

SUPPORTING INFORMATION

Unifying theoretical framework for deciphering the oxygen reduction reaction on platinum

Jun Huang,^{1,2,z} Jianbo Zhang,^{2,3} Michael Eikerling⁴

¹ College of Chemistry and Chemical Engineering, Central South University,
Changsha 410083, PR China

² Department of Automotive Engineering, State Key Laboratory of Automotive
Safety and Energy, Tsinghua University, Beijing 100084, China

³ Beijing Co-innovation Center for Electric Vehicles, Beijing Institute of
Technology, Beijing 100081, China

⁴ Department of Chemistry, Simon Fraser University, Burnaby, BC V5A 1S6,
Canada

Corresponding authors: jhuangelectrochem@qq.com

Lateral interaction effect

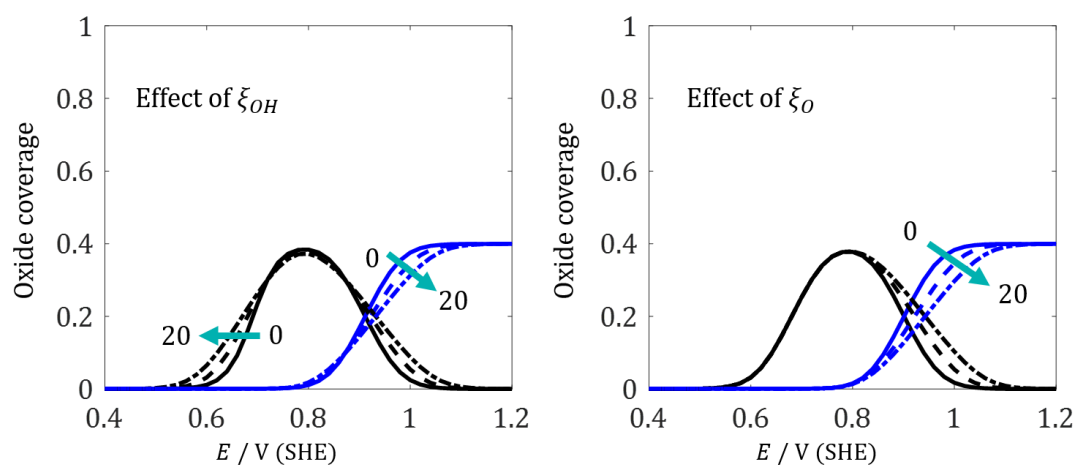


Figure S 1. Effect of ξ_{OH} on the coverage of adsorbed oxygen intermediates (left) with $\xi_O = 10$ kJ mol⁻¹. Effect of ξ_O on the coverage of adsorbed oxygen intermediates (right) with $\xi_{OH} = 10$ kJ mol⁻¹. Other parameters are given in Figure 2 of the main-text.

Interfacial parameters

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

Category	Item	Value	Note
General	Gas constant, R	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$	Constant
	Faraday constant, F	96485 C mol^{-1}	Constant
	Temperature, T	298.15 K	Typical value
	Elementary charge, e	$1.6 \times 10^{-19} \text{ C}$	Constant
	Avogadro's number, N_A	$6.02 \times 10^{23} \text{ mol}^{-1}$	Constant
	Water dipole moment, μ_w	3.1 D	Typical value
	Pt atom density, N_{tot}	$1.6335 \times 10^{19} \text{ m}^{-2}$	Calculated using $4/\sqrt{3}a_{pt}^2$ with $a_{pt} = 3.92 \text{ \AA}$
	Vacuum permittivity, ϵ_0	$8.85 \times 10^{-12} \text{ F m}^{-1}$	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

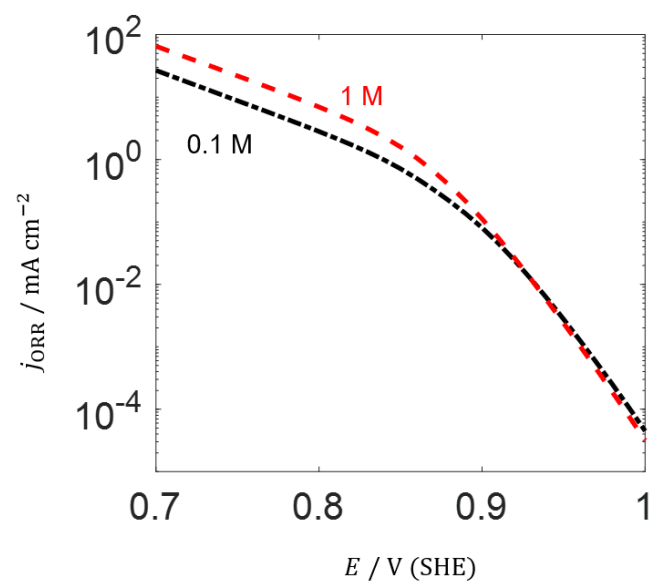


Figure S 2. Effect of ionic strength on the ORR for the case of pH=1.2 in Figure 3.

