SUPPORTING INFORMATION

Unifying theoretical framework for deciphering the oxygen reduction reaction on platinum

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Lateral interaction effect

Figure S1. Effect of $\xi_{OH}$ on the coverage of adsorbed oxygen intermediates (left) with $\xi_O = 10$ kJ mol$^{-1}$. Effect of $\xi_O$ 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 $\sigma_M$.

<table>
<thead>
<tr>
<th>Category</th>
<th>Item</th>
<th>Value</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>General</td>
<td>Gas constant, $R$</td>
<td>$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$</td>
<td>Constant</td>
</tr>
<tr>
<td></td>
<td>Faraday constant, $F$</td>
<td>$96485 \text{ C mol}^{-1}$</td>
<td>Constant</td>
</tr>
<tr>
<td></td>
<td>Temperature, $T$</td>
<td>$298.15 \text{ K}$</td>
<td>Typical value</td>
</tr>
<tr>
<td></td>
<td>Elementary charge, $e$</td>
<td>$1.6 \times 10^{-19} \text{ C}$</td>
<td>Constant</td>
</tr>
<tr>
<td></td>
<td>Avogadro’s number, $N_A$</td>
<td>$6.02 \times 10^{23} \text{ mol}^{-1}$</td>
<td>Constant</td>
</tr>
<tr>
<td></td>
<td>Water dipole moment, $\mu_w$</td>
<td>$3.1 \text{ D}$</td>
<td>Typical value</td>
</tr>
<tr>
<td></td>
<td>Pt atom density, $N_{\text{tot}}$</td>
<td>$1.6335 \times 10^{19} \text{ m}^{-2}$</td>
<td>Calculated using $4/\sqrt{3}a_{\text{Pt}}^2$ with $a_{\text{Pt}} = 3.92\text{Å}$</td>
</tr>
<tr>
<td></td>
<td>Vacuum permittivity, $\varepsilon_0$</td>
<td>$8.85 \times 10^{-12} \text{ F m}^{-1}$</td>
<td>Constant</td>
</tr>
<tr>
<td>Dielectric and structural</td>
<td>Permittivity of oxide layer, $\varepsilon_{\text{PO}}$</td>
<td>$1.0 \varepsilon_0$</td>
<td>Nothing but vacuum inside the oxide layer</td>
</tr>
<tr>
<td></td>
<td>Permittivity of the IHP, $\varepsilon_{\text{IHP}}$</td>
<td>$06.0 \varepsilon_0$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Permittivity of the OHP, $\varepsilon_{\text{OHP}}$</td>
<td>$30.0 \varepsilon_0$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Permittivity of bulk solution, $\varepsilon_s$</td>
<td>$78.5 \varepsilon_0$</td>
<td>Constant (bulk water)</td>
</tr>
<tr>
<td></td>
<td>Thickness of the oxide layer, $\delta_{\text{PO}}$</td>
<td>$0.18 \text{ nm}$</td>
<td>DFT calculation$^2$</td>
</tr>
<tr>
<td></td>
<td>Net charge number per oxide site, $\zeta_{\text{OH}}$</td>
<td>$0.02$</td>
<td>DFT calculation$^2$</td>
</tr>
<tr>
<td></td>
<td>Thickness of the IHP, $\delta_{\text{IHP}}$</td>
<td>$0.275 \text{ nm}$</td>
<td>Constant (the diameter of water dipole) $^1$</td>
</tr>
<tr>
<td></td>
<td>Thickness of the OHP, $\delta_{\text{OHP}}$</td>
<td>$0.515 \text{ nm}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Potential difference between bulk and interfacial metal, $\Delta \phi_M$</td>
<td>$0.3 \text{ V}$</td>
<td></td>
</tr>
</tbody>
</table>
A collection of ORR Tafel slopes of Pt electrocatalysts.

