Density Functional Study of Catalytic Oxygen Reduction Reaction (ORR) on Cathode Electrode for Fuel Cell System

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Density functional studies have performed for the platinum cluster model of cathode catalysts that are used in polymer electrolyte membrane fuel cell (PEMFC). A generalized gradient approximation treatment of total energies denoted that the activation barrier for oxygen dissociation after the proton-transfer step, as intermediate species formation, would have similar magnitude that determined by the temperature dependent oxygen reduction Tafel plot measurements.

The PEMFC is currently considered as a potential alternative energy conversion device for automotive applications because of its high energy density and quick response performance to load instability. However, a breakthrough would be required as regard to the amount of precious metals that are used in the catalyst of membrane electrode assembly (MEA). Detailed understanding of the reaction mechanism, particularly in cathode, would be necessary to promote the progress. Unfortunately, since in situ experiments under the operating condition of PEMFC are fairly difficult, the characterization of three phase boundaries (i.e., catalyst/electrolyte/gas-diffusion-layer), which play the most dominant role in power generation, have, therefore, not yet been satisfactorily achieved.

Here, I introduce some preliminary results of density functional calculation for oxygen reduction reaction (ORR) on precious metal electrocatalyst using the cluster model of metal surfaces. It is already reported that the quantum modeling for the fuel cell catalyst would be effective for the poisoning problem which is caused by the carbon monoxide species.[1] Recently, the ORR also come to be a target of molecular orbital theories, but there still remain quantitative discrepancies from the experimental activation barrier and there is a debate of rate-determining steps in this reaction so far. In this study, I tried to attain relatively high accuracy prediction of activation barrier for ORR by taking account of the factors that are thought to affect the final energy profiles of reactions.

Within the framework of DFT, I can express the total energy of the ground state as

$$E = T + U + Exc$$

where T is the kinetic energy of the system of noninteracting electrons, U is the classical electrostatic energy due to Coulomb interactions, and Exc includes all many-body contributions of electrons. The many-body contribution, Exc, is a function of the electron density ρ,

$$Exc = Exc[\rho] \quad \left(\rho = \sum_i |\phi_i(r)|^2\right)$$

where ϕ is the molecular orbital. Thus, it is apparently important to select a reliable Exc so as to get better energetics. Many quest have already been performed in this relation,[2] and I selected one of the most refined functional, as called PW91 that was based on the generalized gradient approximation. This have already been clarified to give the adequate energetics for variety of problems.[3]

For electrocatalysis modeling, the complex electron-transfer process from a precious metal surface (e.g. Pt) to reactant is a key feature of each elemental reaction. It is notable that the basis set description accuracy would play a crucial role for this kind of problem especially in the adsorption energies. There is a notorious superposition error in the case of localized small gaussian basis sets. So I took numerical approaches for the electron integral as was already confirmed the toughness to the superposition error. Regarding the selection of basis set level, I used split valence numerical basis sets[4] with polarization effect (DNP level) that have reported the similar accuracy of 6-311+G(3df,2pd) in conventional gaussian basis sets.[5]

I note that the relativistic effect for heavy precious metals with 5d orbital, such as Pt, cannot definitely be neglected. For example, from our simple comparison of potential surfaces for $Pt_4 + O_2$ models (with fixed Pt_4 positions), there should be apparent discrepancies whether including the relativistic effect or not, see Table 1. Since computation of an all-electron relativistic calculation for large clusters is far beyond practical, I used the model core potential (DSPP[6]) for Pt, which was parameterized with consideration of the relativistic effect that had relatively modest but satisfactory compensation in comparison to all-electron calculation, as in Table 1.

In order to reduce the computational cost for large clusters, I also used LDA functional, as called PWC, with split valence level basis (DN basis) for geometry optimization. Their validity was represented on Table 2. The quantum solver that I used was DMol3, supplied from Accelrys Inc.[7]

In terms of quantitative estimation of energetics, it is important to apply the enough size cluster for the simulation. Thus, I first calculate the cluster size dependence of adsorption energies for oxygen on Pt(111) surface. As shown in Figure 1, it is evident that when molecular oxygen is adsorbed on a single Pt layer, at least ten surface Pt atoms are required. Furthermore, concerning

Table 1. Energetic differences in oxygen dissociation for Pt_4O_2 with the existence of relativistic effect

Calculation level[a]	Binding energy of molecular oxygen[d] /eV	Barrier for linear oxygen dissociation /eV	Reaction heat from molecular adsorption[d] /eV
PW91/DNP//PW91/DNP	−1.04	1.55	−0.97
PW91/DNP(AESR) //PW91/DNP(AESR)[b]	−2.16	0.41	−3.97
PW91/DNP(DSPP) //PW91/DNP(DSPP)[c]	−1.68	0.64	−3.03

[a]Pt is linearly fixed, as d(Pt–Pt) = 2.77 Å. [b]All electron scalar relativistic[5] calculation. [c]A pseudo potential[4] (*Density Functional Semi-core Pseudo Potential*) is applied for Pt, which include relativistic effect. [d]Minus means exothermic reaction.

Table 2. Effect on the geometry optimization for the energy surfaces of oxygen dissociation in Pt_4O_2

Calculation level[a]	Binding energy of molecular oxygen[b] /eV	Barrier for linear oxygen dissociation /eV	Reaction heat from molecular adsorption[b] /eV
PW91/DNP(DSPP) //PW91/DNP(DSPP)	−1.68	0.64	−3.03
PW91/DNP(DSPP) //PWC/DN(DSPP)	−1.68	0.60	−3.11

[a]Pt is linearly fixed, as d(Pt–Pt) = 2.77 Å. [b]Minus means exothermic reaction.

