Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information for

First principles based mean field model for oxygen reduction reaction

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A. Modeled continuum electrolyte

A.1 Mean field of electrolyte medium

Within the Born-Oppenheimer approximation, a Hamiltonian of an interfacial system is described as follows,

$$H\left[\{\mathbf{P}_i\},\{\mathbf{R}_i\},\{\mathbf{P}_i^m\},\{\mathbf{R}_i^m\}\right]=\sum_i \frac{|\mathbf{P}_i|^2}{2M_i}+\sum_i \frac{|\mathbf{P}_i^m|^2}{2M_i^m}+NE\left[\{\mathbf{R}_i\},\{\mathbf{R}_i^m\}\right], \qquad \text{(A1)}$$

where $\mathbf{P}_i$ and $\mathbf{R}_i$ are momentums and positions of atoms, respectively, N is the number of surface site, and E is the potential energy per surface site of the system. The momentums and positions of atoms in the electrolyte medium are denoted using the superscript m. The partition function of the system can be described as follows,

$$Q=\frac{1}{\prod_i h^{3N_i}\prod_i h^{3N_i^m}}\int\cdots\int \exp\left[-\frac{H\left[\{\mathbf{P}_i\},\{\mathbf{R}_i\},\{\mathbf{P}_i^m\},\{\mathbf{R}_i^m\}\right]}{k_BT}\right]\prod_i d\mathbf{P}_i d\mathbf{R}_i \prod_i d\mathbf{P}_i^m d\mathbf{R}_i^m\,, \qquad \text{(A2)}$$

where N_i and N_i^m are the numbers of atoms outside and inside the electrolyte medium, respectively. For simplifying the equation, all the atoms in the system are assumed to be non-identical in this section, but it is straightforward to extend equations to the system including identical atoms.

By using the Hamiltonian of the system without the electrolyte medium described as,

$$H_0\left[\{\mathbf{P}_i\},\{\mathbf{R}_i\}\right]=\sum_i \frac{|\mathbf{P}_i|^2}{2M_i}+NE_0\left[\{\mathbf{R}_i\}\right], \qquad \text{(A3)}$$

Eq. (A2) can be rewritten as follows,

$$Q=\frac{1}{\prod_i h^{3N_i}}\int\cdots\int \exp\left[-\frac{H_0\left[\{\mathbf{P}_i\},\{\mathbf{R}_i\}\right]+NG_m\left[\{\mathbf{R}_i\}\right]}{k_BT}\right]\prod_i d\mathbf{P}_i d\mathbf{R}_i\,, \qquad \text{(A4)}$$

where G_m is the mean field of the electrolyte medium defined as follows,

$$G_m\left[\{\mathbf{R}_i\}\right]=\frac{k_BT}{N}\ln\frac{1}{\prod_i h^{3N_i^m}}\int\cdots\int \exp\left[-\frac{\sum_i \frac{|\mathbf{P}_i^m|^2}{2M_i^m}+NE\left[\{\mathbf{R}_i\},\{\mathbf{R}_i^m\}\right]-NE_0\left[\{\mathbf{R}_i\}\right]}{k_BT}\right]d\mathbf{P}_i^m d\mathbf{R}_i^m\,. \qquad \text{(A5)}$$

Eq. (A4) indicates that the system is regarded as a system including only atoms outside the electrolyte medium in the mean field G_m. We define a new Hamiltonian described as,

$$H_1\left[\{\mathbf{P}_i\},\{\mathbf{R}_i\}\right]=\sum_i \frac{|\mathbf{P}_i|^2}{2M_i}+NE_1\left[\{\mathbf{R}_i\}\right], \qquad \text{(A6)}$$

$$E_1\left[\{\mathbf{R}_i\}\right]=E_0\left[\{\mathbf{R}_i\}\right]+G_m\left[\{\mathbf{R}_i\}\right], \qquad \text{(A7)}$$

and rewrite the partition function in Eq. (A4) as follows,

$$Q = \frac{1}{\prod_i h^{3N_i}} \int \cdots \int \exp\left[-\frac{H_1[\{\mathbf{P}_i\},\{\mathbf{R}_i\}]}{k_B T} \right] \prod_i d\mathbf{P}_i d\mathbf{R}_i \, . \tag{A8}$$

A.2 Basic equations of modeled continuum electrolyte

One of the most rigorous methods to calculate G_m in Eq. (A5) is executing the integrations with respect to the phase space by a thermodynamic integration scheme using first principles molecular dynamics (FPMD).[S1] Its computational cost, however, is too high to apply it to interfacial systems with long-ranged electric double layers. Instead of the FPMD method, we chose a continuum electrolyte theory, in which atoms in the electrolyte medium are replaced with a continuum medium, and G_m is described as a field of the continuum medium.

The electrolyte surrounding the atoms is described as a medium comprised of a combination of the dielectric medium[30-37] and a modified Poisson-Boltzmann medium,[38, 39] and the potential energy E_1 is defined as follows,

$$E_1[\{f_{i\mathbf{k}\sigma}\},\{\psi_{i\mathbf{k}\sigma}\},\rho_+,\rho_-,\phi,\{\mathbf{R}_i\}] = K + E_{xc} + E_{es} + G_{nel} - TS_e - TS_m , \tag{A9}$$

where K, E_{xc} and E_{es} are the kinetic, exchange-correlation and electrostatic energies, respectively, G_{nel} is the free energy of the non-electrostatic interaction from the electrolyte, S_e is the entropy of electrons, S_m is the entropy of the electrolyte, and T is the temperature. In Eq. (A9), it is explicitly indicated that E_1 depends also on wave functions $\{\psi_{i\mathbf{k}\sigma}\}$, occupation numbers $\{f_{i\mathbf{k}\sigma}\}$ of those wave functions, charge distributions ρ_+ and ρ_- of ions in the electrolyte, and the electrostatic potential ϕ.

K ,E_{xc} and S_e are described as follows,[28, 29]

$$K = \sum_\sigma \sum_\mathbf{k} \sum_i f_{i\mathbf{k}\sigma} \int d\mathbf{r}\, \psi^*_{i\mathbf{k}\sigma}(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 \right) \psi_{i\mathbf{k}\sigma}(\mathbf{r}), \tag{A10}$$

$$E_{xc} = E_{xc}[\rho_\uparrow,\rho_\downarrow] = \int d\mathbf{r} f_{xc}(\rho_\uparrow,\rho_\downarrow,\nabla\rho_\uparrow,\nabla\rho_\downarrow), \tag{A11}$$

$$S_e = \sum_\sigma \sum_\mathbf{k} \sum_i \frac{1}{2\sqrt{\pi}} \exp\left[-\left(\frac{\varepsilon_{i\mathbf{k}\sigma} - \varepsilon_F}{\sigma_e} \right) \right], \tag{A12}$$

$$\rho_\sigma(\mathbf{r}) = \sum_\mathbf{k} \sum_i f_{i\mathbf{k}\sigma} |\psi_{i\mathbf{k}\sigma}(\mathbf{r})|^2 , \tag{A13}$$

where σ_e is the broadening width in the Gaussian smearing method,[S2] $\varepsilon_{i\mathbf{k}\sigma}$ is the one electron energy, and ε_F is the Fermi energy.

E_{es} is the electrostatic energy including the electrostatic interaction from the electrolyte and described as follows,

$$E_{es} = \int d\mathbf{r} [\rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r}) + \rho_c(\mathbf{r}) + \rho_+(\mathbf{r}) + \rho_-(\mathbf{r})] \phi(\mathbf{r}) - \int d\mathbf{r} \frac{\varepsilon(\mathbf{r})}{8\pi} |\nabla\phi(\mathbf{r})|^2 , \tag{A14}$$

where ρ_c is charges of nuclei, and ε is the dielectric permittivity. ε is a function of the position vector **r** and defined to be unity in the region close to the atoms and ε_{bulk} (= 78.36) in the region far from the atoms. At the intermediate region, ε smoothly changes from 1 to ε_{bulk}. An example of the dielectric distribution is shown in Fig. S1 (B). Details of the definition are shown elsewhere.[26]

G_{nel} takes account of all non-electrostatic interactions from the electrolyte medium, such as cavitation, dispersion and repulsive interactions[30-32, 37] from water molecules and repulsive interactions from ions. Details of the function forms are also described elsewhere.[26]

S_m is described by using a lattice gas model for the electrolyte as follows,[38, 39]

$$\begin{aligned} S_m = -\frac{k_B}{a^3}\int d\mathbf{r}[& |\rho_+(\mathbf{r})|a^3 \ln\left(|\rho_+(\mathbf{r})|a^3\right) + |\rho_-(\mathbf{r})|a^3 \ln\left(|\rho_-(\mathbf{r})|a^3\right) \\ & + \left(1-|\rho_+(\mathbf{r})|a^3 - |\rho_-(\mathbf{r})|a^3\right)\ln\left(1-|\rho_+(\mathbf{r})|a^3 - |\rho_-(\mathbf{r})|a^3\right)] \end{aligned}, \tag{A15}$$

where a corresponds to the size of the ions.

