Electrochemical interface

Helmholtz layer

Adsorption of ions

Electric double layer

Redistribution of electrolyte ions

Water conduction band

Electron transfer (redox) reaction

e^-

E_F

Water valence band

Pt

Bias potential

Potential profile

ELUDATION OF THE ENERGY CONVERSION PROCESS

FIGURES

Water splitting is a subject of study in junior high school. When this familiar chemical reaction proceeds in opposite direction, we can get electricity from hydrogen and oxygen. Explanation of those well-known phenomena is the target of modern electrochemistry. Here we use the most sophisticated computational tools to attack this problem.

Electrochemical Interface

The electricity is generated at the interface of the electrode and the electrode. Hydrogen is dissociated into proton and electron at the anode, and the proton and the electron reduce the oxygen at the cathode to produce water, as shown in Fig.1. This phenomenon can be abstractly modeled using one side of the electrode as shown in the above figure. There is unbalance in the forward and back ward reactions at the interface, causing electrified surface and redistribution of the electrolyte from the equilibrium. At the electric double layer thereby generated, the electrode reaction occurs. True understanding of the interface state is the target of our study.

How to model the interface from first-principles?

We need to capture the electron transfer between the electrode and the reactants and the chemical bond formed between them. This requires accurate electronic structure calculation. In addition, water molecules play important role in the formation of the electric double layer. The problem of the modeling is how accurately we need to go.

The effect of bias potential and pH, crucial for the electrochemical research, can be captured in principle, but we cannot incorporate infinite water molecules into the computational cell. It is practical to approximate the water in the off-shore region by a continuum. To establish a corresponding implicit solvent mode, we have spent many years.

Previously we have developed the effective screening medium (ESM) method to describe the off-shore water using a dielectric continuum. This enabled to apply bias potential to the interface and follow the electrode dynamics for the first time. Indeed, by applying negative bias to the electrode acid solution interface, we reproduced an electrochemical reaction $H^+ + e^- \rightarrow H^*$, which is a part of water splitting reaction. The simulation was done not only for the hydrogen evolution, but also for the oxygen reduction reaction. See http://sugino.issp.u-tokyo.ac.jp/public/ for further detail.

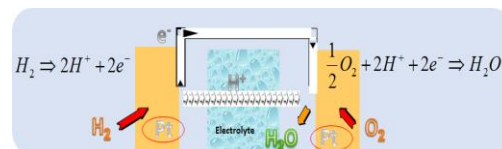$$H_2 \Rightarrow 2H^+ + 2e^- \qquad \frac{1}{2}O_2 + 2H^+ + 2e^- \Rightarrow H_2O$$

Fig.1: Electrode reaction

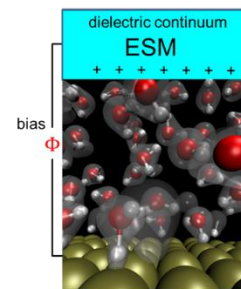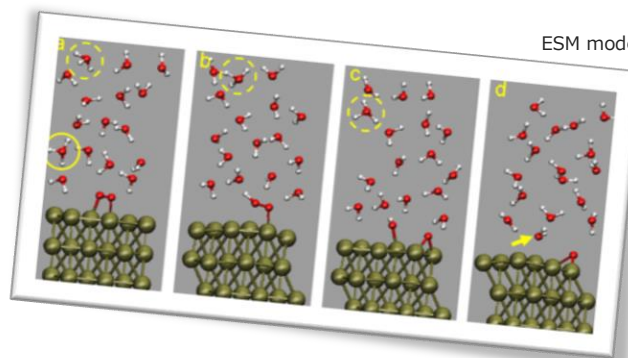Anode reaction (left) and cathode reaction (right).

Fig.2: ESM

ESM modeling of the platinum acid-solution interface.

Target of out post-K computer simulation

Owing to the simulations, we have gradually advanced understanding of the electrode, but the knowledge is not sufficient. We need to further advance the theory to achieve real contribution to electrochemistry. For this purpose, we have been modifying the algorithms and the computer codes for years, and have now reached the phase to performing product run.

The improved simulation code is able to determine the charge distribution using the liquid theory instead of simply describe the solvent using the dielectric continuum as did previously. With this, we can now more realistically describe the pH effect and the effect by electrolyte ions. The bias potential can be more legitimately determined, so that the constant bias simulation can be done meaningfully. We will simulate the anode and the cathode sides of the platinum solution interface systematically taking various surface structures into account. We believe we will be able to significantly advance the microscopic theory of electrochemistry. Because of large number of simulations required, we will intensively use K-computer and post K-computer.

Significance of the study

It is not well known yet how the oxygen reduction reaction will occur; there are various candidates as shown in the right-figure. We will challenge this problem in this project. If our method turns out to be successful and can be applied to other electrochemical processes as well, it is indeed a significant achievement. It will not be so far that we can advance our understanding on the battery and the bioelectricity.

We will try to predict the internal resistance of the fuel cell by calculating the reaction resistance and the electric double layer capacitance. For this purpose, the electrode kinetic equation will be solved together with the mass transport equation, whose parameters will be determined by other groups performing a molecular dynamics simulation. Then, it will be possible to determine the current voltage curve taking the structure of the fuel cell.

Role of the PD

We are looking for a researcher who will perform the simulation using the large supercomputers like K-computer. It is necessary to have an experience with first-principles simulation and have learned basics of computer hardwares and softwares sufficient for handling K-computer. Background of statistical physics or chemical kinetics is also required.
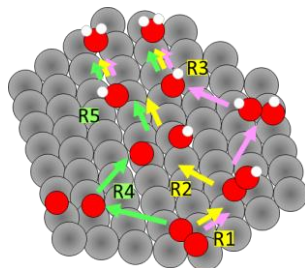
■ Dissociative mechanism

■ Associative mechanism

■ 2nd associative mechanism