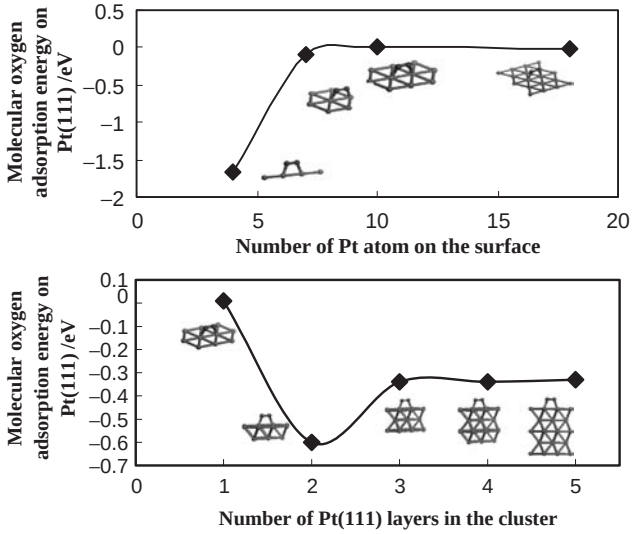

Figure 1. Dependence on Pt(111) cluster size for molecular adsorption energies of $Pt_x + O_2$, where all Pt positions are fixed in its crystal structure.

the number of deeper layers, a size dependent trend also exists. From Figure 1, I find that the three layer Pt_{25} cluster shown in Figure 2, could be the minimum size that required for a reliable energetic analysis.

The reaction that takes place at the cathode catalyst is a water generation reaction from molecular oxygen with the consecutive four-electron reduction reaction. Hence, one important point that strongly related to the concept of rational catalyst design is the plausible reaction pathway from oxygen to water.

$$O_2 + 4H^+ + 4e^- \xrightarrow{Pt} O{\cdot}O + 4H^+ + 4e^- \xrightarrow{Pt} 2O* + 4H^+ + 4e^- \xrightarrow{Pt} \cdots \xrightarrow{Pt} 2H_2O \quad (1)$$

$$O_2 + 4H^+ + 4e^- \xrightarrow{Pt} OOH^+ + 3H^+ + 4e^- \xrightarrow{Pt} O^+{\cdot}OH + 3H^+ + 4e^- \xrightarrow{Pt} O^+ + OH + 3H^+ + 4e^- \xrightarrow{Pt} \cdots \xrightarrow{Pt} 2H_2O \quad (2)$$

$$O_2 + 4H^+ + 4e^- \xrightarrow{Pt} OOH + 3H^+ + 3e^- \xrightarrow{Pt} O{\cdot}OH + 3H^+ + 3e^- \xrightarrow{Pt} O* + OH + 3H^+ + 3e^- \xrightarrow{Pt} \cdots \xrightarrow{Pt} 2H_2O \quad (2')$$

Concerning a possible reaction pathway (1–2′), where reaction (1) involves direct oxygen dissociation, (2) involves the formation of an intermediate before dissociation, such as cationic oxy-hydroxide, and (2′) involves fast electron transfer to an intermediate that results in the formation of neutral oxy-hydroxide, it is apparent that I could not neglect the barrier in the molecular oxygen dissociation on the catalyst. So I first clarified dissociation barrier in this process.

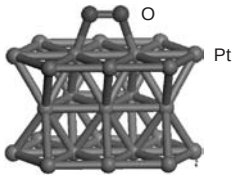

Figure 2. Resulted Pt_{25} cluster that used for the simulation.

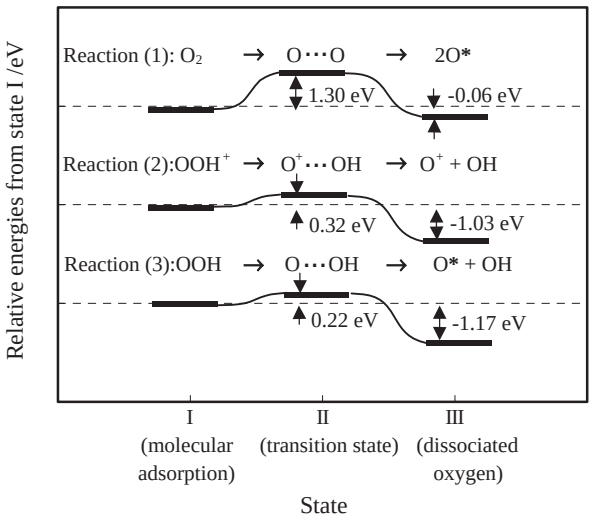

Figure 3. Potential energy profiles for oxygen dissociation on Pt_{25} cluster as regard to the three possible pathways. All calculations were performed under PW91/DNP(DSPP)//PWC/DN(DSPP) condition.

As clearly shown in Figure 3, our results support that the formation of oxy-hydroxide intermediates are more favorable than direct dissociation. The calculated activation barriers for the intermediate formation pathways, 0.22–0.32 eV, are slightly lower than the experimental estimation of 0.22[8,9]–0.44[10] eV, which was determined by the temperature-dependent Tafel plot measurements. The calculated direct dissociation pathway (1.3 eV) is apparently much higher than the experimental values. Thus, considering the quantitative similarity of an apparent activation barrier during the oxygen dissociation, it may be likely that aforementioned barrier is related to the rate-determining step of the cathode reaction. Further studies including water effect are currently investigated.

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