

SUPPORTING INFORMATION

Unifying theoretical framework for deciphering the oxygen reduction reaction on platinum

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Lateral interaction effect

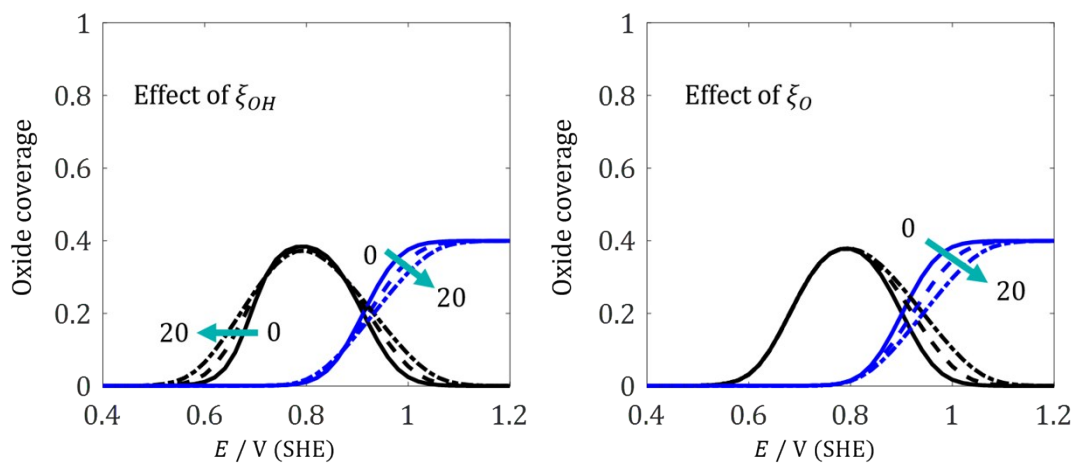


Figure S 1. Effect of ξ_{OH} on the coverage of adsorbed oxygen intermediates (left) with $\xi_O = 10 \text{ kJ mol}^{-1}$. Effect of ξ_O on the coverage of adsorbed oxygen intermediates (right) with $\xi_{OH} = 10 \text{ kJ mol}^{-1}$. Other parameters are given in Figure 2 of the main-text.

Interfacial parameters

Table S1. Parameters of the electrified interface in calculation of σ_M .

Category	Item	Value	Note
General	Gas constant, R	$8.314 J K^{-1} mol^{-1}$	Constant
	Faraday constant, F	$96485 C mol^{-1}$	Constant
	Temperature, T	$298.15 K$	Typical value
	Elementary charge, e	$1.6 \times 10^{-19} C$	Constant
	Avogadro's number, N_A	$6.02 \times 10^{23} mol^{-1}$	Constant
	Water dipole moment, μ_w	$3.1 D$	Typical value
	Pt atom density, N_{tot}	$1.6335 \times 10^{19} m^{-2}$	Calculated using $4/\sqrt{3}a_{Pt}^2$ with $a_{Pt} = 3.92 \text{ \AA}$
	Vacuum permittivity, ϵ_0	$8.85 \times 10^{-12} F m^{-1}$	Constant
Dielectric and structural	Permittivity of oxide layer, ϵ_{PtO}	$1.0 \epsilon_0$	Nothing but vacuum inside the oxide layer
	Permittivity of the IHP, ϵ_{IHP}	$06.0 \epsilon_0$	1
	Permittivity of the OHP, ϵ_{OHP}	$30.0 \epsilon_0$	1
	Permittivity of bulk solution, ϵ_s	$78.5 \epsilon_0$	Constant (bulk water)
	Thickness of the oxide layer, δ_{PtO}	$0.18 nm$	DFT calculation ²
	Net charge number per oxide site, ζ_{OH}	0.02	DFT calculation ²
	Thickness of the IHP, δ_{IHP}	$0.275 nm$	Constant (the diameter of water dipole)
	Thickness of the OHP, δ_{OHP}	$0.515 nm$	1
Potential difference between bulk and interfacial metal, $\Delta\phi_M$	$0.3 V$	1	

A collection of ORR Tafel slopes of Pt electrocatalysts.

Table S2. A collection of ORR Tafel slopes of Pt electrocatalysts.