E_1 is minimized with respect to $\{f_{i\mathbf{k}\sigma}\}$, $\{\psi_{i\mathbf{k}\sigma}\}$, $\rho_\pm$ and ϕ by self-consistently solving the equations derived by variational principles with respect to $\{f_{i\mathbf{k}\sigma}\}$, $\{\psi_{i\mathbf{k}\sigma}\}$, $\rho_\pm$ and ϕ as follows,

$$\left[-\frac{1}{2}\nabla^2 + \phi(\mathbf{r}) + \frac{\delta E_{xc}}{\delta \rho_\sigma}\right]\psi_{i\mathbf{k}\sigma}(\mathbf{r}) = \varepsilon_{i\mathbf{k}\sigma}\psi_{i\mathbf{k}\sigma}(\mathbf{r}), \tag{A16}$$

$$f_{i\mathbf{k}\sigma} = \frac{1}{2}\left(1 - erf\left[\frac{\varepsilon_{i\mathbf{k}\sigma} - \varepsilon_F}{\sigma_e}\right]\right), \tag{A17}$$

$$\nabla\cdot\left(\varepsilon(\mathbf{r})\nabla\phi(\mathbf{r})\right) = -4\pi\left(\rho_\uparrow(\mathbf{r}) + \rho_\downarrow(\mathbf{r}) + \rho_c(\mathbf{r}) + \rho_-(\mathbf{r}) + \rho_+(\mathbf{r})\right), \tag{A18}$$

$$\rho_\pm(\mathbf{r}) = \mp\frac{c_{bulk}e^{\left(\pm\phi(\mathbf{r}) - \phi_{rep}(\mathbf{r})\right)/k_BT}}{1 - 2a^3c_{bulk} + 2a^3c_{bulk}\cosh\left(\phi(\mathbf{r})/k_BT\right)e^{-\phi_{rep}(\mathbf{r})/k_BT}}, \tag{A19}$$

where c_{bulk} is the ion concentration in the bulk electrolyte and set as 0.1 mol· L^{-1}, and ϕ_{rep} is the potential function describing the repulsive interaction from ions in the electrolyte.

Within the continuum electrolyte theory, G_m is obtained as follows,

$$G_m[\{f_{i\mathbf{k}\sigma}\},\{\psi_{i\mathbf{k}\sigma}\},\{\mathbf{R}_i\}] = E_1[\{f_{i\mathbf{k}\sigma}\},\{\psi_{i\mathbf{k}\sigma}\},\{\mathbf{R}_i\}] - E_0[\{f_{i\mathbf{k}\sigma}\},\{\psi_{i\mathbf{k}\sigma}\},\{\mathbf{R}_i\}], \tag{A20}$$

where E_0 is the potential energy of the system without the modeled continuum electrolyte obtained by setting $G_{nel} = \rho_\pm(\mathbf{r}) = S_m = 0$ and $\varepsilon(\mathbf{r}) = 1$ in Eq. (A9).

A.3 Definition of region for modeled continuum electrolyte

For computations, we need to define the region regarded as the modeled continuum electrolyte. The simplest definition is to regard all the water molecules and ions surrounding the adsorbates and surface as the modeled continuum electrolyte. It was, however, shown in a previous study[27] that OH(ads) and HO_2(ads) have specifically strong hydrogen-bonds with water molecules, and those bonds cannot be accurately described by the modeled continuum electrolyte. Hence, a few explicit water molecules handled by DFT are placed to saturate the hydrogen bonds of those adsorbates as shown in Fig. S1. Although the accuracy of this methodology is not fully verified yet, previous applications to H(ads), OH(ads) and O(ads) showed that the reversible potentials were reproduced well within ±0.13 V.[27, 43-44]

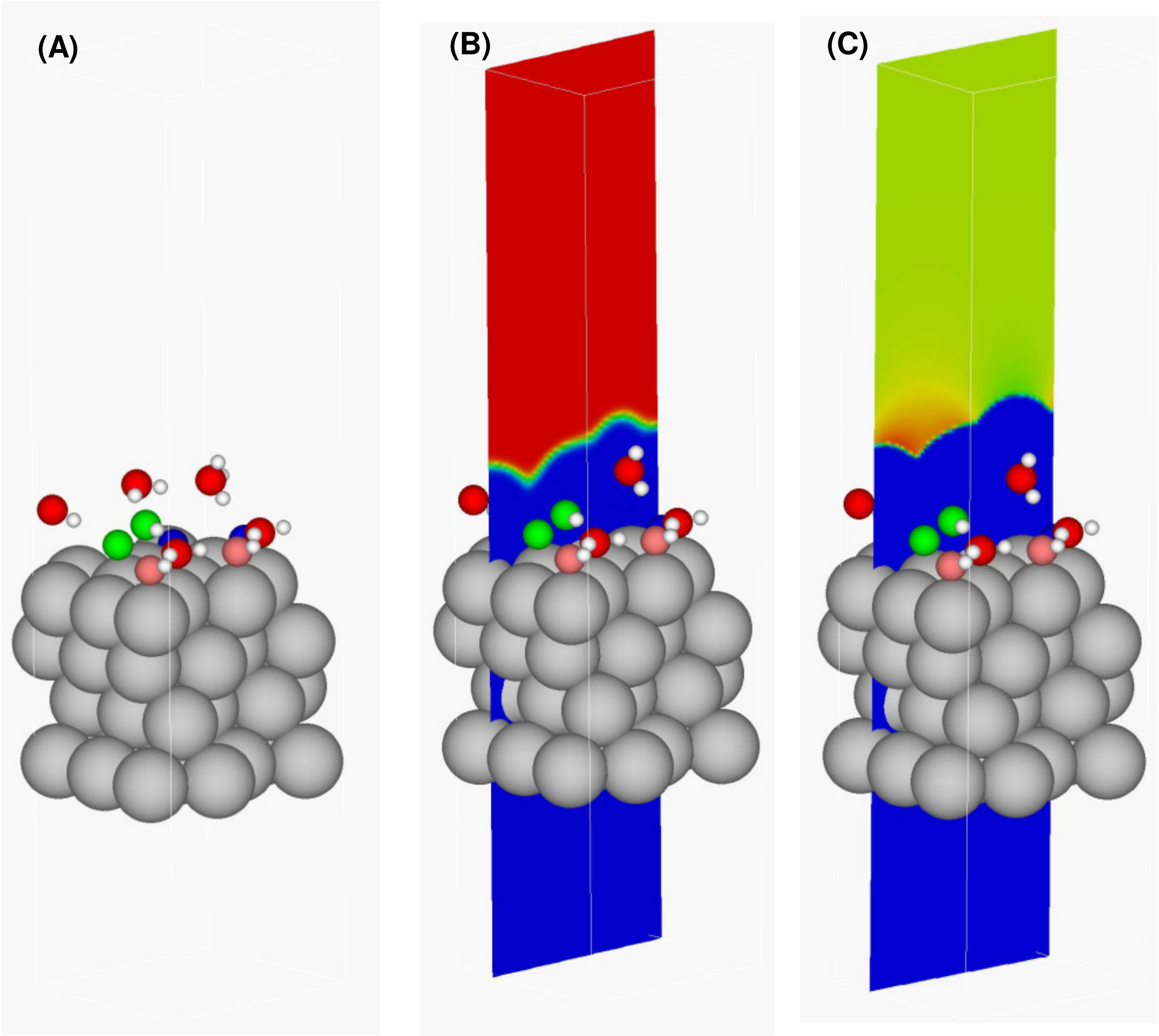

Fig. S1 A surface model with $\theta_O = \theta_{OH} = 1/6$ and $\theta_{HO2} = 1/12$. Positions of atoms in the unit cell are show in (A), and distributions of the dielectric permittivity and concentration of cation in a cross section of the unit cell are shown in (B) and (C), respectively. Gray large spheres are Pt, medium red spheres are O in H_2O, medium peach spheres are O in OH(ads), blue medium spheres are O(ads), medium light green spheres are O in HO_2(ads) and small white spheres are H. The blue and red regions in the dielectric distribution shown in (B) indicate ε=1 and 78.36, respectively. The blue and red regions in the cation distribution shown in (C) indicate $\rho_+ = 0$ and 0.15 mol·L^{-1}, respectively.

B. Gas phase potential energy and solvation free energy

From the assumption (ii), the Hamiltonian described as Eq. (A6) can be rewritten using the harmonic oscillator model as follows,

$$H_1\left[\{\mathbf{P}_i\},\{\mathbf{R}_i\},\{\mathbf{P}_i^w\},\{\mathbf{R}_i^w\}\right]=\sum_i\frac{|\mathbf{P}_i|^2}{2M_i}+\sum_i\frac{|\mathbf{P}_i^w|^2}{2M_i^w}+NE_1\left[\{\mathbf{R}_{i0}\},\{\mathbf{R}_{i0}^w\}\right]+\sum_i\sum_j\frac{k_{ji}}{2}|\Delta\mathbf{R}_i|^2+\sum_i\sum_j\frac{k_{ji}^w}{2}|\Delta\mathbf{R}_i^w|^2, \tag{B1}$$

where k_{ji} is the force constant for jth vibration mode in ith specie, and $\mathbf{R}_{i0}$ is the equilibrium positions of atoms in ith specie, and $\Delta\mathbf{R}_i$ is defined as $\mathbf{R}_i - \mathbf{R}_{i0}$. In Eq. (B1), all variables for the explicit water molecules described in the section A.3 are indicated using superscript w. By using Eqs. (A8) and (B1) and the assumption (iii), the partition function can be rewritten as follows,

$$Q=\frac{N!}{\left(N-\sum_i N_i\right)!\prod_i N_i!}\exp\left[-\frac{NE_1\left[\{\mathbf{R}_{i0}\},\{\mathbf{R}_{i0}^w\}\right]}{k_BT}\right]\prod_i {Q_{vib,i}}^{N_i}{Q_{vib,w}}^{N_w}, \tag{B2}$$

where $Q_{vib,w}$ is the vibrational partition function of the single explicit water molecule near the adsorbates, and N_w is the number of the explicit water molecules..

