Nano-Simulation of Electrode Reactions in Fuel Cells

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In the second year of this project, 2006, we could simulate an electrode reaction by 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 achieve an electron transfer reaction with hydrogen atom adsorption on Pt electrode after adding a bias. This adsorption reaction is the first step of the hydrogen evolution reaction (Volmer step). The detailed analysis and more calculations are necessary to understand the electrode reaction in the fuel cells.

Keywords: fuel cell, first principles molecular dynamics, electrode 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 realized their potentially high efficiency in the conversion from chemical to electric energy, when they are used for practical purposes. They are also very expensive. Thus, there are a lot of points that must be improved to achieve the higher energy-conversion efficiency. 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. The electrochemical reactions take place at anode and cathode as:

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

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

Protons pass through a proton selective ion conductor located between the anode and the cathode, and electrons 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 improved is a small output current. It is necessary to find good electrode materials, i.e. highly active catalysis with lower activation energy, which give higher exchange current. The present oxygen electrodes have various problems; low output current and lower output voltage than thermodynamically expected value. About the hydrogen electrode side, platinum is a very good electrode, though it is expensive. A problem of platinum is CO (carbon monoxide) poisoning; 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. The big difference of the electrochemical reactions from the other chemical reactions on surfaces, i.e. ordinary catalytic reactions, is that the former reaction takes place on the surface of which electric potential is controlled from the outside. A purpose of the simulation is to obtain kinetic properties of the reaction (non-equilibrium property). These properties, however, need a high computational load to be calculated at a certain temperature, since molecular dynamics (MD) with electronic state calculation, i.e. first principles MD (FPMD), is necessary. Another problem to be solved for the simulation is to find a method to have the voltage difference in a unit cell under the periodic boundary conditions of FPMD. We have developed effective screening medium (ESM) method and tested it in 2005. Hydrogen electrode is the target for the simulation with FPMD and ESM in 2006, since its reaction mechanism is simpler and more known than the oxygen side.

2. Calculation method and system

2.1 Method

Since fundamentals of chemical reactions lie in 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 Schrödinger 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),1) in which wave function Ψ is expanded by plane waves with ultra-soft pseudopotentials 2) for the inner core electrons. Generalized gradient approximation (GGA) is used with PBE functional.3) 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.

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. The total system is as follows.

$$\mathrm{EMS}(\varepsilon=1)\ \|\ \mathrm{vacuum}\ |\ 36\mathrm{Pt}\ |\ 32\mathrm{H_2O}+\mathrm{H}\ |\ \mathrm{vacuum}\ \|\ \mathrm{EMS}(\varepsilon=\infty)$$

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 gradient, with keeping the neutrality of the whole system. Divergence of energy under the periodic boundary conditions is, thus, avoided.

3. Results and Discussion

3.1 Water structure near the Pt electrode

Different structures of water on electrodes from those in the bulk have been experimentally observed by X-ray diffraction and STM. Our simulation also showed that water molecules are structured on the Pt electrode under a certain bias and give higher density than that in the bulk.5) These results support qualitatively the experiments but they are somewhat different quantitatively from the experiments.

3.2 Adsorption reaction

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

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

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

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

and

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

In our simulation, we could observe the hydrogen atom adsorption from the hydronium ion with the charge transfer under a certain condition. In order to have such a condition, water reorganization was necessary. The detailed analysis is now on going.

4. Conclusion

We could simulate an electrode reaction by the first principles molecular dynamics combined with effective screening media. The detailed analysis will be done in 2007 with more simulations to have quantitative data.

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燃料電池の電極反応ナノシミュレーション

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本プロジェクトの2年目である2006年は、燃料電池の水素極の電極反応を解析するために、森川ら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、シミュレーションした。その結果、ユニットセル中に白金36原子、水32分子、水素原子1個が周期境界条件下で存在する系に対して、ある程度の電位をかけることで、電荷移動とともに、プロトンから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。燃料電池内の電極反応を理解するために、さらに、詳細なシミュレーションと解析が継続中である。

キーワード：燃料電池, 第一原理分子動力学, 電極反応, 有効遮蔽体