Sample	Method & condition	Tafel slope / $mV\ dec^{-1}$	Potential range / V	Potential dependence	Reference
Pt/Vulcan	RDE, O_2 -saturated $0.1M\ HClO_4$, mass- transfer corrected	60~90	0.75 – 0.95	Decreasing	3
Pt(111)	RDE, O_2 -saturated $0.1M\ HClO_4$	77	0.7 – 0.9	Not shown	4
50% wt Pt/Vulcan	IR-free voltage of a catalyst layer in H_2/O_2 gas condition at 100% RH and 80°C	60 – 110	0.75 – 0.90	Decreasing	5
Pt(111)	RDE, O_2 -saturated $0.1M\ HClO_4$ at 296 K, intrinsic kinetic current	~60 – 118	0.5 – 1.0	Decreasing	6
Pt-poly, Pt_3Ni , Pt_3Co	RDE, O_2 -saturated $0.1M\ HClO_4$ at 293 K, mass-transfer corrected	90 – 110	0.80 – 0.92	Decreasing	7
Pt disk electrode	RDE, $HClO_4$ and H_2SO_4	60 – 120	0.4 – 1.0	Decreasing	8

Effect of ionic strength

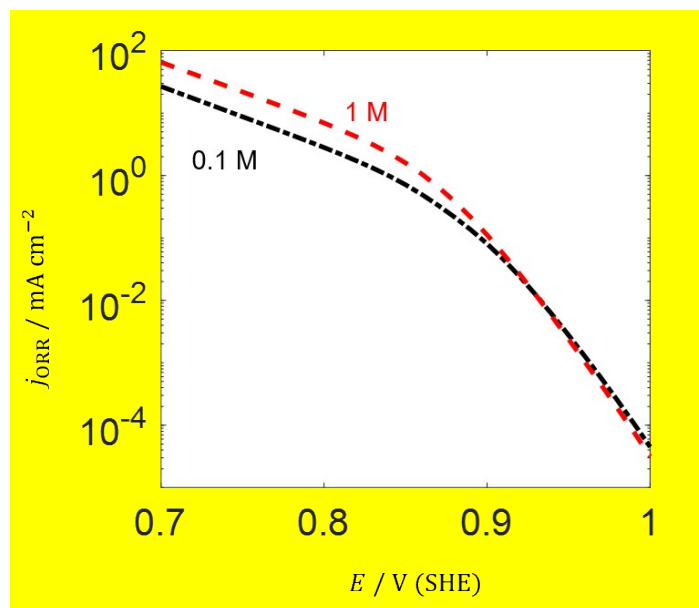


Figure S 1. Effect of ionic strength on the ORR for the case of $\text{pH}=1.2$ in Figure 3.

Rate constants

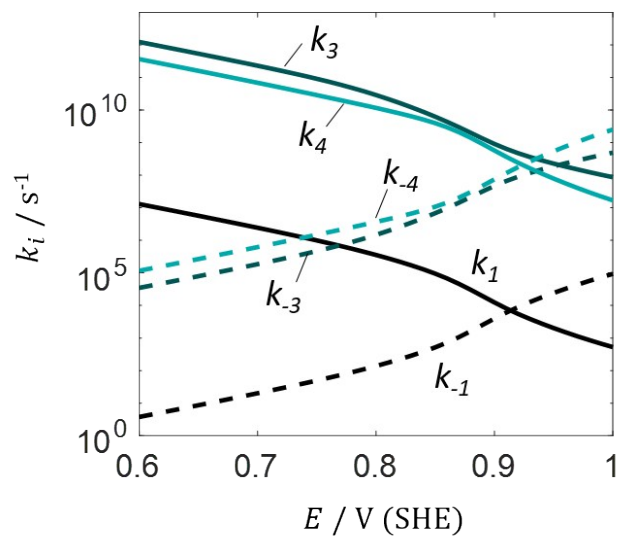


Figure S 3. Variations in the rate constants as a function of electrode potential for $\text{pH}=1.2$ in Figure 3.