For simplifying equations, we define a gas phase potential energy ${E_a}^{gas}$ and a solvation free energy ${G_a}^{solv}$ as follows,

$$E_a^{gas}\equiv E_0\left[\{\mathbf{R}_{i0}\}\right], \tag{B3}$$

$$G_a^{solv}\equiv E_1\left[\{\mathbf{R}_{i0}\},\{\mathbf{R}_{i0}^w\}\right]-E_0\left[\{\mathbf{R}_{i0}\}\right]-\frac{N_i^w}{N}k_BT\ln Q_{vib,i}^w, \tag{B4}$$

where $E_0[\{\mathbf{R}_{i0}\}]$ is the potential energy of the system without the explicit water molecules and the modeled continuum electrolyte. By using Eqs. (B3) and (B4), Eq. (B2) can be rewritten as follows,

$$Q=\frac{N!}{\left(N-\sum_i N_i\right)!\prod_i N_i!}\exp\left[-\frac{NE_a^{gas}+NG_a^{solv}}{k_BT}\right]\prod_i {Q_{vib,i}}^{N_i}. \tag{B5}$$

This equation corresponds to Eq. (2) in the section 2.2.

The data on $-k_BT\ln Q_{vib,i}$ obtained by vibration analysis are compiled in Table S1. This table also contains $-k_BT\ln Q_{trans,i}\,Q_{rot,i}\,Q_{vib,i}$ for isolated molecules.

Table S1 Free energies $-k_BT \ln Q_i = H_i - TS_i$ at T=298.15, where H_i and S_i are the enthalpies and entropies. The units are eV.

i	H_i	TS_i
H_2(g)	0.359	0.403
O_2(g)	0.184	0.579
H_2O(g)	0.668	0.584
H_2O(ads)	0.723	0.149
O(ads)	0.098	0.041
OH(ads)	0.400	0.130
HO_2(ads)	0.527	0.144

C. Reaction free energies and reversible potentials

C.1 Reaction free energies of the reactions (R3), (R4) and (R6)

ΔG_1 is obtained by integrating an infinitesimal change in the summation of $G^0{}_i$ terms caused by a reaction,

$$\begin{aligned}&(dN'_{\mathrm{O}} + dN'_{\mathrm{OH}})\mathrm{H_2O(aq)} + N'_{\mathrm{O}}\mathrm{O(ads)} + N'_{\mathrm{OH}}\mathrm{OH(ads)} \\ &\quad\rightarrow (N'_{\mathrm{O}} + dN'_{\mathrm{O}})\mathrm{O(ads)} + (N'_{\mathrm{OH}} + dN'_{\mathrm{OH}})\mathrm{OH(ads)} + (2dN'_{\mathrm{O}} + dN'_{\mathrm{OH}})\mathrm{H^+(aq)} + (2dN'_{\mathrm{O}} + dN'_{\mathrm{OH}})\mathrm{e^-},\end{aligned} \tag{C1}$$

along a path from $(N'_{\mathrm{O}}, N'_{\mathrm{OH}})$ = (0, 0) (a point O) to $(N_{\mathrm{O}}, N_{\mathrm{OH}})$ (a point X), a coordinate of which is denoted as λ, as follows,

$$\begin{aligned}\Delta G_1(\theta_{\mathrm{O}}, \theta_{\mathrm{OH}}) &= \int_{\mathrm{O}}^{\mathrm{X}} \left(\frac{\partial \Delta G_1}{\partial \theta'_{\mathrm{O}}} \frac{d\theta'_{\mathrm{O}}}{d\lambda} + \frac{\partial \Delta G_1}{\partial \theta'_{\mathrm{OH}}} \frac{d\theta'_{\mathrm{OH}}}{d\lambda} \right) d\lambda \\ &= \int_{\mathrm{O}}^{\mathrm{X}} \left[\left(\frac{\partial E_a}{\partial \theta'_{\mathrm{O}}} - k_BT \ln Q_{vib,\mathrm{O}} + G^0_{\mathrm{H_2}} - G^0_{\mathrm{H_2O}} \right) \frac{d\theta'_{\mathrm{O}}}{d\lambda} + \left(\frac{\partial E_a}{\partial \theta'_{\mathrm{OH}}} - k_BT \ln Q_{vib,\mathrm{OH}} + \frac{1}{2} G^0_{\mathrm{H_2}} - G^0_{\mathrm{H_2O}} \right) \frac{d\theta'_{\mathrm{OH}}}{d\lambda} \right] d\lambda, \\ &= \left[\left\{ E_a(\theta_{\mathrm{O}}, \theta_{\mathrm{OH}}, 0) - k_BT\theta_{\mathrm{O}} \ln Q_{vib,\mathrm{O}} - k_BT\theta_{\mathrm{OH}} \ln Q_{vib,\mathrm{OH}} \right\} + \frac{2\theta_{\mathrm{O}} + \theta_{\mathrm{OH}}}{2} G^0_{\mathrm{H_2}} \right] - \left[E_a(0,0,0) + (\theta_{\mathrm{O}} + \theta_{\mathrm{OH}}) G^0_{\mathrm{H_2O}} \right]\end{aligned} \tag{C2}$$

where ΔG_1 and E_a are described as functions of the surface coverages θ_{O}, θ_{OH} and $\theta_{\mathrm{HO_2}}$ in this equation. From Eqs. (4) and (C2), following equations are obtained,

$$\frac{\partial \Delta G_1}{\partial \theta_{\mathrm{O}}} = \left(\frac{\partial E_a}{\partial \theta_{\mathrm{O}}} - k_BT \ln Q_{vib,\mathrm{O}} \right) + G^0_{\mathrm{H_2}} - G^0_{\mathrm{H_2O}} = G^0_{\mathrm{O}} + G^0_{\mathrm{H_2}} - G^0_{\mathrm{H_2O}}, \tag{C3}$$

$$\frac{\partial \Delta G_1}{\partial \theta_{\mathrm{OH}}} = \left(\frac{\partial E_a}{\partial \theta_{\mathrm{OH}}} - k_BT \ln Q_{vib,\mathrm{OH}} \right) + \frac{1}{2} G^0_{\mathrm{H_2}} - G^0_{\mathrm{H_2O}} = G^0_{\mathrm{OH}} + \frac{1}{2} G^0_{\mathrm{H_2}} - G^0_{\mathrm{H_2O}}. \tag{C4}$$

Substituting Eqs. (C3) and (C4) into Eqs. (11)-(13) gives following equations:

$$\Delta G_{\mathrm{RD}} = G_{\mathrm{H_2O}} - G_{\mathrm{OH}} - G_{\mathrm{H^+ + e^+}}\,, \tag{C5}$$

$$\Delta G_{\mathrm{RT}} = G_{\mathrm{OH}} - G_{\mathrm{O}} - G_{\mathrm{H^+ + e^+}}\,, \tag{C6}$$

$$\Delta G_{\mathrm{DA}} = 2G_{\mathrm{O}} - G_{\mathrm{O_2}}\,. \tag{C7}$$

C.2 Reaction free energy of the reaction (R5)

Similarly to ΔG_1, ΔG_2 is obtained by integrating an infinitesimal change in the summation of $G^0{}_i$ terms caused by a reaction,

$$\begin{aligned} &dN'_{\mathrm{HO_2}}\mathrm{O_2(g)} + dN'_{\mathrm{HO_2}}\mathrm{H^+(aq)} + dN'_{\mathrm{HO_2}}\mathrm{e^-} + N'_{\mathrm{HO_2}}\mathrm{HO_2(ads)} + N'_{\mathrm{O}}\mathrm{O(ads)} + N'_{\mathrm{OH}}\mathrm{OH(ads)} \\ &\qquad \leftrightarrow \left(dN'_{\mathrm{HO_2}} + N'_{\mathrm{HO_2}}\right)\mathrm{HO_2(ads)} + N'_{\mathrm{O}}\mathrm{O(ads)} + N'_{\mathrm{OH}}\mathrm{OH(ads)} \end{aligned}\,, \tag{C8}$$

along a path from (N'_{O}, N'_{OH}, N'_{HO2}) = (N_{O}, N_{OH}, 0) (a point X) to (N_{O}, N_{OH}, N_{HO2}) (a point Y) as follows,

$$\begin{aligned} \Delta G_2\left(\theta_{\mathrm{O}}, \theta_{\mathrm{OH}}, \theta_{\mathrm{HO_2}}\right) &= \int_{\mathrm{X}}^{\mathrm{Y}} \frac{\partial \Delta G_2}{\partial \theta'_{\mathrm{HO_2}}} \frac{d\theta'_{\mathrm{HO_2}}}{d\lambda} d\lambda \\ &= \int_{\mathrm{X}}^{\mathrm{Y}} \left(\frac{\partial E_a}{\partial \theta'_{\mathrm{HO_2}}} - k_B T \ln Q_{vib,\mathrm{HO_2}} - \frac{1}{2} G^0_{\mathrm{H_2}} - G^0_{\mathrm{O_2}} \right) \frac{d\theta'_{\mathrm{HO_2}}}{d\lambda} d\lambda \\ &= \left[\left\{ E_a\left(\theta_{\mathrm{O}}, \theta_{\mathrm{OH}}, \theta_{\mathrm{HO_2}}\right) - k_B T \theta_{\mathrm{HO_2}} \ln Q_{vib,\mathrm{HO_2}} \right\}\right] - \left[E_a\left(\theta_{\mathrm{O}}, \theta_{\mathrm{OH}}, 0\right) + \frac{\theta_{\mathrm{HO_2}}}{2} G^0_{\mathrm{H_2}} + \theta_{\mathrm{HO_2}} G^0_{\mathrm{O_2}} \right] \end{aligned}\,. \tag{C9}$$

