attention in the last decade. However, it is not straightforward to translate state of the art simulations into electrocatalysis. As the simulations normally are done at constant number of ions and electrons rather than at constant potential and constant pH, which represent the real physical conditions. In fact, due to this, the electrochemical interface presents one of the frontiers for electronic structure simulations.

In this chapter we describe how standard simulations can provide atomic-scale understanding of electrocatalytic reactions. We introduce the computational version of reference electrodes, which are key in the interpretation of simulations. Furthermore, the reference electrodes are used to create phase diagrams and reaction free energy diagrams for electrocatalytic reactions. The chapter will focus on simulations which can be done without any special implementation of the electronic structure method. This means that we focus on explicit solvent and charge-neutral interfaces. The connection to the electrode potential is introduced in the analysis of the simulations rather than in the simulations themselves.