Oxide coverage as a function of the chemisorption energy

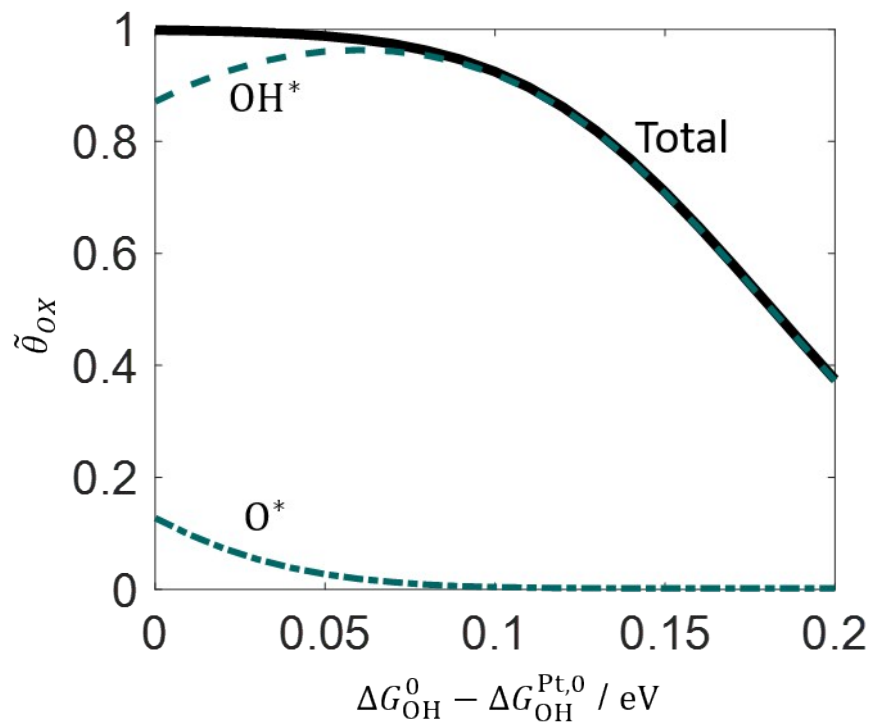


Figure S 4. Normalized total oxide coverage, $\tilde{\theta}_{\text{OX}} = (\theta_{\text{OH}} + \theta_{\text{O}}) / \theta_{\text{max}}$, as a function of hydroxyl binding energy. The data are calculated at $E = 0.9 \text{ V (RHE)}$ using the same parameter set as in Figure 7.

Relation between ORR activity and G_{OH}^0

According to the definition we obtain,

$$K_3^* = \frac{k_3^*}{k_{-3}} = [H^+] \exp\left(\frac{E_{a,-3} - E_{a,3}}{RT}\right) = [H] \quad (S1)$$

Based on the scaling relation, E_3^{eq} of a catalyst having a different ΔG_{OH}^0 relative to $\Delta G_{OH}^{Pt,0}$ is expressed as,

$$E_3^{eq} = E_3^{Pt,eq} + \frac{(\zeta_0 - 1)(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0})}{F} \quad (S2)$$

where $E_3^{Pt,eq} = 0.95 \text{ V}$ as in Table 1.

Substituting Eq.(S2) into Eq.(S1) leads to,

$$K_3^* = [H^+] \exp\left(-\frac{F(E - E_3^{Pt,eq})}{4RT}\right) \exp\left(\frac{\delta G_\zeta}{RT}\right) \quad (S3)$$

with $K_3^{Pt,*} = [H^+] \exp\left(-\frac{F(E - E_3^{Pt,eq})}{RT}\right) \exp\left(\frac{\delta G_0 - \delta G_{OH}}{RT}\right)$.

Similarly, we have,

$$K_4^* = K_4^{Pt,*} \exp\left(\frac{(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0})}{RT}\right) \quad (S4)$$

with $K_4^{Pt,*} = [H^+] \exp\left(-\frac{F(E - E_4^{Pt,eq})}{RT}\right) \exp\left(\frac{-\delta G_{OH}}{RT}\right)$.

For step (1),

$$k_1^* = k_1^{Pt,*} \exp\left(\frac{-\beta_1 \zeta_{OOH}(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0})}{RT}\right), \quad (S5)$$

$$\text{with } k_1^{Pt,*} = k_1^0 \exp\left(\frac{-E_{a,i}^0 - \beta_1 F(E - E_1^{Pt,eq})}{RT}\right) [O_2][H^+]$$

For step (3),

$$k_3^* = k_3^{Pt,*} \exp\left(\frac{\beta_3(\zeta_O - 1)(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0})}{RT}\right), \quad (S6)$$

$$\text{with } k_3^{Pt,*} = k_3^0 \exp\left(\frac{-E_{a,3}^0 - \beta_3 F(E - E_3^{Pt,eq})}{RT}\right) \theta_O [H^+]$$

For step (4),

$$k_4^* = k_4^{Pt,*} \exp\left(\frac{\beta_4(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0})}{RT}\right), \quad (S7)$$

$$\text{with } k_4^{Pt,*} = k_4^0 \exp\left(\frac{-E_{a,4}^0 - \beta_4 F(E - E_4^{Pt,eq})}{RT}\right) \theta_{OH} [H^+]$$