From Eq. (C9), a following equation is obtained:

$$\frac{\partial \Delta G_2}{\partial \theta_{\mathrm{HO_2}}} = \left(\frac{\partial E_a}{\partial \theta_{\mathrm{HO_2}}} - k_B T \ln Q_{vib,\mathrm{HO_2}} \right) - \frac{1}{2} G^0_{\mathrm{H_2}} - G^0_{\mathrm{O_2}} = G^0_{\mathrm{HO_2}} - \frac{1}{2} G^0_{\mathrm{H_2}} - G^0_{\mathrm{O_2}}\,. \tag{C10}$$

Substituting Eq. (C10) into Eq. (18) gives a following equation:

$$\Delta G_{\mathrm{RA}} = G_{\mathrm{HO_2}} - G_{\mathrm{O_2}} - G_{\mathrm{H^+ + e^+}}\,. \tag{C11}$$

C.3 Reversible potentials at a low surface coverage conditions

Reversible potentials in Eqs. (14), (15) and (19) at a low coverage condition are approximated by a finite difference method as follows,

$$U^0_{\mathrm{RD}} = \frac{1}{e} \left. \frac{\partial \Delta G_1}{\partial \theta_{\mathrm{OH}}} \right|_{\theta_i = 0} \cong \frac{1}{e} \frac{\Delta G_1\left(0, \delta\theta_{\mathrm{OH}}\right)}{\delta\theta_{\mathrm{OH}}}\,, \tag{C12}$$

$$U^0_{\mathrm{RT}} = \frac{1}{e} \left(\left. \frac{\partial \Delta G_1}{\partial \theta_{\mathrm{O}}} \right|_{\theta_i = 0} - \left. \frac{\partial \Delta G_1}{\partial \theta_{\mathrm{OH}}} \right|_{\theta_i = 0} \right) \cong \frac{1}{e} \left(\frac{\Delta G_1\left(\delta\theta_{\mathrm{O}}, 0\right)}{\delta\theta_{\mathrm{O}}} - \frac{1}{e} \frac{\Delta G_1\left(0, \delta\theta_{\mathrm{OH}}\right)}{\delta\theta_{\mathrm{OH}}} \right), \tag{C13}$$

$$U^0_{\mathrm{RA}} = -\frac{1}{e} \left. \frac{\partial \Delta G_2}{\partial \theta_{\mathrm{HO_2}}} \right|_{\theta_i = 0} \cong -\frac{1}{e} \frac{\Delta G_2\left(0, 0, \delta\theta_{\mathrm{HO_2}}\right)}{\delta\theta_{\mathrm{HO_2}}}\,. \tag{C14}$$

C.4 Gas phase and solvation contribution in ΔG_1 and ΔG_2

The reversible potentials in Eqs. (C12)-(C14) for various materials can be efficiently calculated through the first principles method by dividing ΔG_1 and ΔG_2 into gas phase and solvation contributions as follows,

$$\Delta G_1(\theta_{\mathrm{O}},\theta_{\mathrm{OH}}) = \Delta G_1^{gas}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}}) + \Delta G_1^{solv}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}}), \tag{C15}$$

$$\Delta G_2(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},\theta_{\mathrm{HO_2}}) = \Delta G_2^{gas}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},\theta_{\mathrm{HO_2}}) + \Delta G_2^{solv}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},\theta_{\mathrm{HO_2}}), \tag{C16}$$

where each contribution is described as follows,

$$\begin{aligned}&\Delta G_1^{gas}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}})\\ &= \left[\left\{E_a^{gas}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},0) - k_B T\theta_{\mathrm{O}}\ln Q_{vib,\mathrm{O}} - k_B T\theta_{\mathrm{OH}}\ln Q_{vib,\mathrm{OH}}\right\} + \frac{2\theta_{\mathrm{O}}+\theta_{\mathrm{OH}}}{2}G_{\mathrm{H_2}}^0\right] - \left[(\theta_{\mathrm{O}}+\theta_{\mathrm{OH}})G_{\mathrm{H_2O}}^0 + E_a^{gas}(0,0,0)\right]'\end{aligned} \tag{C17}$$

$$\Delta G_1^{solv}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}}) = \left\{E_a(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},0) - E_a^{gas}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},0)\right\} - \left\{E_a(0,0,0) - E_a^{gas}(0,0,0)\right\}, \tag{C18}$$

$$\begin{aligned}&\Delta G_2^{gas}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},\theta_{\mathrm{HO_2}})\\ &= \left[\left\{E_a^{gas}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},\theta_{\mathrm{HO_2}}) - k_B T\theta_{\mathrm{HO_2}}\ln Q_{vib,\mathrm{HO_2}}\right\}\right] - \left[\frac{\theta_{\mathrm{HO_2}}}{2}G_{\mathrm{H_2}}^0 + \theta_{\mathrm{HO_2}}G_{\mathrm{O_2}}^0 + E_a^{gas}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},0)\right]'\end{aligned} \tag{C19}$$

$$\Delta G_2^{solv}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},\theta_{\mathrm{HO_2}}) = \left\{E_a(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},\theta_{\mathrm{HO_2}}) - E_a^{gas}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},\theta_{\mathrm{HO_2}})\right\} - \left\{E_a(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},0) - E_a^{gas}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},0)\right\}. \tag{C20}$$

Eqs. (C18) and (C20) can be simplified using Eq. (1) as follows,

$$\Delta G_1^{solv}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}}) = G_a^{solv}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},0) - G_a^{solv}(0,0,0), \tag{C21}$$

$$\Delta G_2^{solv}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},\theta_{\mathrm{HO_2}}) = G_a^{solv}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},\theta_{\mathrm{HO_2}}) - G_a^{solv}(\theta_{\mathrm{O}},\theta_{\mathrm{OH}},0), \tag{C22}$$

where $G_a{}^{solv}$ is also shown as a function of θ_{O}, θ_{OH} and θ_{HO2} in this equation. Eqs. (C21) and (C22) indicate that $\Delta G_1{}^{solv}$ and $\Delta G_2{}^{solv}$ correspond to changes in the solvation free energies caused by the formations of O(ads) and OH(ads) and the formation of $\mathrm{HO_2}$(ads), respectively.

D. Derivation of Eq. (24)

D.1 Activation free energy and activation energy of reaction (R6)

Before the application of the Brønsted-Evans-Polanyi (BEP) equation, we describe definitions of the activation free energy and activation energy in this section.

From the assumption (x), the Gibbs free energy of the transition state is described as follows,

$$G_{\mathrm{O_2(TS)}} = \frac{\partial E_a}{\partial \theta_{\mathrm{O_2(TS)}}} - k_B T\ln Q_s Q_{vib,\mathrm{O_2(TS)}}^{*} + k_B T\ln\frac{\theta_{\mathrm{O_2(TS)}}}{1-\sum_i \theta_i}, \tag{D1}$$

where $\theta_{\mathrm{O2(TS)}}$ is the surface coverage of the transition state, Q_s is the partition function with respect to the reaction coordinate s, and $Q^*_{vib,\mathrm{O2(TS)}}$ is the partition function with respect to coordinates except for the coordinate s. Q_s is described by a 1-dimensional translational partition function as $(2\pi\mu_s k_B T)^{1/2}\delta_s/h$,[40, 41] where μ_s is the effective mass, and δ_s is the length where the specie is regarded as the transition state. According to the transition state theory, in which the transition state is assumed to be in quasi-equilibrium with the reactant ($G_{\mathrm{O2(TS)}} = G_{\mathrm{O2}}$), and a half of the transition state is assumed to move towards the product state with a mean velocity of $v_s = (2k_BT/\pi\mu_s)^{1/2}$,[40, 41] the rate of the forward reaction (R6) is obtained as follows,

$$v_{\mathrm{DA}} = \frac{k_BT}{h} p_{\mathrm{O_2}} \left(1 - \sum_i \theta_i\right) \exp\left(-\frac{\Delta G_{\mathrm{DA},f}}{k_BT}\right), \tag{D2}$$

$$\Delta G_{\mathrm{DA},f} = \Delta E_{\mathrm{DA},f} - k_BT \ln \frac{Q^*_{vib,\mathrm{O_2(TS)}}}{Q_{trans,\mathrm{O_2}} Q_{rot,\mathrm{O_2}} Q_{vib,\mathrm{O_2}}}, \tag{D3}$$

$$\Delta E_{\mathrm{DA},f} = \frac{\partial E_a}{\partial \theta_{\mathrm{O_2(TS)}}} - E_{\mathrm{O_2}}, \tag{D4}$$

where $\Delta G_{\mathrm{DA},f}$ is the activation free energy, and $\Delta E_{\mathrm{DA},f}$ is the activation energy.

