A Cluster Model DFT Study for Oxygen Reduction Reactions

Hisayoshi Kobayashi,*[1] Toshiko Miura,[1] Nobuyuki Takeuchi,[1] and Tokio Yamabe[2]
[1]*Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585*
[2]*Nagasaki Institute of Applied Science, 536, Amibacho, Nagasaki 851-0123*

(Received January 20, 2009; CL-090070; E-mail: kobayashi@chem.kit.ac.jp)

The equilibrium (reversible) potential for oxygen reduction reaction (ORR) on Pt electrodes was evaluated using small cluster models and DFT calculations. For the five elementary reactions, $O_2 \rightarrow OOH$, $OOH \rightarrow O + H_2O$, $OOH \rightarrow HOOH$, $O \rightarrow OH$, and $OH \rightarrow H_2O$, the estimated equilibrium potentials were 0.41, 1.99, −0.35, 1.36, and −0.01 V. Comparing to the standard electrode potential for O_2 reduction, 1.23 V, the OOH and H_2O formations contribute to the overpotential, and HOOH formation does not prevail.

Application of quantum chemical methods to electrode reactions is an important subject for microscopic understanding of electrochemistry and further development of fuel cell systems. Although a few sophisticated treatments have been published so far,[1,2] we propose a simple method to estimate the equilibrium electrode potential for five reductive elementary reactions composing ORR.

Clusters of composition $Pt_5He_8X_2$ and $Pt_6He_9X_2$ are used as models of a Pt electrode, as shown in Figure 1. X_2 means various hetero-diatoms such as F_2, Cl_2, and Li_2, and are used to modify the ionization potential (IP) of Pt clusters without building up charge. The negative value of work function is equal to the electrode potential, and the work function is approximated by the IP. Hence, the IP can be in parallel with the electrode potential, which reflects the imposed outer potential. He atoms are employed as "the fence," which prevents adspecies from bonding to the "second layer" Pt atoms. All the positions of Pt, He, and X atoms are those of Pt atoms in bulk crystal, and are fixed during the calculation.

The reductive reaction is generally written as eq 1.

$$\text{PtX–}\boldsymbol{R} + [O_4H_9]^+ + e^-(E_F) \rightarrow \text{PtX–}\boldsymbol{R}\text{H} + O_4H_8 \quad (1)$$

To simply the notation of electrode Pt clusters, $Pt_5He_8X_2$ and $Pt_6He_9X_2$ are abbreviated as PtX. ***R*** is a reducing precursor representing O_2, OOH, O, and OH. $e^-(E_F)$ means an electron with an energy of the Fermi energy, E_F of electrode. The total energies of PtX–***R*** and PtX–***R***H are calculated by optimizing ***R*** and ***R***H moieties.

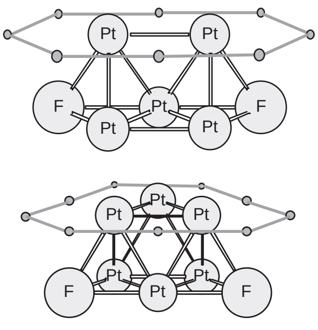

Figure 1. $Pt_5He_8F_2$ and $Pt_6He_9F_2$ clusters. Small gray spheres mean He atoms.

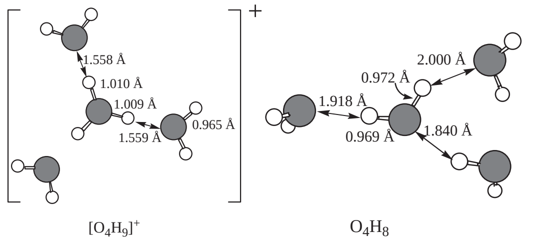

Figure 2. Oxonium ion model (left) and water cluster model (right).

The oxonium ion and deprotonated water cluster are modeled by $[O_4H_9]^+$ and O_4H_8, and their optimized structures are shown in Figure 2. The overall ORR is written as eq 2.

$$1/4O_2 + [O_4H_9]^+ + e^- \rightarrow 1/2H_2O + O_4H_8 \quad (2)$$

The reaction energy is calculated to be −7.62 eV for eq 2. This value is converted to 3.02 V vs. SHE using the absolute value of hydrogen electrode potential (4.6 V).[3] The calculated result overestimates the experimental value (1.23 V vs. SHE) by 1.79 V. The major part of error is ascribed to the absence of solvation effects, which leads to underestimation in stability for cationic species compared to neutral ones. So the calculated 3.02 V is matched to the experimental 1.23 V vs. SHE for all the reactions since $[O_4H_9]^+$ and O_4H_8 appears always in the left and right sides of eq 1.