Combining Eqs. (S3)-(S7) into the relation $v_{ORR} = (K_3^*)^v (K_4^*)^\mu k_i^*$ gives,

$$v_{ORR} = v_{ORR}^0 \exp\left(\frac{(v(\zeta_O - 1) + \mu - \zeta_i)(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0})}{RT}\right), \quad (S8)$$

with $v_{ORR}^0 = (K_3^{Pt,*})^v (K_4^{Pt,*})^\mu k_i^{Pt,*}$ and

$$\zeta_i = \begin{cases} \beta_1 \zeta_{OOH}, & i = 1 \\ -\beta_3(\zeta_O - 1), & i = 3, \\ -\beta_4, & i = 4 \end{cases} \quad (S9)$$

Rate determining term

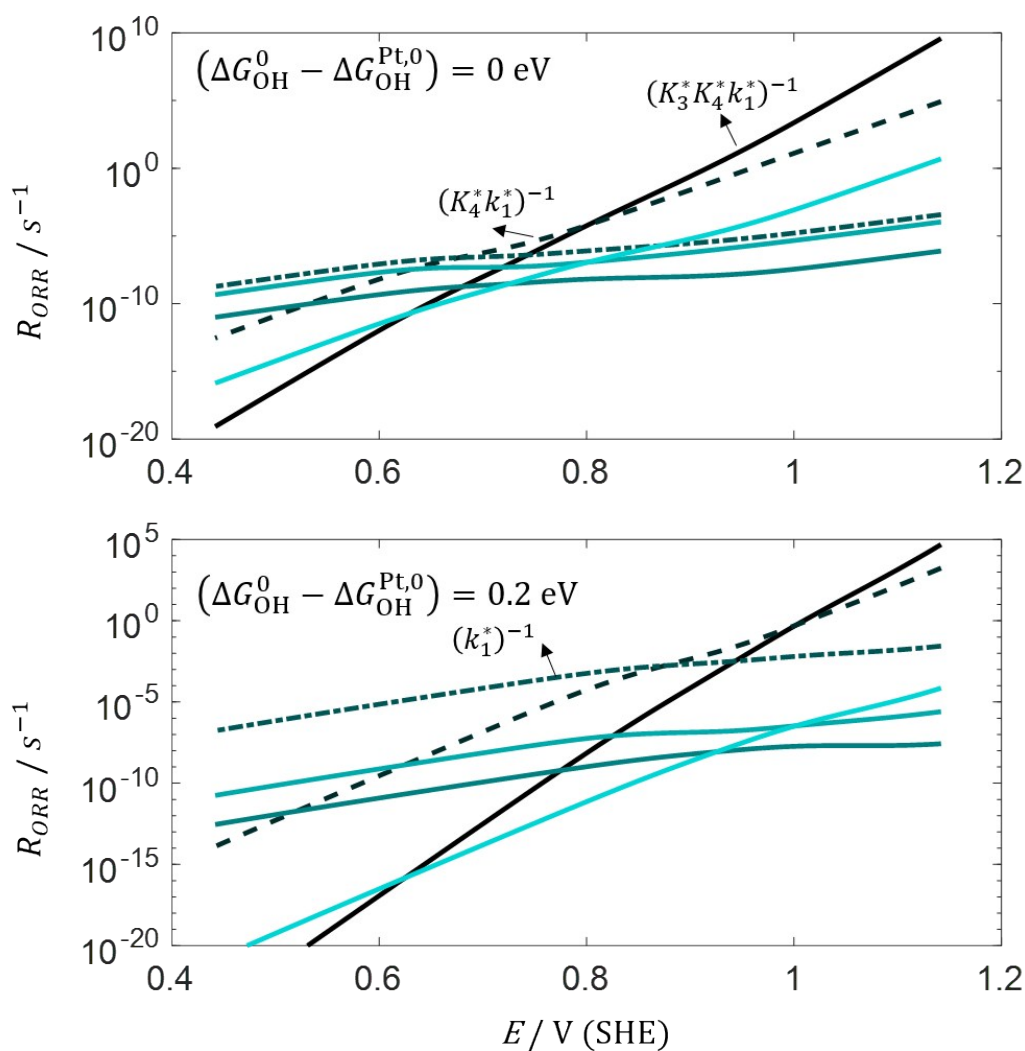


Figure S 5. Rate-determining term of the ORR rate expression for $(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0}) = 0$ and 0.2 eV. Labels for the curves are the same as in Figure 5.

References

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