D.2 Application of Brønsted-Evans-Polanyi equation

We rewrite Eq. (D3) as,

$$\Delta G_{\mathrm{DA},f} = \Delta G^0_{\mathrm{DA},f} + \left(\Delta E_{\mathrm{DA},f} - \Delta E^0_{\mathrm{DA},f}\right), \tag{D5}$$

and apply the BEP equation (23) to the second term in the right hand side of Eq. (D5) as follows,

$$\Delta G_{\mathrm{DA},f} = \Delta G^0_{\mathrm{DA},f} + a\left(\Delta E_{\mathrm{DA}} - \Delta E^0_{\mathrm{DA}}\right), \tag{D6}$$

where ΔE_{DA} and ΔE^0_{DA} are the reaction energies of the reaction (R6) and described as follows,

$$\Delta E_{\mathrm{DA}} = 2\frac{\partial E_a}{\partial \theta_{\mathrm{O}}} - E_{\mathrm{O_2}}, \tag{D7}$$

$$\Delta E^0_{\mathrm{DA}} = 2\left.\frac{\partial E_a}{\partial \theta_{\mathrm{O}}}\right|_{\theta_i=0} - E_{\mathrm{O_2}}. \tag{D8}$$

The second term in the right hand side of Eq. (D6) can be rewritten using Eqs. (16), (C3), (D7) and (D8) as follows,

$$\Delta E_{\mathrm{DA}} - \Delta E^0_{\mathrm{DA}} = 2\left(\frac{\partial E_a}{\partial \theta_{\mathrm{O}}} - \left.\frac{\partial E_a}{\partial \theta_{\mathrm{O}}}\right|_{\theta_i=0}\right) = 2\left(\frac{\partial \Delta G_1}{\partial \theta_{\mathrm{O}}} - \left.\frac{\partial \Delta G_1}{\partial \theta_{\mathrm{O}}}\right|_{\theta_i=0}\right) = 2\frac{\partial \Delta\Delta G_1}{\partial \theta_{\mathrm{O}}}. \tag{D9}$$

Substituting Eq. (D9) into Eq. (D6) gives Eq. (24).

E. Parameters and models for first principles calculations

E.1 Parameters and models for calculating changes in free energies ΔG_1 and ΔG_2 in Eqs. (C2) and (C9)

Surfaces were modeled by a 4 layer slab of Pt(111) with a periodic structure of (3×2√3) containing several patterns of O(ads), OH(ads) and HO_2(ads). θ_O and θ_{OH} were changed from 0 to 1/3 ML with an increment of 1/12 ML, while θ_{HO2} was set as 0 or 1/12 ML. The coverage θ_{H2O} of the explicit water molecules was set as $\theta_{H2O} = 2/3 - \theta_{OH} - \theta_{HO2}$. The remaining electrolyte was described by the modeled continuum electrolyte as written in the sections A and B. Fig. S2 is an example of the surface pattern at $\theta_O = \theta_{OH} = 1/6$, $\theta_{HO2} = 1/12$ and $\theta_{H2O} = 5/12$.

The exchange-correlation energy E_{xc} was described by a revised generalized gradient approximation,[46] which gives more accurate adsorption energies than other functionals using the generalized gradient approximation. A quasi-Newton optimizer was used to obtain meta-stable structures.[S3] The optimizations were carried out with a threshold of 0.05 eV·Å^{-1} for the maximum forces acting on atoms. A 3×3 Monkhorst-Pack mesh was used.[S4] Double zata plus polarization (DZP) basis sets[26] were applied to H, O and Pt in the calculations. All the potential energies were extrapolated to $k_BT = 0$ eV. Calculations were executed by a first principles code using linear-combinations of pseudo-atomic orbitals[26] and norm-conserving pseudopotentials.[S5]

Among the parameters described above, the use of the incomplete basis sets causes the largest error, but increasing the size of the basis sets from DZP to triple zeta plus polarization (TZP) basis sets changed the binding energies of O(ads), OH(ads) and HO_2(ads) only less than 0.03 eV, which corresponds to the change in ΔG_1 and ΔG_2 by less than 0.003 eV and is smaller than the errors caused by the assumption described in the section 2.2.1. We also investigated the effects of other parameters, such as the **k**-point mesh and threshold for the structural optimizations, and found that the effects are sufficiently small (less than 0.001 eV errors in ΔG_1 and ΔG_2).

Details of the computational results on $\Delta\Delta G_1$ and $\Delta\Delta G_2$ are compiled in Tables S2 and S3.

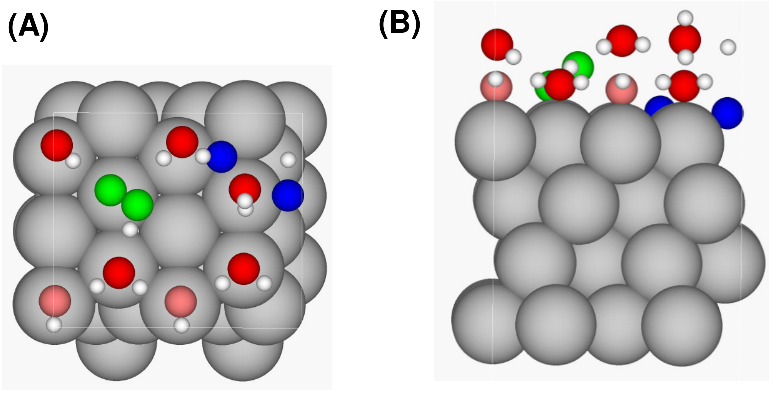

Fig. S2 An example of the surface model for calculating ΔG_1 and ΔG_2. $\theta_O = \theta_{OH} = 1/6$, $\theta_{HO2} = 1/12$ and $\theta_{H2O} = 5/12$. Atoms only in the unit cell are shown in this figure.

Table S2 $\Delta\Delta G_1$ as a function of θ_O and θ_{OH}. The unit of $\Delta\Delta G_1$ is eV.

θ_O	θ_{OH}	$\Delta\Delta G_1$
2/12	0	0.003
3/12	0	0.017
4/12	0	0.036
5/12	0	0.091
6/12	0	0.135
7/12	0	0.211
1/12	1/12	0.004
2/12	1/12	0.002
3/12	1/12	0.031
4/12	1/12	0.115
0	2/12	0.006
1/12	2/12	0.011
2/12	2/12	0.019
3/12	2/12	0.089
4/12	2/12	0.193
0	3/12	0.011
1/12	3/12	0.013
2/12	3/12	0.051
3/12	3/12	0.149
4/12	3/12	0.213
0	4/12	0.025
1/12	4/12	0.081
2/12	4/12	0.168
3/12	4/12	0.242
4/12	4/12	0.356
0	5/12	0.066
0	6/12	0.118
0	7/12	0.192

Table S3 $\Delta\Delta G_2$ at $\theta_{HO2} = 1/12$ as a function of θ_O and θ_{OH}. The unit of $\Delta\Delta G_2$ is eV.

θ_O	θ_{OH}	$\Delta\Delta G_2$
1/12	0	0.005
2/12	0	–0.001
3/12	0	0.019
4/12	0	0.045
0	1/12	0.011
1/12	1/12	–0.008
2/12	1/12	–0.002
3/12	1/12	0.029
4/12	1/12	0.043
0	2/12	0.013
1/12	2/12	0.009
2/12	2/12	0.014
3/12	2/12	0.035
4/12	2/12	0.079
0	3/12	0.008
1/12	3/12	0.007
2/12	3/12	0.009
3/12	3/12	0.041
4/12	3/12	0.054
0	4/12	0.011
1/12	4/12	0.022
2/12	4/12	0.052
3/12	4/12	0.056
4/12	4/12	0.064
0	5/12	0.013
0	6/12	0.029

E.2 Parameters and models for calculating reversible potentials described in Eqs. (C12)-(C14) and related physical properties described in Eqs. (C15) and (C16)

We used a similar methodology to that proposed by Nørskov et al,[1, 2] in which the gas phase and solvation contributions were separately calculated as described in Eqs. (C.15) and (C.16).

Gas phase free energies ΔG_1^{gas} and ΔG_2^{gas} were calculated by using 6 layer slabs with a small unit cell of a (2×2) periodic structure in vacuum. The use of a larger unit cell of (3×2√3) changed the free energies by only less than 0.02 eV, and increasing the slab thickness up to 10 layer also changed the binding energies by only less than 0.02 eV. For Pt alloys, concentrations of Pt are 100 % in the 1st layer, 25 % in the 2nd layer and 75 % in further inner layers.[4] For Pt core-shell catalysts, the concentrations are 100 % in the 1st layer and 0 % in inner layers.[5] A 5×5 Monkhorst-Pack mesh[S4] with a Gaussian broadening[S2] with an energy width of 0.1 eV was applied. Changes in the binding energies caused by increasing the **k**-point mesh up to 20×20 were less than 0.001 eV.

Solvation contributions of ΔG_1^{solv} and ΔG_2^{solv} were calculated by using the same slab as that described in the previous section. In this model, explicit water molecules were placed to form the 2-dimensional hexagonal ice-like structure as shown in Fig. S3. The parameters described in previous section were also used in the calculations.

Table S4 summarizes the results on $\Delta G_1^{solv}(\delta\theta_{\rm O},0)$, $\Delta G_1^{solv}(0,\delta\theta_{\rm OH})$ and $\Delta G_2^{solv}(0,0,\delta\theta_{\rm HO2})$, which correspond to the changes in the solvation free energy caused by formations of isolated O(ads), OH(ads) and HO_2(ads), respectively. Other theoretical results are also shown in this table.[S6, S7] Our results indicate that OH(ads) and HO_2(ads) are stabilized by the solvation, while O(ads) is not significantly affected by the solvation. The trend for O(ads) and OH(ads) agree well with a result in a previous theoretical study.[2]

$\Delta G_1^{solv}(\delta\theta_{\rm O},0)$ is estimated to be larger than −0.06 eV by using an experimental data on the reaction enthalpy of $\Delta H_{ads,{\rm O}}^{gas} \approx -1.70$ eV for forming 2O(ads) at $\theta_{\rm O} = 0.25$ ML from O_2(g) on Pt(111) in gas phase,[S8] an experimental electrode potential larger than 0.90 V (SHE) for forming O(ads) on Pt(111) in the electrolyte,[8] and the reversible potential $U^0_{\rm ORR} = 1.229$ V (SHE) for the oxygen reduction reaction[47] as follows,

$$U = \frac{\Delta H_{ads,{\rm O}}^{gas}/2 + \Delta G_1^{solv}(\delta\theta_{\rm O},0) - T\left(S_{\rm O} - S_{{\rm O}_2}/2\right)}{2e} + U_{\rm ORR}^0 > 0.9\ {\rm V}\ ({\rm SHE}), \qquad ({\rm E1})$$

where $S_{\rm O}$ and $S_{\rm O2}$ are entropies of O(ads) and O_2(g), respectively, and shown in Table S1. This semi-empirical estimation supports the theoretical results.

