Nano-Simulation of Electrode Reactions in Fuel Cells

Project Representative

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Electrode reaction on the hydrogen electrode in the fuel cell was, at first, simulated by the first principles molecular dynamics using the STATE (Simulation Tool for Atom TEchnology) code developed by Morikawa et al. with newly developed effective screening medium (ESM) method proposed by Otani and Sugino to control the electrode potential in a similar way as real electrodes do. A starting configuration was comprised of 36 Pt atoms, 32 water molecules and a proton under the periodic boundary conditions. It was possible to have an electron transfer reaction with hydrogen atom adsorption on Pt electrode after adding 0.95 electrons. This adsorption reaction is the first step of the hydrogen evolution reaction (Volmer step). Electron transfer reaction was analyzed in detail.

Keywords: fuel cell, first principles molecular dynamics, electrode reaction, Volmer reaction, effective screening medium

1. Introduction

Fuel cells are expected to provide a solution to some current energy problems because they are environment-friendly. But, the present fuel cells have not achieved their potentially high efficiency in the conversion from chemical to electric energy, when they are used for practical purposes. Their cost is also very high because of expensive platnium electrode. Thus, there are a lot of points that must be improved. The purpose of our project started from 2005 is to understand electrode reactions and properties by the first principles way for further development of fuel cells.

1.1 Electrode reactions

"Electrode reaction" is a chemical reaction associated with electron transfer on electrodes in an electrochemical cell. A typical fuel cell uses hydrogen gas as a fuel and oxygen gas from the air as an oxidizing agent. The electrode reactions take place at anode and cathode as:

$H_2 \rightarrow 2H^+ + 2e^-$ on anode (negative terminal)

$O_2 + 4H^+ + 4e^- \, 2H_2O$ on cathode (positive terminal)

Protons H^+ pass through a proton selective ion conductor located between the anode and the cathode, and electrons e^- pass through an outer electric circuit to give an electric power. Total reaction is, then, a simple oxidation reaction of hydrogen molecules.

$2H_2 + O_2 \rightarrow 2H_2O$ Total reaction

1.2 Technological problems in fuel cells

One of the biggest problems which must be solved is a small output current. It is necessary to find good electrode materials, which give higher exchange current, i.e. highly active catalysis having lower activation energy. This is a common problem in the hydrogen and oxygen electrodes. At present, platinum or its alloy is used for the both electrodes. The oxygen electrodes have another problem that is lower output voltage than thermodynamically expected value. About the hydrogen electrode side, a problem is CO (carbon monoxide) poisoning of platinum; deactivation of electrode because of adsorption of CO on platinum when CO is included in the hydrogen gas as an impurity.

1.3 How to solve these problems by simulations

Since electrode reactions are basically the nano-scale phenomena, atomic and electronic scale understanding is necessary to improve the system performance. The chemical reaction associated with the electron transfer must be simulated. It takes in a complex system, i.e. solution, at a certain temperature. Molecular dynamics (MD) with electronic state

calculation, which is called first principles MD (FPMD), is necessary. In order to add the voltage difference to make the electron transfer, effective screening medium (ESM) method[1] developed in 2005 is implemented in FPMD code, STATE[2]. Hydrogen electrode is the target for the simulation with FPMD and ESM, since its reaction mechanism is simpler and known better than that in the oxygen side.

2. Calculation method and system

2.1 Method

Since chemical reactions fundamentally take place because of movement of atoms, we need to calculate trajectories of all atoms concerned. Such a calculation is possible by the first principles MD in which atom i of mass m_i at position $\mathbf{q}_i$ moves by Newtonian equation

$$m_i \frac{d^2 \mathbf{q}_i}{dt^2} = \mathbf{f}_i .$$

Force $\mathbf{f}_i$ on atom i with charge z_i is calculated from the electronic state calculation of the whole system by solving the Schrodinger equation for electrons,

$$\hat{H}\Psi = E\Psi$$
$$\hat{H} = \sum_j \frac{\partial^2}{\partial^2 \mathbf{r}_j} + \sum_j \sum_{k(k>j)} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} - \sum_j \sum_i \frac{z_i}{|\mathbf{r}_j - \mathbf{q}_i|},$$

