Nano-Simulation of Electrode Reactions in Fuel Cells

Project Representative

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In the first year of this project, 2005, the computational environment for the first principles molecular dynamics simulations for electrochemical reactions in fuel cells was set up. We have implemented into STATE (Simulation Tool for Atom TEchnology) code developed by Morikawa et al. 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 which was comprised of 36 Pt atoms, 48 water molecules and a proton under the periodic boundary conditions was obtained after the long-time annealing. Beside this very hard and rigorous calculation, we have also done more practical simulations to help developments and understandings of nano particle (cluster) electrodes used in fuel cells. We could calculate a "whole" Pt_{147} cluster on which a H atom is adsorbed by the same code.
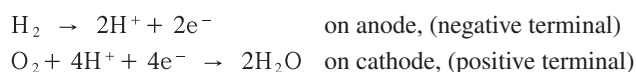
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1. Introduction

Fuel cells are expected to provide a solution to some current energy problems because of their high efficiency and 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 in 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 electrode properties for further development of fuel cells by the first principles way.

1.1 Electrode reactions

"Electrode reaction" is a chemical reaction associated with electron transfer on electrodes in a 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 with lower inner resistance. It is necessary to find good electrode materials, i.e. higher active catalysis with lower activation energy, which give higher exchange current. The present oxygen electrodes have various problems; low output current and low output voltage. 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. This is also the case for direct methanol fuel cells in which methanol is used

as a fuel instead of hydrogen. This type of cell is expected to be commercialized as a battery for mobile equipments like laptop computers, mobile phones, etc, in near future.

1.3 How to solve these problems

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 reaction 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. We need to calculate kinetic properties of the reaction (non-equilibrium property) at the certain temperature. These properties, however, need the high computational load to be calculated, since molecular dynamics (MD) with electronic state calculation, i.e. first principles MD, is necessary. The more practical approach is to calculate energies of initial and final configurations and the intermediate states by the first principles method at 0 K. Hydrogen electrode is the target in 2005, since its reaction mechanism is simpler and more known than the oxygen side.

2. Calculation 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 $\mathbf{q}_i$ with charge z_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 is calculated from the electronic state calculation of the whole system by solving the Schrödinger equation for electrons,

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

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.

3. Calculation systems

3.1 Platinum-liquid water system

A system of 36 Pt atoms ($3 \times 2\sqrt{3}$) and 48 H_2O molecules in a periodic unit cell of 8.4Å × 9.7Å × 24.6Å was used as a model of a water/electrode interface. In order to prepare a well equilibrated geometry of liquid water, we annealed the system at 600 K for 1ps, cooled it down to 300 K within another 1 ps, then annealed it again at 300 K for 2–3 ps. We also added a hydrogen atom in the system to have a hydronium ion H_3O^+ as shown in Fig. 1.

3.2 Platinum clusters

Since a platinum crystal is in the fcc structure, we prepared the fcc clusters of platinum atoms as shown in Fig. 2. Adsorption energy of H, and O was calculated using "STATE". The cluster was located in a large super cell under the periodic boundary conditions.
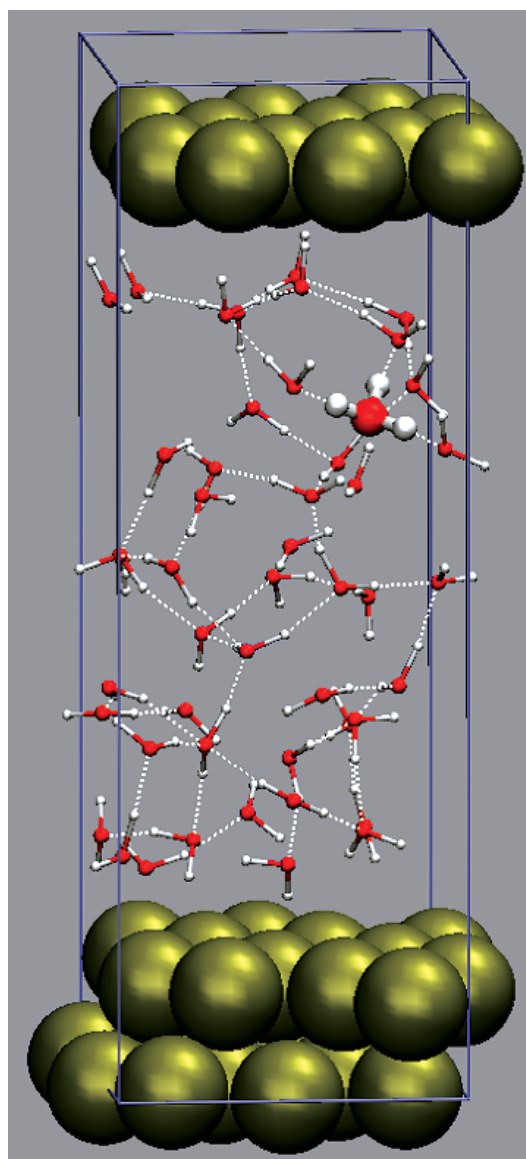