For $\Delta G_1^{solv}(0,\delta\theta_{\rm OH})$, we could not find any experimental data which can be quantitatively compared with our result, but several experimental studies combined with DFT calculations reported that the mixed adlayer of OH and H_2O is energetically more favorable than adlayers of only OH or H_2O due to specifically strong hydrogen bonds between OH and H_2O.[11, S6, S9] Our results are consistent with those experimental suggestions.

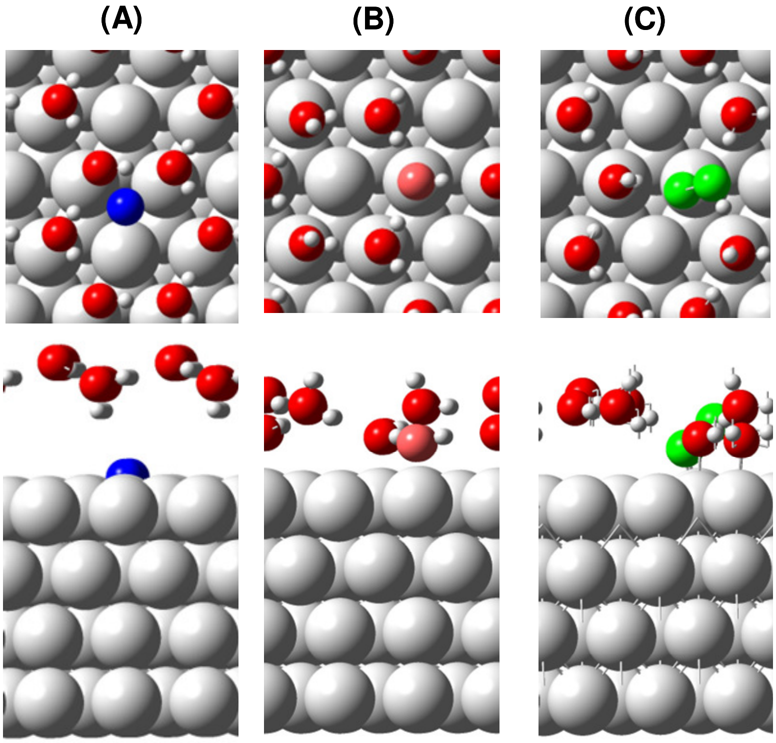

Fig. S3 Top and side views of surface models for calculating (A) $\Delta G_1^{solv}(\delta\theta_{\rm O},0)$, (B) $\Delta G_1^{solv}(0,\delta\theta_{\rm OH})$ and (C) $\Delta G_2^{solv}(0,0,\delta\theta_{\rm HO2})$.

Table S4 $\Delta G_1^{solv}(\delta\theta_{\mathrm{O}},0)$, $\Delta G_1^{solv}(0,\delta\theta_{\mathrm{OH}})$ and $\Delta G_2^{solv}(0,0,\delta\theta_{\mathrm{HO2}})$, which correspond to changes in the solvation free energy by formations of isolated O(ads), OH(ads) and HO_2(ads), respectively. Units of free energies are eV.

$\Delta G_1^{solv}(\delta\theta_{\mathrm{O}},0)$	$\Delta G_1^{solv}(0,\delta\theta_{\mathrm{OH}})$	$\Delta G_2^{solv}(0,0,\delta\theta_{\mathrm{HO2}})$
–0.005[a]	–0.544[a]	–0.287[a]
–0.03[b]	–0.59[b]	
> –0.06[e]	–0.59[c]	
	–0.59[d]	

a. Results in this work.

b. Results in Ref. 2.

c. Results in Ref. S7.

d. Results in Ref. S8.

e. Estimation using Eq. (E1).

E. 3 Parameters and models for calculating activation energies of the reaction (R6)

The same slab models as those used in the gas phase calculations described in the previous section were used for calculating the activation energies $\Delta E^0_{\mathrm{DA},f}$ and reaction energies ΔE^0_{DA} of the reaection (R6). A nudged elastic band (NEB) method$^{\mathrm{S10-S12}}$ was used to obtain minimum energy pathways. Other parameters are the same as those described in the previous subsection.

Fig. S4 shows the results on the single crystal surfaces of Pt, Pt alloys and core-shell surfaces, and Fig. S5 shows the results on the single crystal surface of pure Pt pre-covered by O(ads).

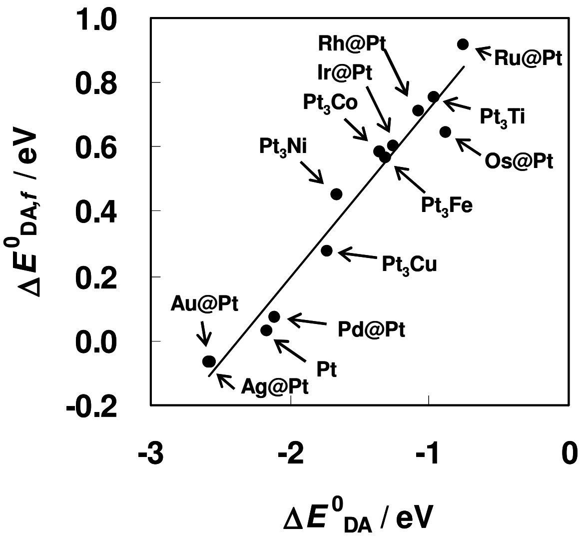

Fig. S4 The activation energy $\Delta E^0_{\mathrm{DA},f}$ as a function of the adsorption energy ΔE^0_{DA} on single crystal surfaces of Pt, Pt alloy and Pt core-shells. Circles are the first principles results, and the solid line is the fitted BEP relationship described as Eq. (23) with a=0.52 and b=1.25 eV.

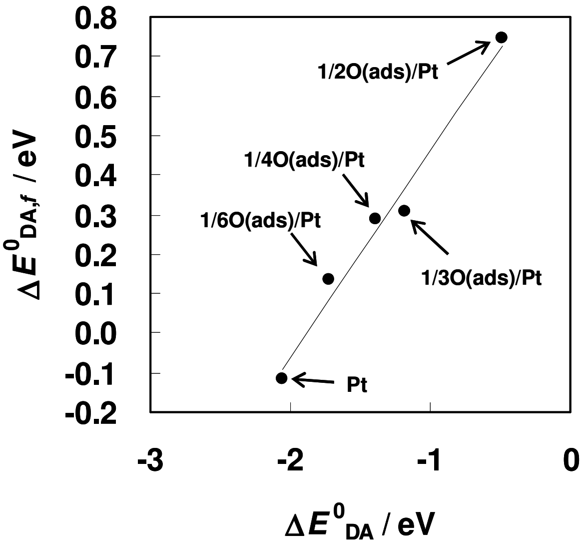

Fig. S5 The activation energy $\Delta E^0_{\mathrm{DA},f}$ as a function of the adsorption energy ΔE^0_{DA} on Pt(111). Circles are the first principles results, and the solid line is the fitted BEP relationship described as Eq. (23) with the parameters of a=0.52 and b=0.98 eV.

F. Flowchart for solving simultaneous equations (31)-(35)

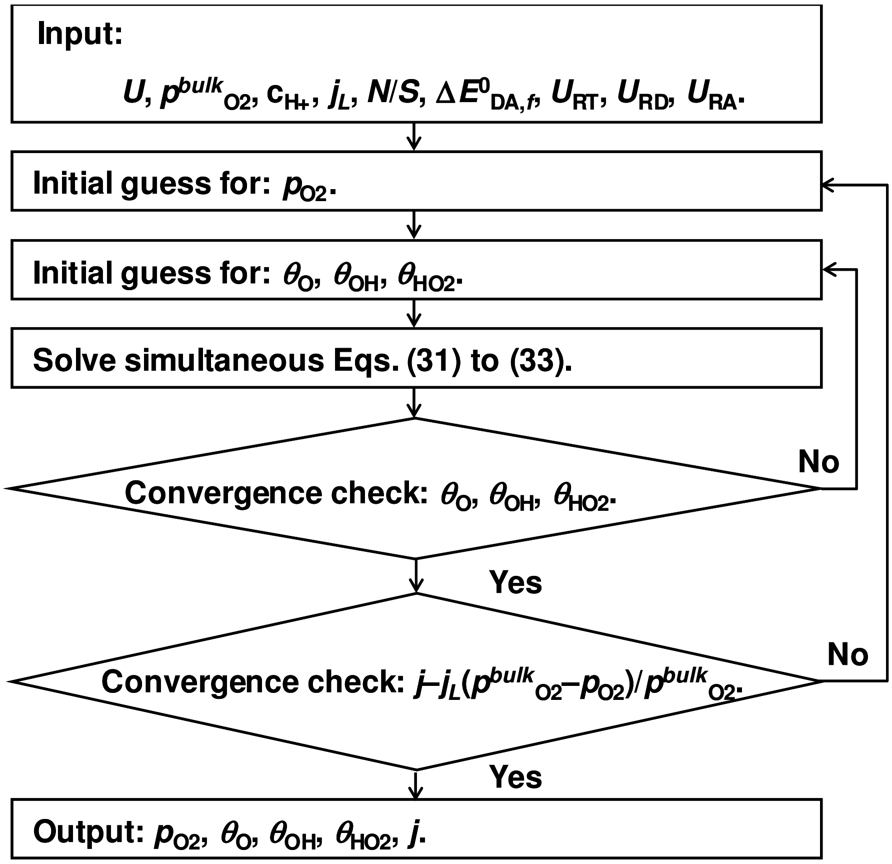

Fig. S6 A flowchart of the iterative solution to obtain the steady state current density and surface coverages.