Rate constants

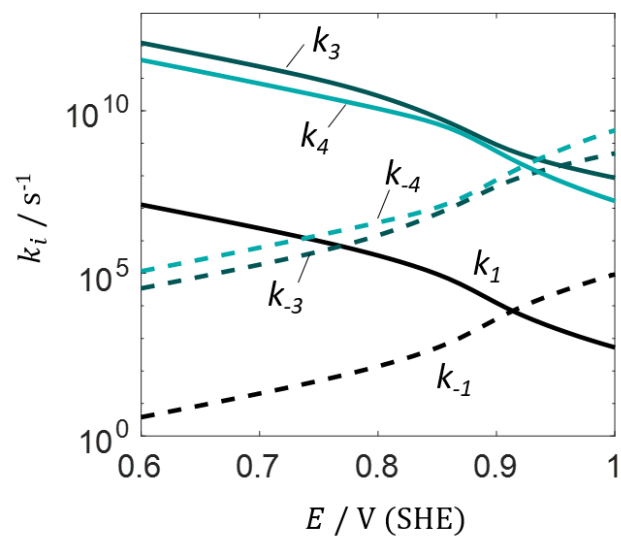


Figure S 3. Variations in the rate constants as a function of electrode potential for $\text{pH}=1.2$ in Figure 3.

Oxide coverage as a function of the chemisorption energy

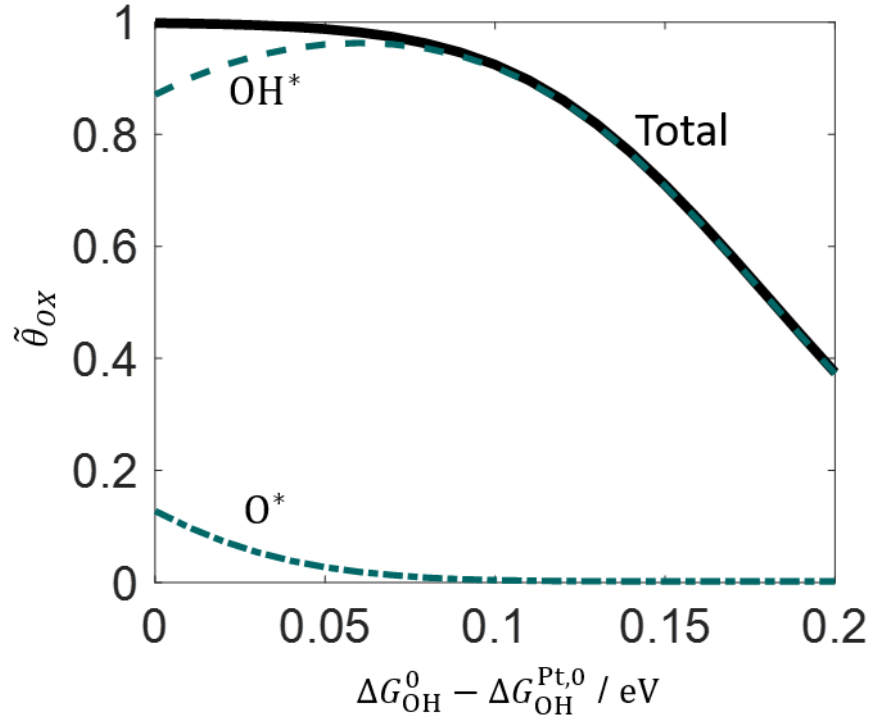


Figure S 4. Normalized total oxide coverage, $\tilde{\theta}_{\text{ox}} = (\theta_{\text{OH}} + \theta_{\text{O}})/\theta_{\text{max}}$, as a function of hydroxyl binding energy. The data are calculated at $E = 0.9 \text{ V}$ (RHE) using the same parameter set as in Figure 7.

Relation between ORR activity and G_{OH}^0

According to the definition we obtain,

$$\begin{aligned} K_3^* &= \frac{k_3^*}{k_{-3}} = [H^+] \exp\left(\frac{E_{a,-3} - E_{a,3}}{RT}\right) = [H^+] \exp\left(-\frac{\Delta G_3}{RT}\right) \\ &= [H^+] \exp\left(-\frac{F(E - E_3^{eq}) + \delta G_{OH} - \delta G_O}{RT}\right). \end{aligned} \quad (S1)$$

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,

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

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

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

$$\begin{aligned} K_3^* &= [H^+] \exp\left(-\frac{F(E - E_3^{Pt,eq})}{4RT}\right) \exp\left(\frac{\delta G_O - \delta G_{OH}}{RT}\right) \exp\left(\frac{F}{eRT} (\zeta_O \right. \\ &\quad \left. - 1)(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0})\right) \\ &= K_3^{Pt,*} \exp\left(\frac{1}{RT} (\zeta_O - 1)(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0})\right), \end{aligned} \quad (S3)$$

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

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),

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

$$\text{with } k_1^{\text{Pt},*} = k_1^0 \exp\left(\frac{-E_{\text{a},1}^0 - \beta_1 F(E - E_1^{\text{Pt,eq}})}{RT}\right) [\text{O}_2][\text{H}^+].$$