To explain the term $e^-(E_F)$, eq 1 is decomposed into two steps, i.e., the proton transfer and electron addition.

$$\text{PtX–}\boldsymbol{R} + [O_4H_9]^+ \rightarrow [\text{PtX–}\boldsymbol{R}\text{H}]^+ + O_4H_8 \quad (1a)$$

$$[\text{PtX–}\boldsymbol{R}\text{H}]^+ + e^-(E_F) \rightarrow \text{PtX–}\boldsymbol{R}\text{H} \quad (1b)$$

The energy change by eq 1a shows whether the proton transfer is stable or not, and the calculation is straightforward. Equation 1b indicates that the electron comes from the E_F of PtX–***R*** rather than the vacuum level. The total energy of PtX–***R***H is, however, more stable than that of [PtX–***R***H]$^+$ by several eV's. This is because the electron is added from the vacuum level. To fulfill the condition of $e^-(E_F)$, the IP of PtX–***R*** must be added to the total energy difference between [PtX–***R***H]$^+$ and PtX–***R***H. Finally the reaction energy, E_R is defined by eq 3.

$$\begin{aligned} E_R = {} & E\{\text{PtX–}\boldsymbol{R}\text{H}\} + E\{O_4H_8\} - E\{\text{PtX–}\boldsymbol{R}\} \\ & - E\{[O_4H_9]^+\} + \text{IP}\{\text{PtX–}\boldsymbol{R}\} \end{aligned} \quad (3)$$

where $E\{\mathbf{A}\}$ and $\text{IP}\{\mathbf{A}\}$ are the total energy and IP of **A**.

The E_R is evaluated using various cluster models. If the IP of PtX–***R*** is large (deep E_F), the reaction is endothermic. On the other hand, if the IP is small (higher E_F), the reaction is exothermic and the reduction will proceed easily. For a cluster with an

Table 1. Calculated values for IP, U_{el}, and E_{R} for O_2, OOH, O, and OH reduction to OOH, $O + H_2O$, HOOH, OH, and H_2O

	PtX–***R***	IP	U_{el}[a]	E_{R}	E'_{R}[b]
1	$Pt_5He_8F_2O_2$	8.17	1.78	1.29	
	$Pt_5He_8FClO_2$	7.70	1.31	0.31	
	$Pt_5He_8Cl_2O_2$	7.40	1.01	0.20	
	$Pt_5He_8Br_2O_2$	7.18	0.79	0.17	
	$Pt_5He_{10}O_2$	6.91	0.52	0.15	
	$Pt_5He_8Li_2O_2$	5.55	−0.84	−1.75	
2	$Pt_5He_8F_2OOH$	9.01	2.62	1.17	2.96
	$Pt_5He_8FClOOH$	8.81	2.42	0.50	—
	$Pt_5He_8Cl_2OOH$	8.39	2.00	0.01	—
	$Pt_5He_8Br_2OOH$	7.88	1.49	−0.67	—
	$Pt_5He_{10}OOH$	7.46	1.07	−0.60	1.53
	$Pt_5He_8I_2OOH$	7.42	1.03	—	1.51
	$Pt_5He_8Be_2OOH$	6.93	0.53	—	1.05
	$Pt_5He_8BeMgOOH$	6.43	0.04	—	0.55
	$Pt_5He_8Mg_2OOH$	6.05	−0.34	—	0.20
	$Pt_5He_8Li_2OOH$	6.03	−0.36	—	−1.61
3	$Pt_5He_8F_2O$	8.63	2.24	0.53	
	Pt_5He_8FClO	7.99	1.60	0.05	
	$Pt_5He_{10}O$	7.75	1.36	−0.25	
	$Pt_5He_8Cl_2O$	7.72	1.33	−0.37	
	$Pt_5He_8Br_2O$	6.99	0.60	−2.33	
4	$Pt_6He_9F_2O$	8.11	1.72	0.24	
	Pt_6He_9FClO	7.81	1.42	0.11	
	$Pt_6He_9Cl_2O$	7.50	1.11	−0.45	
	$Pt_6He_9Br_2O$	7.28	0.89	−0.46	
	Pt_6He_9O	7.05	0.65	−0.88	
5	$Pt_5He_8Br_2OH$	9.30	2.91	3.27	
	$Pt_5He_8F_2OH$	9.08	2.69	2.31	
	$Pt_5He_{10}OH$	7.86	1.47	1.58	
	$Pt_5He_8I_2OH$	7.78	1.37	1.58	
	$Pt_5He_8Be_2OH$	7.37	0.98	1.01	
	$Pt_5He_8BeMgOH$	6.79	0.40	0.70	
	$Pt_5He_8Mg_2OH$	6.36	−0.03	−0.03	
	$Pt_5He_8Li_2OH$	6.20	−0.19	−0.03	

[a] IP and U_{el} are related by $U_{\mathrm{el}} = \mathrm{IP}/e^- - 4.6 - 1.79$. [b] E'_{R} shows results for OOH reduction to HOOH.