G. Effects of symmetry factors on surface coverages in a low potential range

In a low potential range, the associative pathway is dominant as shown in Fig. 7, and the rates of the backward reactions of (R3), (R4) and (R5) can be neglected because of the large overpotential for the reduction reactions. Hence, the simultaneous equations (31)-(33) can be simplified to simultaneous equations with respect to θ_{O} and θ_{OH} as follows,

$$a_{11}\theta_{\mathrm{O}} + a_{21}\theta_{\mathrm{OH}} = 1, \tag{G1}$$

$$a_{12}\theta_{\mathrm{O}} + a_{22}\theta_{\mathrm{OH}} = 1, \tag{G2}$$

$$a_{11} = 1 + \frac{c_{\mathrm{RT}}}{c_{\mathrm{RA}}}\exp\left\{-\frac{e(\alpha_{\mathrm{RT}} - \alpha_{\mathrm{RA}})U}{k_B T}\right\}, \tag{G3}$$

$$a_{21} = 1, \tag{G4}$$

$$a_{12} = 1 - \frac{c_{\mathrm{RT}}}{c_{\mathrm{RA}}}\exp\left\{-\frac{e(\alpha_{\mathrm{RT}} - \alpha_{\mathrm{RA}})U}{k_B T}\right\}, \tag{G5}$$

$$a_{22} = 1 + \frac{c_{\mathrm{RD}}}{c_{\mathrm{RA}}}\exp\left\{-\frac{e(\alpha_{\mathrm{RD}} - \alpha_{\mathrm{RA}})U}{k_B T}\right\}, \tag{G6}$$

$$c_{\mathrm{RA}} = p_{\mathrm{O}_2}\exp\left(-\frac{\Delta G_{\mathrm{RA}}^{rev} - e\alpha_{\mathrm{RA}}U_{\mathrm{RA}}}{k_B T}\right), \tag{G7}$$

$$c_{\mathrm{RT}} = \exp\left(-\frac{\Delta G_{\mathrm{RT}}^{rev} - e\alpha_{\mathrm{RT}}U_{\mathrm{RT}}}{k_B T}\right), \tag{G8}$$

$$c_{\mathrm{RD}} = \exp\left(-\frac{\Delta G_{\mathrm{RD}}^{rev} - e\alpha_{\mathrm{RD}}U_{\mathrm{RD}}}{k_B T}\right), \tag{G9}$$

where the coefficients a_{ij} depend on the potential, while the coefficients c_i do not.

If $\alpha_{\mathrm{RT}} = \alpha_{\mathrm{RD}} = \alpha_{\mathrm{RA}}$, all the potential-dependent exponential terms in Eqs. (G3)-(G6) become unity; hence, all the coefficients become independent of the potential, and θ_{O} and θ_{OH} also become independent of the potential. The use of Eqs. (G1)-(G9) with single symmetry factor gives $\theta_{\mathrm{O}} = 0.191$ and $\theta_{\mathrm{OH}} = 0.051$, which are very close to the solution of the simultaneous equations (31)-(33) of $\theta_{\mathrm{O}} = 0.188$ and $\theta_{\mathrm{OH}} = 0.049$ at 0.40 V (RHE).

When the symmetry factors are changed to $\alpha_{\mathrm{RT}} = 0.40$, $\alpha_{\mathrm{RD}} = 0.40$ and $\alpha_{\mathrm{RA}} = 0.60$ following suggestions by pervious DFT calculations on small clusters,[13, 19] θ_{O} and θ_{OH} do not remain constant in the low potential region, and several kinetic properties, such as the current density and Tafel slope in the low potential region, change quantitatively as shown in Fig. S7. However, the changes in the symmetry factors do not affect the important trends discussed in the section 3 [i.e., $\Delta\theta_{\mathrm{O}}$ is larger than $\Delta\theta_{\mathrm{OH}}$, $\Delta\theta_{\mathrm{O}} + \Delta\theta_{\mathrm{OH}}$ increases when the potential decreases, the Tafel slop increases when the potential decreases, and the current density at the high potential region do not largely change].

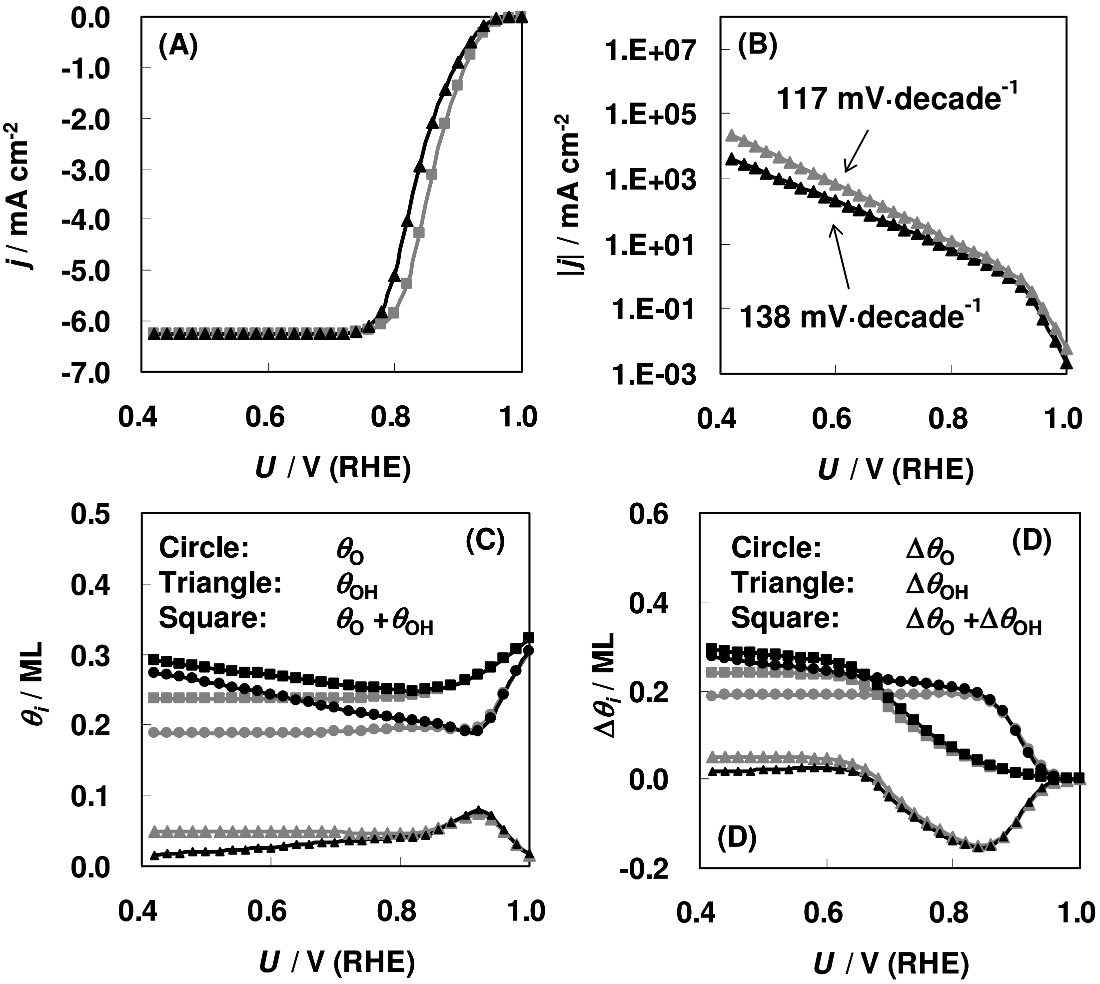

Fig. S7 Summary of effects of changes in α_i from $\alpha_{\mathrm{RT}} = \alpha_{\mathrm{RD}} = \alpha_{\mathrm{RA}} = 0.50$ (gray) to $\alpha_{\mathrm{RT}} = 0.40$, $\alpha_{\mathrm{RD}} = 0.40$ and $\alpha_{\mathrm{RA}} = 0.60$ (black). (A) Current density at $j_L = 6.26$ mA· cm^{-2}, (B) Current density at $j_L = 10^6$ mA· cm^{-2}, (C) surface coverages at $j_L = 10^6$ mA· cm^{-2}, and (D) differences in surface coverages at $j_L = 10^6$ mA· cm^{-2}. Tafel slopes in the low potential region are shown in (B).

