

Supplementary Information

Toward full simulation of the electrochemical oxygen reduction reaction on Pt with first-principles and kinetic calculations

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1 Computations

The cutoff energies for the DFT calculations were 3060 and 340 eV for electron density and plane waves, respectively. The SCF criterion and smearing factor were set at $0.5 - 2.7 \times 10^{-7}$ eV/atom and 0.14 - 0.27 eV, respectively. The MD temperature was controlled at 353 K with simple velocity scaling or a N ose-Hoover thermostat [1]. The MD timestep was 1.0 fs with the mass of deuterium used for the hydrogen atoms. To calculate the redox potential and activation energy, the time-averaged values of the total energy and forces across about 0.5 ps and 2 ps, respectively, were obtained after equilibration. The cell size in the z -direction must be long enough to avoid influences from the Pt-water and water-vacuum interfaces. FPMD calculations were typically carried out with 128 cores in parallel on supercomputers mentioned in Acknowledgement. 1 ps calculation needed one week without a waiting time.

In the redox potential calculation, a hydrogen atom of a randomly selected adsorbed-H₂O was removed to make OH adsorption. In order to make O adsorption, a hydrogen atom of a randomly selected OH(ad) was removed. Total energy becomes stable after 200-300 MD steps. Then, a H atom is removed gain. After producing each configuration having the different number of O and OH adsorption, these different configurations were independently equilibrated. OH(ad) and H₂O(ad) sometimes exchange the H atom between them. OH(ad) is located on an atop site, and O(ad) is on a hollow site.

In the activation energy calculation, a configuration of $n = 2$ in Fig. 2(a) was used for reaction *R1* and that of $n = 1$ in Fig. 2(b) was used for reaction *R2*. The atomic distance between H of OH or H₂O on Pt and O of the nearest water molecule was constrained. The distance was step-by-step shortened from the initial atomic distance. After selecting several configurations, constraint FPMD calculation was carried out at each distance. Atomic distance was constrained by the SHAKE algorithm [3].

2 Change in coverage of adsorbed O and OH during CV

The degree of coverage of adsorbed OH and O species during CV are shown in Fig. S1. Here, the normalized coverage, $\theta/\theta_{\text{sat}}$, was defined with a saturated coverage value of $\theta_{\text{sat}} = 2/3$.

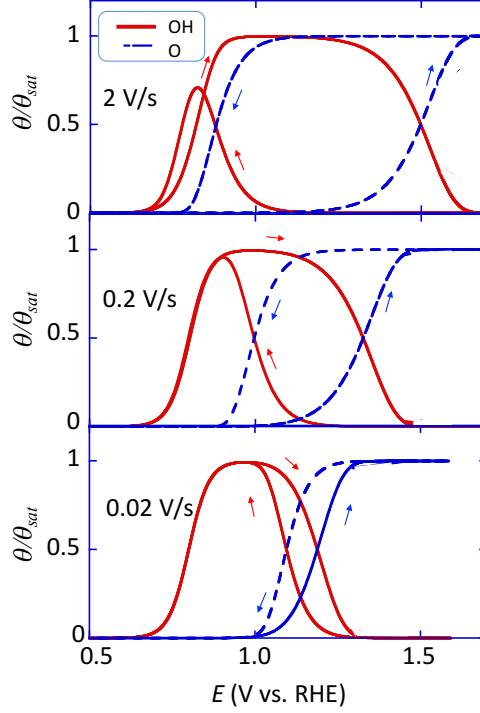


Figure S1: Changes in normalized coverage ($\theta/\theta_{\text{sat}}$) of OH(ad) and O(ad) for CV results using scan rates, $v = 0.02, 0.2,$ and 2 V/s.

3 Calculating the activation energy and symmetry factor from two energy profiles

We consider two energy profiles shown in Fig. S2. The red curve is at the equilibrium; the energy levels at the initial and final states are the same. The blue broken curve is the general case. E_a in the Butler–Volmer equation is the activation energy for the equilibrium case. When the energy level of the final state (E_{final}) is different from that initial (E_{initial}), the energy level at the transition state ($E_{\text{transition}}$) will change by β , as widely detailed in electrochemistry textbooks, e.g. [4] as

$$E_{\text{transition}} = E_{\text{initial}} + \beta(E_{\text{final}} - E_{\text{initial}}). \quad (1)$$

With two energy profiles, 1 and 2, of differing energy levels for the final and transition states, they will be:

$$E_{\text{transition},1} = E_a + \beta E_{\text{final},1} \quad E_{\text{transition},2} = E_a + \beta E_{\text{final},2} \quad (2)$$

where the energy levels for the transition and final states are measured from the baseline of the initial energy level. From these two equations, E_a and β are obtained as follows.