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method &amp; condition</th>
<th>Tafel slope / mV dec(^{-1})</th>
<th>Potential range / V</th>
<th>Potential dependence</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Vulcan</td>
<td>RDE, O(_2)-saturated 0.1M HClO(_4), mass-transfer corrected</td>
<td>60~90</td>
<td>0.75 – 0.95</td>
<td>Decreasing</td>
<td>3</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>RDE, O(_2)-saturated 0.1M HClO(_4)</td>
<td>77</td>
<td>0.7 – 0.9</td>
<td>Not shown</td>
<td>4</td>
</tr>
<tr>
<td>50% wt Pt/Vulcan</td>
<td>IR-free voltage of a catalyst layer in H(_2)/O(_2) gas condition at 100% RH and 80(^\circ)C</td>
<td>60 – 110</td>
<td>0.75 – 0.90</td>
<td>Decreasing</td>
<td>5</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>RDE, O(_2)-saturated 0.1M HClO(_4) at 296 K, intrinsic kinetic current</td>
<td>~60 – 118</td>
<td>0.5 – 1.0</td>
<td>Decreasing</td>
<td>6</td>
</tr>
<tr>
<td>Pt-poly, Pt(_3)Ni, Pt(_3)Co</td>
<td>RDE, O(_2)-saturated 0.1M HClO(_4) at 293 K, mass-transfer corrected</td>
<td>90 – 110</td>
<td>0.80 – 0.92</td>
<td>Decreasing</td>
<td>7</td>
</tr>
<tr>
<td>Pt disk electrode</td>
<td>RDE, HClO(_4) and H(_2)SO(_4)</td>
<td>60 – 120</td>
<td>0.4 – 1.0</td>
<td>Decreasing</td>
<td>8</td>
</tr>
</tbody>
</table>
**Effect of ionic strength**

Figure S2. 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 pH=1.2 in Figure 3.
Oxide coverage as a function of the chemisorption energy

Figure S 4. Normalized total oxide coverage, $\tilde{\theta}_{OX} = (\theta_{OH} + \theta_O)/\theta_{max}$, as a function of hydroxyl binding energy. The data are calculated at $E = 0.9 \ V$ (RHE) using the same parameter set as in Figure 7.
**Relation between ORR activity and \(G_{0H}^0\)**

According to the definition we obtain,

\[
K_3^* = \frac{k_3^*}{k_{-3}} = [H^+] \exp \left( \frac{E_{a,3} - E_{a,3}^{eq}}{RT} \right) = [H^+] \exp \left( -\frac{\Delta G_3}{RT} \right)
\]

(S1)

\[
= [H^+] \exp \left( -\frac{F(E - E_3^{eq} + \delta G_{OH} - \delta G_0)}{RT} \right)
\]

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

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

(S2)

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

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

\[
K_3^* = [H^+] \exp \left( -\frac{F(E - E_3^{Pt,eq})}{4RT} \right) \exp \left( \frac{\delta G_0 - \delta G_{OH}}{RT} \right) \exp \left( \frac{F}{eRT} (\zeta_0 - 1)(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0}) \right)
\]

(S3)

\[
= k_3^{Pt,*} \exp \left( \frac{1}{RT} (\zeta_0 - 1)(\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0}) \right)
\]

with \(k_3^{Pt,*} = [H^+] \exp \left( -\frac{F(E - E_3^{Pt,eq})}{RT} \right) \exp \left( \delta G_0 - \delta G_{OH} \right) \).

Similarly, we have,

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

(S4)

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

For step (1),
\[ k_1^* = k_1^{pt,*} \exp \left( -\frac{\beta_1 \zeta_{OOH} (\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0})}{RT} \right), \]  

(S5)

with \( k_1^{pt,*} = k_1^0 \exp \left( -\frac{E_{a,1}^0 - \beta_1 F (E - E_{1,eq}^{Pt})}{RT} \right) \) \([O_2][H^+].\)

For step (3),

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

(S6)

with \( k_3^{pt,*} = k_3^0 \exp \left( -\frac{E_{a,3}^0 - \beta_3 F (E - E_{3,eq}^{Pt})}{RT} \right) \theta_3[H^+].\)

For step (4),

\[ k_4^* = k_4^{pt,*} \exp \left( \frac{\beta_4 (\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0})}{RT} \right), \]  

(S7)

with \( k_4^{pt,*} = k_4^0 \exp \left( -\frac{E_{a,4}^0 - \beta_4 F (E - E_{4,eq}^{Pt})}{RT} \right) \theta_4[H^+].\)

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

\[ v_{ORR} = v_{ORR}^0 \exp \left( \frac{(\nu (\zeta_O - 1) + \mu - \zeta_i) (\Delta G_{OH}^0 - \Delta G_{OH}^{Pt,0})}{RT} \right), \]  

(S8)

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

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

(S9)
**Rate determining term**

\[
\left( \Delta G_{\text{OH}}^0 - \Delta G_{\text{OH}}^{\text{Pt},0} \right) = 0 \text{ eV} \\
\left( K_4^* k_1^* \right)^{-1}
\]

\[
\left( \Delta G_{\text{OH}}^0 - \Delta G_{\text{OH}}^{\text{Pt},0} \right) = 0.2 \text{ eV} \\
\left( k_1^* \right)^{-1}
\]

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

References
985-1007.

