

First principles description of electrochemical reactions at water/Pt(111) interface

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To elucidate microscopic details of an electrochemical reaction that takes place at the electrode-electrolyte interface has been an issue of long standing in the electrochemistry as well as the surface science. One of the reasons for this is the following: An electrochemical reaction is promoted by an applied bias in an experiment whereas it is difficult to control the bias potential in a conventional first principles molecular dynamics (FPMD) simulation. Thus we cannot simulate and analyze the electrochemical reaction, which would not occur spontaneously, by a FPMD simulation. To overcome this problem two of the present authors have developed a new method, effective screening (ESM) method [1], to calculate biased surface/interface. This method can directly treat the nonrepeated slab model with use of a Green's function technique. In this research, we have carried out FPMD simulations for the initial step of the hydrogen evolution reaction (HER) at water/Pt(111) interface by utilizing the ESM method. We model the water/Pt(111) interface as a slab model and put one more hydrogen atom in the form of H_3O^+ into the calculation cell.

In the present talk, after characterizing the ESM method and our simulation model, we will present following results. With increasing applied potential, the excess proton is bound in the first water layer and diffuses in this layer region via the H_5O_2^+ complex. When we applied substantially strong potential, the excess proton is adsorbed onto the Pt surface. The adsorption is accompanied by a transfer of an electron from the interface state. These results show that we have succeeded in simulating one of the electrochemical reactions by the FPMD+ESM simulation.

[1] M. Otani and O. Sugino, *Phys. Rev. B* (2006) **73**, 115407.