E_{R} of zero, the reaction is in equilibrium. Thus the purpose of calculations is to find the IP value where the reaction is "thermoneutral," and this IP corresponds to the equilibrium electrode potential.

Gaussian 03 was employed with a hybrid B3LYP DFT method.[4] For Pt and various hetero atoms, the LanL2DZ basis set is used. The 6-311++G(d,p) basis set is used for H and O atoms, and the STO-3G basis is used for He atoms. Table 1 shows the IP, the electrode potential (U_{el}), and E_{R} for the five elementary reduction reactions.

In the second block of Table 1, both results for $O + H_2O$ decomposition and HOOH formation are shown in the fifth and sixth columns. The O atom reduction to OH species is examined with $Pt_5He_8X_2$ and $Pt_6He_9X_2$ clusters, and shown in the third and forth blocks. All the results are shown in Figure 3 as the U_{el} vs. E_{R} relationship.

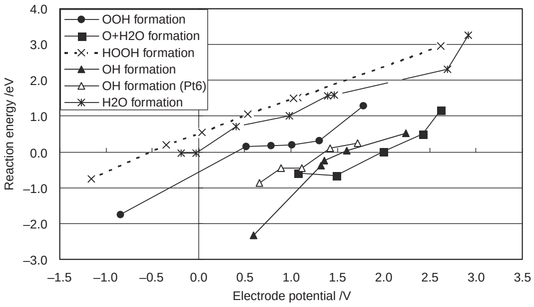

Figure 3. Relation between electrode potential and reaction energy for the five reduction reactions. The vertical dashed line indicates 1.23 V.

The equilibrium electrode potential is determined from the intercept with the $E_{\mathrm{R}} = 0$ line. They are 0.41, 1.99, −0.52, 1.56 (1.36), and −0.01 V for $O_2 \rightarrow$ OOH, OOH $\rightarrow O + H_2O$, OOH $\rightarrow$ HOOH, O $\rightarrow$ OH, and OH $\rightarrow H_2O$, respectively. If the value is lager than 1.23 V, that elementary reaction does not contribute to the overpotential. The OOH and H_2O formation may be the origin of the overpotential. The former is often suggested by other researchers.[5] The difficulty of H_2O formation is ascribed to a strong bonding of OH species like catalyst poison. The OH formation from O atom does not contribute to the overpotential in the present calculation, although it is suggested in the literature.[5] One possible reason is that the O atom cannot be adsorbed to the most stable hollow site with $Pt_5He_8X_2$ cluster. To improve this situation, the calculation is repeated using $Pt_6He_9X_2$ as shown in Figure 1. The equilibrium electrode potential is shifted from 1.56 to 1.36 V, but it is still larger than 1.23 V, and our conclusion is that OH formation does not contribute to the overpotential. Other factors which are not considered here may be coadsorbed species and surface reconstruction. For HOOH formation from OOH, we can say that the reaction hardly occurs owing to a very negative value of the equilibrium potential.

Although the present calculation is based on a rough model for electrochemical systems, especially neglecting the solvents and the electric double layer, it can estimate the equilibrium electrode potentials qualitatively. Refinement of models is the first priority in future work.

The authors are grateful to Prof. Yasukazu Saito for instructive discussion. This work was supported by the Grant-in-Aid (Nos. 20038035 and 20350089).

References

1 J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jónsson, *J. Phys. Chem. B* **2004**, *108*, 17886.
2 R. Jinnouchi, A. B. Anderson, *Phys. Rev. B* **2008**, *77*, 245417.
3 J. O'M. Bockris, S. U. M. Kahn, *Surface Electrochemistry*, Plenum, New York, **1993**, p. 493.
4 M. J. Frisch, et al., *Gaussian 03, Revision B.03*, Gaussian, Inc., Pittsburgh PA, **2003**.
5 Y. Wang, P. B. Balbuena, *J. Chem. Theory Comput.* **2005**, *1*, 935.