# Supporting Information: Field effects explain the unintuitive potential response of electrochemical oxygen evolution in acid

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# 1. Computational details

Total energy calculations for all systems are performed using both spin-polarized and non-spinpolarized DFT within the RPBE exchange-correlation functional.<sup>1</sup> We note that all DFT results shown in the main article are a result of spin-paired calculations, while we also show spinpolarized results in the SI. The choice of using spin-paired results throughout the main article was made since  $IrO_2$  is non-magnetic. Further, the effect of explicitly including spin polarization only affected the formation energy of \*O, (over-)stabilizing it by 0.2 eV, leading to an underestimation of the phase transition potential from \*OH to \*O. Finally, including spin polarization leads to the lack of convergence with an applied electric field.

We did not consider solvent effects in our calculations, since our previous study has shown that changes in the energetics of the reaction pathway are minor with the inclusion of explicit solvent for the oxygen evolution reaction on  $IrO_2(110)$ .<sup>2</sup> Further, we did not explicitly include van der Waals corrections, as all considered reaction intermediates are only composed of up to three atoms and chemisorbed.

The Kohn–Sham equations are solved using the Projected Augmented Wave (PAW) method, implemented in the Vienna Ab Initio Simulation Package (VASP, version 5.4.4).<sup>3</sup> A plane wave basis set with a kinetic energy cutoff of 500 eV is employed for bulk, surface, and surface-adsorbed species calculations. Geometry optimization is performed until the force on each atom is less than 0.05 eV/Å, with a total energy convergence threshold of  $1.0 \times 10^{-5}$  eV.

For bulk IrO<sub>2</sub>, a  $5 \times 5 \times 7$  k-point grid is used, yielding optimized lattice constants of a = 4.58 Å and c = 3.20 Å, with relative errors of 1.77% and 1.59%, respectively.<sup>4</sup>The IrO<sub>2</sub>(110) surface is modeled with a  $1 \times 4$  slab containing four atomic layers, where the bottom two layers are fixed to the bulk geometry and 12 Å of vacuum in the z-direction between slabs is included. Dipole corrections are applied,<sup>5</sup> and a  $3 \times 3 \times 1$  k-points grid is employed. The same setup is used to model adsorbates on the surface.

For all systems, vibrational calculations are performed to obtain the zero-point energy  $(E^{ZPE})$ , enthalpic temperature correction  $(\int^{C_p dT})$ , and entropy  $(TS^{harm})$ . For non-adsorbed species, these quantities are obtained in the ideal gas limit at 298.15 K, following the approach detailed by Peterson *et al.* <sup>6</sup>For the adsorbates on the surface, these terms are obtained under the harmonic approximation at 298.15, using the thermochemistry module from the Atomic Simulation Environment (ASE) package.<sup>7</sup>

Calculations using a sawtooth potential implemented in VASP are performed to incorporate the effects of the electric field on the adsorbates. The electric field is applied within the range of -1.0 to 1.0 VÅ<sup>-1</sup>, and the adsorbates are allowed to relax using the same convergence thresholds mentioned earlier. To determine the Gibbs free energy at each applied field,  $E^{ZPE}$ ,  $\int C_p dT$ , and  $TS^{harm}$  contributions are assumed to remain constant across all fields.

Finally, the barrier for the O-O bond formation via the Langmuir Hinshelwood (LH) mechanism was calculated under oxygen coverage conditions by the climbing image nudge elastic band (CI-NEB) method.

# 2. Theoretical Analysis for Lattice Oxygen Mechanism

The involvement of lattice oxygen in the reaction mechanism, often associated with the Marsvan Krevelen mechanism, is a widely considered hypothesis. We calculated the oxygen desorption energies at different depths within IrO<sub>2</sub>. Our results indicate a thermodynamic penalty of approximately 1.5 eV for desorbing bulk-lattice oxygen compared to surface-bound oxygen (see Table S1).



