How to Model the Oxygen Evolution at the Solid-liquid Interface?

Xueqing Zhang[1,2], Thijs J. H. Vlugt[1], and Anja Bieberle-Hütter[2]
[1]*Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, Delft, The Netherlands*
[2]*Electrochemical Materials and Interfaces, Dutch Institute for Fundamental Energy Research, Eindhoven, the Netherlands*

The design of highly efficient electrodes for photoelectrochemical (PEC) water splitting is of both fundamental and practical importance.[1-4] The solid-gas model simulations of the oxygen evolution reaction (OER) have demonstrated that the water splitting activity can be enhanced strongly by tuning of surface properties,[5-6] such as surface orientation, surface steps, nano-structure (nano-cluster and nano-cavity), co-catalyst and oxygen vacancies.[5-7] This is how the electrode morphology affects the adsorption energies of the intermediate species during the OER. However, it is a solid-liquid (usually semiconductor-water for the PEC cell) interface at experimental condition. Therefore, to simulate the experimental PEC condition the solid-liquid interface, as shown in Figure 1 (a), should be considered instead of state-of-the-art solid-gas interface. This is very challenging, since we are dealing here with a photo-activated system and semiconductor materials in a reacting solid-liquid environment. To stimulate the discussion in this field of research, we propose here the rump discussion of oxygen evolution at the solid-liquid interface within the topic of solute/electrode interaction. Our preliminary ab-initio molecular dynamics simulations predict that the free energy step (Figure 1 (b)) is much lower than earlier determined by the solid-gas model (1.9 eV)[5]. However, it is very difficult to rationally calculate the activation energy and the reaction rate constant due to the complexity of the solid-liquid interface and the very dynamic proton transfers. We propose at the rump session to discuss among others the following aspects, which are important and not well understood in the field of PEC water splitting. (a) How can we calculate the free energy, activation energy and rate constants at the solid-liquid interface considering the reactive environment in the surrounding of water molecules (compared to the solid-gas model)? (b) How do the physical/chemical parameters (for example pre-factors) of the solid-liquid interface affect the simulation results (such as coverage of intermediate species)? (c) What is the difference between the light excitation and electrical excitation (since the PEC process is typically assumed as an electro-catalytic process in the OER simulations)? and (d) Does the OER reaction mechanism obtained at the solid-gas model still hold for the solid-liquid interface? At the end of the rump discussion we will be able to formulate a clear story about how to solve the challenges in the simulation of solid-liquid interface. In addition to the discussion for PEC system, the discussion results obtained can be widely applied to other systems with the solute/electrode interaction.
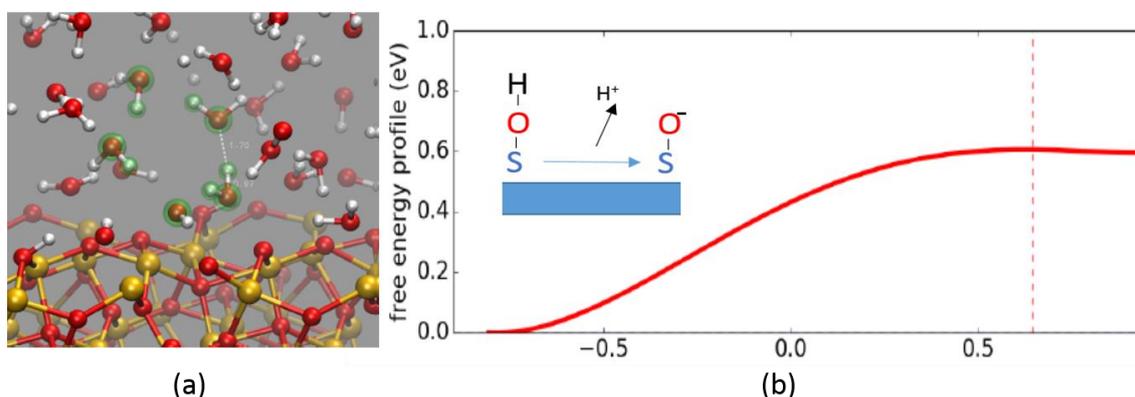

(a)

(b)

Figure 1 a) the solid-liquid interface with the proton transfer process highlighted in green, (b) the free energy profile of the proton transfer from the surface to the water solution.

1.	Zhang, X.; Bieberle-Hütter, A., Modeling and Simulations in Photoelectrochemical Water Oxidation: From Single Level to Multiscale Modeling. *ChemSusChem* **2016**, *9*, 1223-1242.

2.	Rossmeisl, J.; Qu, Z. W.; Zhu, H.; Kroes, G. J.; Nørskov, J. K., Electrolysis of Water on Oxide Surfaces. *J. Electroanal. Chem.* **2007**, *607*, 83-98.

3.	van de Krol, R.; Liang, Y.; Schoonman, J., Solar Hydrogen Production with Nanostructured Metal Oxides. *J. Mater. Chem.* **2008**, *18*, 2311-2320.

4.	Cheng, J.; Liu, X.; VandeVondele, J.; Sulpizi, M.; Sprik, M., Redox Potentials and Acidity Constants from Density Functional Theory Based Molecular Dynamics. *Acc. Chem. Res.* **2014**, *47*, 3522-3529.

5.	Zhang, X.; Klaver, P.; van Santen, R.; van de Sanden, M. C. M.; Bieberle-Hütter, A., Oxygen Evolution at Hematite Surfaces: The Impact of Structure and Oxygen Vacancies on Lowering the Overpotential. *J. Phys. Chem. C* **2016**, *120*, 18201-18208.

6.	Zhang, X.; Cao, C.; Bieberle-Hütter, A., Orientation Sensitivity of Oxygen Evolution Reaction on Hematite. *J. Phys. Chem. C* **2016**, *120*, 28694-28700.

7.	Zhang, X.; Cao, C.; Bieberle-Hutter, A., Enhanced Electrochemical Water Oxidation: The Impact of Nanoclusters and Nanocavities. *Phys. Chem. Chem. Phys.* **2017**, *19*, 31300-31305.