$$\beta = \frac{E_{\text{transition},2} - E_{\text{transition},1}}{E_{\text{final},2} - E_{\text{final},1}} \quad (3)$$

$$E_a = \frac{E_{\text{transition},1}E_{\text{final},2} - E_{\text{transition},2}E_{\text{final},1}}{E_{\text{final},2} - E_{\text{final},1}} \quad (4)$$

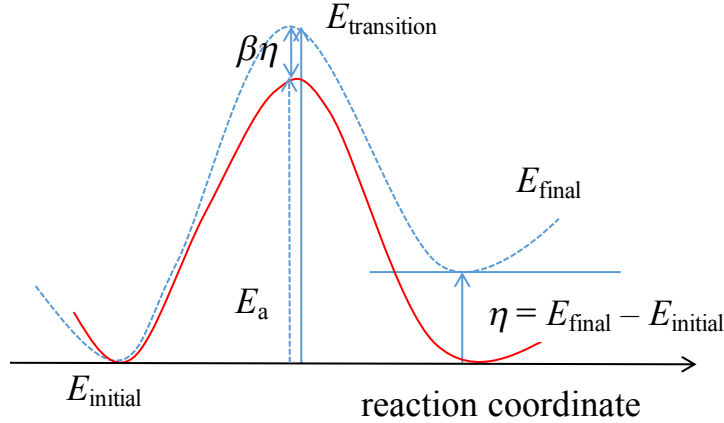


Figure S2: Schematic showing two different energy profiles at equilibrium (red line) and in the general case (broken blue line) along the reaction coordinate.

4 Parameters for rate equations

The O_2 saturation concentration was taken from the literature [6], as were diffusion coefficients for both H_3O^+ and O_2 [7]. The activity coefficients of all species were assumed to be unity. All parameters were assumed to be at 353 K, a typical working temperature for a fuel cell. In the LSV calculations, the diffusion layer thickness was set to 20 μm . The parameters used in the CV and LSV calculations are summarized in Tables S1 and S2.

Table S1: Parameter set used in CV and LSV calculations (353 K)

reaction	$R1$	$R2$	$R3$
E_0/eV	0.80 ^a	1.14 ^a	0.92 ^a
E_a/eV	0.09 ^a	0.28 ^a	0.48 ^b
κ	2.0×10^{4c}	2.0×10^{4c}	7.4×10^{12d}
β	0.5 ^a	0.4 ^a	-

^acalculated in this work, ^b ref. [5].

^cfrom $(k_{\text{B}}T/h) \exp(-0.6 \text{ eV}/RT)$, ^dfrom $(k_{\text{B}}T/h)$

Table S2: Parameters used for calculations of the bulk (353 K)

parameter	unit	H ⁺	O ₂	O(ad), OH(ad)
diffusion coefficient ^a	cm ² s ⁻¹	1.81 × 10 ⁻⁴	6.76 × 10 ⁻⁵	
concentration in the bulk ^b	M	1.00 × 10 ⁻¹	1.59 × 10 ⁻³ (for LSV) 1.59 × 10 ⁻¹⁵ (for CV)	
saturated concentration ^c	M		1.59 × 10 ⁻³	
saturated coverage ^e	mol cm ⁻²			1.64 × 10 ⁻⁹

^afrom ref.[7], ^bcalculation conditions, ^cfrom ref.[6], ^e2/3 of the surface Pt density.

5 Rate and diffusion equations

Rate equations for electrochemical reactions are given in the main text. Rate equation for O adsorption from O₂, *R3*, is:

$$J^{(3)} = \kappa^{(3)} \left[-c_{\text{O}_2}^{x=0} (1 - \sigma_{\text{O}} - \sigma_{\text{OH}})^2 \exp \left(-\frac{1}{RT} E_a^{(3)} \right) \right] \quad (5)$$

O₂ formation reaction is not considered here. Another equations used to calculate CV and LSV are the following diffusion equations for diffusion flux J_{diff} of H⁺ and O₂.

$$J_{\text{diff}} = D \frac{\partial C}{\partial x} \quad (6)$$

Where C is a molar concentration, which has the following relation with molar fraction, c , and molar density, ρ .

$$C = \rho c \quad (7)$$

Terms used in the paper are summarized below.

J ; current density

J_0 ; exchange current density

E ; electrode potential

E_0 ; redox potential

E_a ; activation energy

η ; overpotential

κ ; prefactor in rate equation

β ; symmetry factor

F ; Faraday constant

R ; gas constant

T ; temperature

c ; molar fraction

C ; molar concentration

σ ; surface concentration normalized by saturated concentration

θ ; surface coverage

OH, O, H⁺, O₂; parameters or variables for the species in the subscript

⁽¹⁾, ⁽²⁾, ⁽³⁾; parameters or variables for the reactions given in *R1*, *R2*, and *R3* in the main text

^{x=0}; parameter value at the electrode

References

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