where $\mathbf{r}_j$ is position of electron j. This equation is solved using the density functional theory (DFT) with some approximations. In this calculation we used the standard DFT code, STATE (Simulation Tool for Atom TEchnology),[2] in which wave function Ψ is expanded by plane waves with ultra-soft pseudopotentials[3] for the inner core electrons. Generalized gradient approximation (GGA) is used with PBE functional[4] Energy E was calculated with cutoff energies 225 Ry and 25 Ry for electron density and wave functions, respectively. Time step of the molecular dynamics was 1.2 fs.
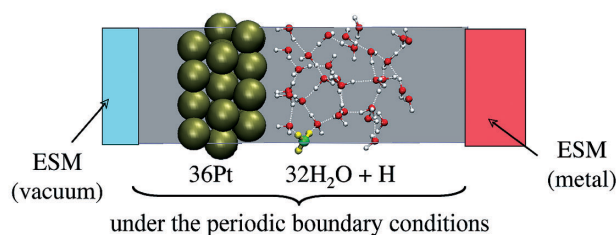

Fig. 1 A unit cell of first principles molecular dynamics simulation.

2.2 Platinum-liquid water system with ESM

A system of 36 Pt atoms ($3 \times 2\sqrt{3}$) and 32 H_2O molecules in a periodic unit cell was used as a model of a water/electrode interface. We added a hydrogen atom in the system to have a hydronium ion H_3O^+. This unit cell was placed between two ESMs of vacuum and metal, which have dielectric constant $\varepsilon = 1$ and $\varepsilon = \infty$, respectively, as shown in Fig. 1.

Since the ESM acts as a medium having the given dielectric constant, the counter charge is induced in ESM($\varepsilon = \infty$) when a certain number of electrons are added to the Pt/water system. Then, it gives a bias, in another word, the potential difference, with keeping the neutrality of the whole system.

3. Results and Discussion

3.1 Water orientation near the Pt electrode

By adding the potential difference, water molecules rotate as their dipole moment directing toward the negatively charged platinum surface. Such a rotation makes a screening of the outer potential, resulting in an increase of the potential difference in the electric double layer between the platinum and the water layer. Therefore, water molecules attached on the negatively charged Pt surface take their H atoms toward the Pt atoms (Fig. 2b), though they are randomly oriented on the neutral Pt surface (Fig. 2a).
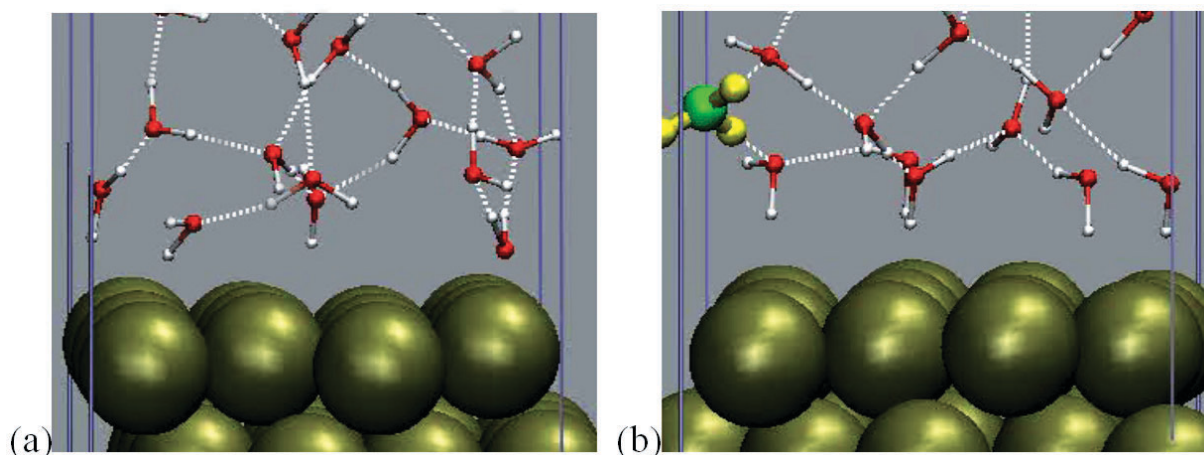