H. Potential-dependent reaction order

The apparent reaction order $\gamma_{\mathrm{O}2}$ is a function of U and is related to the reaction current j as follows,

$$j\left(p_{\mathrm{O}_2}^{bulk},U\right)=k(U)p_{\mathrm{O}_2}\left(p_{\mathrm{O}_2}^{bulk},U\right)^{\gamma_{\mathrm{O}_2}(U)}. \qquad \text{(H1)}$$

Furthermore, the kinetic current density j_k is defined as follows,

$$j_k\left(p_{\mathrm{O}_2}^{bulk},U\right)=k(U)p_{\mathrm{O}_2}^{bulk\,\gamma_{\mathrm{O}_2}(U)}. \qquad \text{(H2)}$$

From Eqs. (34), (H1) and (H2), following equations are derived:

$$Y\left(p_{\mathrm{O}_2}^{bulk},U\right)=\gamma_{\mathrm{O}_2}(U)X\left(p_{\mathrm{O}_2}^{bulk},U\right)+\ln\left|j_k(1,U)\right|, \qquad \text{(H3)}$$

$$X\left(p_{\mathrm{O}_2}^{bulk},U\right)=\ln\left\{1-\frac{\left|j\left(p_{\mathrm{O}_2}^{bulk},U\right)\right|}{j_L\left(p_{\mathrm{O}_2}^{bulk}\right)}\right\}+\ln p_{\mathrm{O}_2}^{bulk}, \tag{H4}$$

$$Y\left(p_{\mathrm{O}_2}^{bulk},U\right)=\ln\left|j\left(p_{\mathrm{O}_2}^{bulk},U\right)\right|. \tag{H5}$$

Accordingly, the potential-dependent reaction order $\gamma_{\mathrm{O}2}$ is calculated as the slope of the *X*-*Y* plot obtained by changing $p^{bulk}{}_{\mathrm{O}2}$. These equations are similar to the one used by Zecevic et al.[77] except that we include the change in j_k by the change in $p^{bulk}{}_{\mathrm{O}2}$.

I. List of notations and symbols

DA:	Dissociative adsorption reaction (R6).
DT:	Dissociative transition reaction (R7).
RA:	Reductive adsorption reaction (R5).
RD:	Reductive desorption reaction (R4).
RT:	Reductive transition reaction (R3).
a:	Parameter in Eq. (23) or diameter of ions in the modeled continuum electrolyte.
c_{H^+}:	Concentration of proton.
c_{bulk}:	Concentration of ions in the continuum electrolyte.
e:	Elementary charge.
$f_{i\mathbf{k}\sigma}$:	Occupation number of the wave function specified by *i*th band index, **k** vector and spin index σ.
E_0:	Potential energy without the modeled continuum electrolyte.
E_1:	Potential energy including the mean field of the modeled continuum electrolyte.
E_a:	Potential energy including the solvation free energy of the adsorbates and surface at an equilibrium position.
E_{es}:	Electrostatic energy.
$E_a{}^{gas}$:	Potential energy of the adsorbates and surface at an equilibrium position without any explicit water molecules and modeled continuum electrolyte.
E_{xc}:	Exchange-correlation energy.
G_m:	Mean field of the modeled continuum electrolyte.
G_{nel}:	Non-electrostatic interaction energy between atoms and the modeled continuum electrolyte.
G_i:	Gibbs free energy of *i*th specie (i = O, OH, HO_2, H_2, O_2, H_2O, H^++e^-, or w, where w indicates the explicit water molecule near the adsorbates).

$G^0{}_i$: Gibbs free energy of *i*th specie without the concentration terms. Definitions are in Eqs. (4), (7) and (9) (i = O, OH, HO_2, H_2, O_2, H_2O, $H^+ + e^-$ or w, where w indicates the explicit water molecule near the adsorbates).

$G_a{}^{solv}$: Solvation free energy defined as Eq. (B4).

H: Hamiltonian.

h: Plank constant.

H_1: Hamiltonian defined as Eq. (B1).

H_i: Enthalpy of the internal motions of *i*th specie shown in Table S1.

j: Current density. A reductive current density is defined as a negative value.

j_L: Limiting current density.

j_k: Kinetic current density defined as Eq (H2).

j_{Pt}: Current density at 0.9 V (RHE) on Pt(111).

K: Electronic kinetic energy.

k_B: Boltzmann constant.

k_{ji}: Force constant for *j*th vibration mode in *i*th specie.

N: Number of surface site.

N_i: Number of *i*th specie (i = O, OH, HO_2, H_2, O_2, H_2O or w, where w indicates the explicit water molecule near the adsorbates).

$\mathbf{P}_i$: Momentum of *i*th atom.

$\mathbf{P}_i^m$: Momentum of *i*th atom in the modeled continuum electrolyte.

$\mathbf{P}_i^w$: Momentum of *i*th atom in the explicit water molecule.

p_i: Pressure of *i*th specie (i = H_2, O_2 or H_2O).

$p^0{}_i$: Pressure of *i*th specie at the standard state (i = H_2, O_2 or H_2O).

$p^{bulk}{}_{\mathrm{O2}}$: Bulk pressure of O_2(g).

Q: Partition function.

$Q^*{}_{vib,\mathrm{O_2(TS)}}$: Partition function of O_2 at the transition state with respect to the coordinates except for the reaction coordinate s of the reaction (R6).

$Q_{rot,i}$: Rotational partition function of *i*th specie (i = O, OH, HO_2, H_2, O_2, H_2O or w, where w indicates the explicit water molecule near the adsorbates).

Q_s: Partition function with respect to the reaction coordinate s of the reaction (R6).

$Q_{trans,i}$: Translational partition function of *i*th specie (i = O, OH, HO_2, H_2, O_2, H_2O or w, where w indicates the explicit water molecule near the adsorbates).

$Q_{vib,i}$: Vibrational partition function of ith specie (i = O, OH, HO_2, H_2, O_2, H_2O or w, where w indicates the explicit water molecule near the adsorbates).

$Q_{vib,w}$: Vibrational partition function of the explicit water molecule near the adsorbates.

$\mathbf{R}_{i0}$: Equilibrium positions of ith atom.

$\mathbf{R}_{i0}^{w}$: Equilibrium positions of ith atom in the explicit water molecule.

$\mathbf{R}_{i}^{m}$: Position of ith atom in the modeled continuum electrolyte.

$\mathbf{R}_{i}^{w}$: Position of ith atom in the explicit water molecule.

S: Surface area of the electrode.

S_e: Entropy of electrons.

S_i: Entropy of the internal motions of ith specie shown in Table S1.

S_m: Entropy of the modeled continuum electrolyte.

T: Temperature.

t: Time or a coefficient in Eq. (16).

U: Electrode potential.

U_i: Reversible potential (i = RA, RD or RT).

$U^0{}_i$: Reversible potential in a low coverage condition (i = RA, RD or RT).

$U^0{}_{\mathrm{ORR}}$: Reversible potential of ORR at the standard state.

v_i: Reaction rate (i = DA, DT, RA, RD or RT).

v_{sweep}: Sweep rate of the cyclic voltammetry.

x_{ass}: Ratio of the current density caused by the associative pathway to the overall current density.

α_i: Symmetry factor (i = RA, RD or RT).

ΔE: Reaction energy.

ΔE_f: Activation energy.

$\Delta E^0{}_{\mathrm{DA}}$: Reaction energy of the reaction (R6) at a low surface coverage condition.

ΔG_1: Change in the summation of $G^0{}_i$ terms caused by the reaction (R8).

ΔG_2: Change in the summation of $G^0{}_i$ terms caused by the reaction (R9).

$\Delta G_1{}^{gas}$: Gas phase contribution in ΔG_1 defined as Eq. (C17).

$\Delta G_2{}^{gas}$: Gas phase contribution in ΔG_2 defined as Eq. (C19).

$\Delta G_1{}^{solv}$: Solvation contribution in ΔG_1 defined as Eq. (C21).

ΔG_2^{solv}: Solvation contribution in ΔG_2 defined as Eq. (C22).

ΔG_i: Reaction free energy (i = DA, RA, RD or RT).

$\Delta G_{i,f}$: Activation free energy of a forward reaction (i = DA, RA, RD or RT).

$\Delta G_{i,b}$: Activation free energy of a backward reaction (i = RA, RD or RT).

ΔG^{rev}_i: Activation free energy at $U = U_i$ (i = RA, RD or RT).

$\Delta H_{ads,\mathrm{O}}^{gas}$: Enthalpy change for forming 2O(ads) from O_2(g) in gas phase.

$\Delta \mathbf{R}_i$: Displacement vectors of atoms.

$\Delta \mathbf{R}^w_i$: Displacement vectors of atoms in the explicit water molecule.

$\Delta\Delta G_1$: Lateral interaction contribution in ΔG_1 defined as Eq. (15).

$\Delta\Delta G_2$: Lateral interaction contribution in ΔG_2 defined as Eq. (19).

$\Delta\theta_i$: Difference in the surface coverage between under O_2 atmosphere and under Ar atmosphere: $\Delta\theta_i = \theta_i$ (O_2 atmosphere) − θ_i (Ar atmosphere) (i = O, OH or HO_2).

δ_s: Effective length along the reaction coordinate s, where O_2 is regarded as the transition state of the reaction (R6).

ε: Dielectric permittivity.

ϕ: Electrostatic potential.

ϕ_{rep}: Non-electrostatic repulsive interaction potential between atoms and ions in the modeled continuum electrolyte.

γ_{O_2}: Apparent reaction order with respect to the pressure of O_2(g).

λ: Coordinate used in the line integrals of Eqs. (C2) and (C9).

μ_s: Effective mass for the translational motion along the reaction coordinate s of the reaction (R6)

ρ_+: Charge distribution of cation in the modeled continuum electrolyte.

ρ_-: Charge distribution of anion in the modeled continuum electrolyte.

ρ_σ: Electron density with spin index σ.

θ_i: Surface coverage defined as N_i/N (i = O, OH, HO_2 or O_2(TS)).

σ_e: Parameter for the Gaussian broadening method.

$\psi_{i\mathbf{k}\sigma}$: Wave function specified by ith band index, $\mathbf{k}$ vector and spin index σ.

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