For step (3),

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

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

For step (4),

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

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

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

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

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

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

Rate determining term

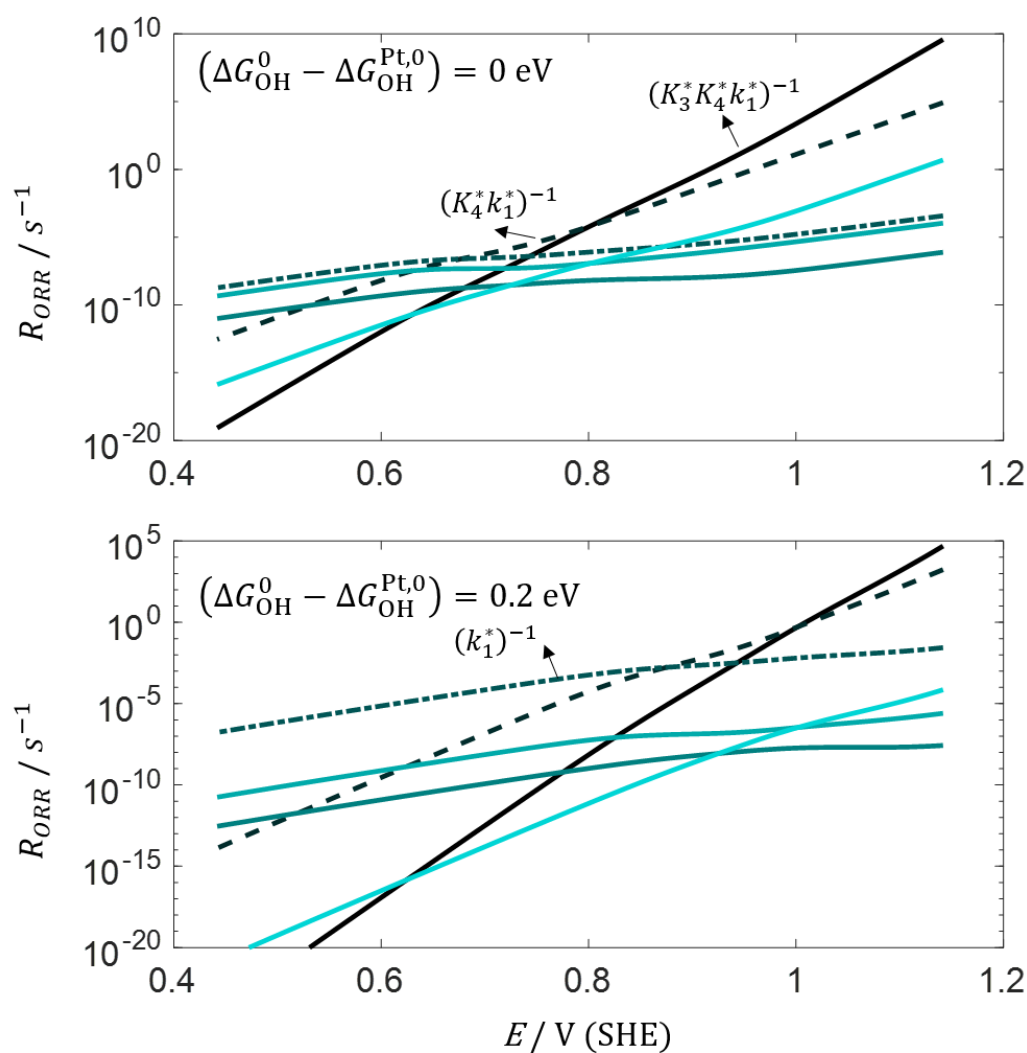


Figure S 5. Rate-determining term of the ORR rate expression for $(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0}) = 0$ and 0.2 eV. Labels for the curves are the same as in Figure 5.

References

1. J. Huang, A. Malek, J. Zhang and M. H. Eikerling, *The Journal of Physical Chemistry C*, 2016, **120**, 13587-13595.
2. A. Malek and M. H. Eikerling, *Electrocatalysis*, 2017, DOI: 10.1007/s12678-017-0436-0.
3. E. J. Coleman and A. C. Co, *ACS Catalysis*, 2015, **5**, 7299-7311.
4. A. M. Gomez-Marin, R. Rizo and J. M. Feliu, *Catalysis Science & Technology*, 2014, **4**, 1685-1698.
5. N. P. Subramanian, T. Greszler, J. Zhang, W. Gu and R. R. Makharia, *ECS Transactions*, 2011, **41**,

985-1007.

6. J. X. Wang, J. Zhang and R. R. Adzic, *The Journal of Physical Chemistry A*, 2007, **111**, 12702-12710.
7. N. Markovic, T. Schmidt, V. Stamenkovic and P. Ross, *FUEL CELLS-WEINHEIM-*, 2001, **1**, 105-116.
8. D. B. Sepa, M. V. Vojnovic and A. Damjanovic, *Electrochimica Acta*, 1981, **26**, 781-793.