Fig. 2 Water structure near the Pt surface.
(a) On neutral Pt surface. (b) On negatively charged Pt surface.
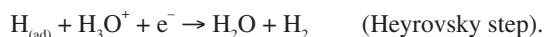
3.2 The first step of the hydrogen evolution reaction

Hydrogen oxidation in the fuel cell and proton reduction in the hydrogen evolution reaction (HER) take place in the same scheme. The latter consists, at first, of the Volmer step, in which a hydrogen atom is adsorbed with a charge transfer from a hydronium ion as

$$H_3O^+ + e^- \rightarrow H_2O + H_{(ad)} \qquad \text{(Volmer step).}$$

This adsorbed hydrogen atom makes dimerization to generate H_2 or it reacts with another hydronium ion with the charge transfer as

$$2H_{(ad)} \rightarrow H_2 \qquad \text{(Tafel step)}$$

and

$$H_{(ad)} + H_3O^+ + e^- \rightarrow H_2O + H_2 \qquad \text{(Heyrovsky step).}$$

In our simulation, we could observe the hydrogen atom adsorption from the hydronium ion, when 0.95 electron is added to the system (Fig. 3). Electron transfer took place at this adsorption process. Electrode potential at this electron transfer reaction was estimated to be –0.8 V vs. SHE. This very high over potential is due to a "rare event" in a short time, ~ps. The electron transfer rate in this simulation corresponds to extremely high current density, ~10^7 A/cm^3, under which condition very high over potential is necessary.

4. Conclusion

We could, at the first time, simulate the *real* electrode reaction by the first principles molecular dynamics combined with effective screening media.

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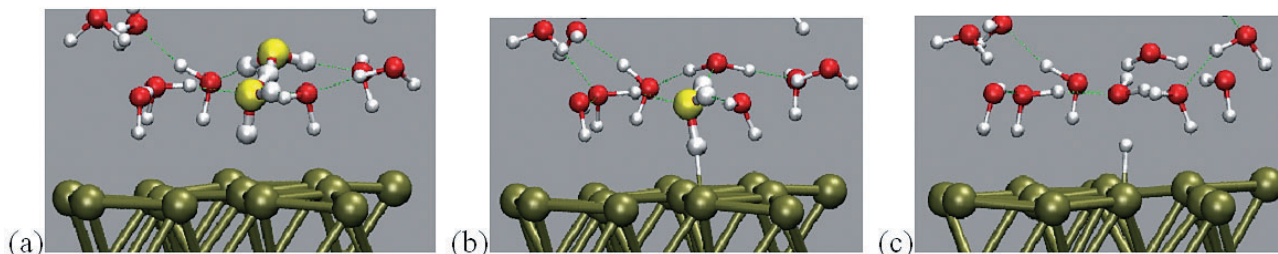
Fig. 3 The first adsorption step with the electron transfer in the hydrogen evolution reaction.
(Reaction takes place from (a) to (c).)

燃料電池の電極反応ナノシミュレーション

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　燃料電池の水素極の電極反応を、森川が開発している第一原理分子動力学計算コードSTATE (Simulation Tool for Atom TEchnology)に、大谷・杉野が新たに開発したeffective screening medium (ESM)法を導入して、初めてシミュレーションできた。周期境界条件下に置かれた計算ユニット中に白金36原子、水32分子、水素原子1個が存在する系に対して、電子を0.95個入れたところ、電荷移動とともに、溶液中のプロトンが、水素原子として白金上に吸着するフォルマー過程が再現できた。これは、バルクの水の電気分解による水素発生反応の第一段階である。電子移動反応を詳しく解析した。

キーワード：燃料電池, 第一原理分子動力学, 電極反応, Volmer反応, 有効遮蔽体