Fig. 1 Simulation cell for the first principles MD. (Pt, gold ball; O, red ball; H, white ball; hydrogen bond, white dotted line)
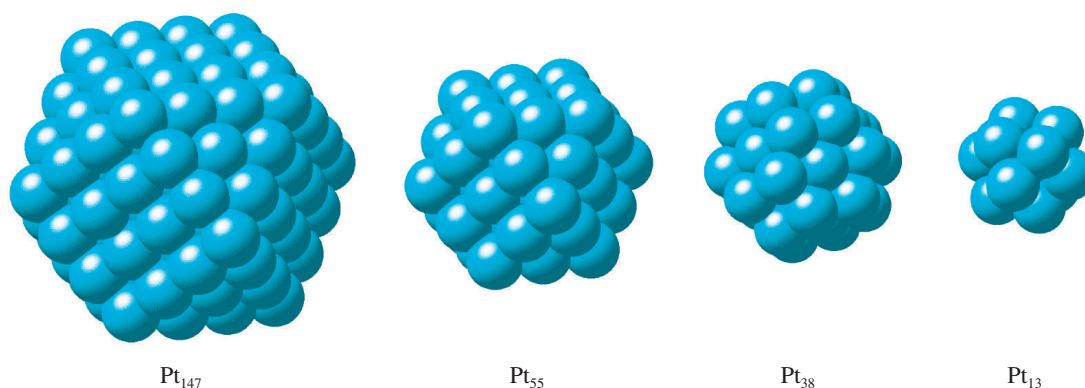
252

Fig. 2 Platinum clusters up to Pt_{147} calculated.

4. Results and Discussion

4.1 Electrode reaction

In order to simulate the electrode reaction more precisely and effectively than previous calculations by the charged slab model, we implemented Effective Screening Medium (ESM) method[4] into STATE. We could prepare the system consisting of Pt | water | vacuum | Pt for the ESM calculation. Hydronium ion movement was found in the liquid water with no chemical reaction.

4.2 Platinum clusters

We found that cohesive energy of Pt cluster as well as Pt-Pt bond length converges slowly with respect to the number of Pt atoms. Hydrogen atom adsorption energy on the clusters gradually decreases as Pt cluster size increases. The adsorption energy on (111) and (100) facets of Pt_{147} approaches the energy on corresponding Pt surfaces. On the other hand, smaller Pt_{13}, Pt_{38}, and Pt_{55} clusters were found to behave quite differently concerning hydrogen adsorption.[5] Icosahedral (Ih) Pt_{147} was also examined. Ih Pt_{147} is more stable than fcc Pt_{147}, which suggests the possibility of a structural transition from fcc to Ih when the Pt cluster size is minimized.

5. Conclusion

We could prepare the starting atomic configuration for the further calculations by ESM in 2006. The larger size clusters than Pt_{147} are also targets in 2006.

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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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　本プロジェクトの最初の年である2005年は、燃料電池の中で起こる電極反応を第一原理分子動力学で解析するために必要な計算環境を整えた。森川らが開発しているSTATE（Simulation Tool for Atom TEchnology）コードに、大谷・杉野が新たに開発したeffective screening medium（ESM）法を導入した。白金36原子、水48分子、プロトン1個を周期境界条件下で長時間アニールして、電極反応のシミュレーションのための出発構造を作ることができた。このような非常に厳密であるが計算負荷の高い計算のほかに、燃料電池に使われるナノ粒子（金属クラスター）電極の開発とその理解にとって必要なより現実的計算も行った。上記と同じコードを用いて、白金147原子のクラスター（その上に水素原子が吸着して電極反応が進む）をまるごと計算することができた。

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