Figure S1 Representation of the removal of different lattice oxygen in  $IrO_2(110)$ . The red dashed circle highlights the removed oxygen position, oxygen bridge (O<sub>b</sub>) in 1, oxygen in the plane of the first layer in 2, and different positions of oxygens in the third layer in 3 and 4. Images 5 and 6 show one and two oxygens on the Ir CUS sites, respectively.

Table S1: Desorption thermodynamics of varying oxygens ranging from bulk to surface  $IrO_2(110)$ . Values for non-spin polarized calculations and, in parentheses, the results for spin polarized calculations.

Process		∆ <i>E</i> (eV)	$\Delta G (U=0) (eV)$	$\Delta G (U = 1.23)$
				(eV)
	1	0.04 (0.03)	0.07 ( 0.06)	2.52 ( 2.53)
$IrO_2 + 2(H^+ + e^-) \rightarrow IrO_2(vac) +$	2	0.40 (0.40)	0.43 (0.43)	2.89 (2.89)
H <sub>2</sub> O(l)	3	0.58 (0.58)	0.61 (0.61)	3.07 (3.07)
	4	0.89 (0.89)	0.92 (0.92)	3.38 (3.38)
$0-IrO_2 + *CUS + 2(H^+ + e^-) → IrO_2 + H_2O(l)$	5	-1.53 (-1.42)	-1.54 (-1.43)	0.92 (1.03)
$0^* - IrO_2 + 0 - CUS + 2(H^+ + e^-) \rightarrow$ IrO <sub>2</sub> + H <sub>2</sub> O(l)	6	-1.84 (-1.47)	-1.86 (-1.49)	0.60 (0.97)

### 3. Field interaction properties



Figure S2 a) Potential of zero charge,  $U_{PZC}$  vs. SHE, at different coverages calculated using non-spin-polarized DFT data. Numbers beside the adsorbates indicate how many were adsorbed on a slab with 4 Ir<sub>CUS</sub> sites (1x4 slab), and work functions are represented by  $\Phi$ . b) Field effect for average Gibbs free energies of different coverages.

Table S2: Work function ( $\Phi$ ) at different coverage on IrO<sub>2</sub>(110) surface.

Adsorbed species	4H <sub>2</sub> O	4*	40H*	10*	20*	30*	40*
Φ (eV)	5.9	6.0	6.3	6.4	6.8	7.1	7.5

#### 4. Equations to determine the strength of field effects

The energy of a given reaction intermediate within a homogeneous electric field is influenced by the change of surface dipole,  $\Delta \mu$ , and surface polarizability  $\Delta \eta$ , upon its formation, as shown in Figure S2b) and defined by

 $\Delta G - \Delta G_{PZC} = \Delta \mu E_z + \frac{\Delta \eta}{2} E_z^2 \#(1)$ here,  $\Delta G_{PZC}$  refers to the binding energy of an adsorbate at the PZC which corresponds to the energy calculated with no applied field.  $\Delta \mu$  and  $\Delta \eta$  for each species can be estimated by the fits shown in Figure S2 a, b. Finally, the applied electric field,  $E_z$ , can be related to the potential vs SHE, U<sub>SHE</sub>, via the simple Helmholtz model, leading to  $E_z = -\frac{C_H}{\varepsilon_r \varepsilon_0} (U_{SHE} - U_{PZC})$ . The following values were used for  $U_{PZC}$ , C<sub>H</sub>,  $\varepsilon_r$ , and  $\varepsilon_0$  when calculating

 $E_{z} = -\frac{C_{H}}{\varepsilon_{r}\varepsilon_{0}}(U_{SHE} - U_{PZC})$ The following values were used for  $U_{PZC}$ ,  $C_{H}$ ,  $\varepsilon_{r}$ , and  $\varepsilon_{0}$  when calculating the electric field: 1.5 V vs SHE,  $\frac{25.0 \frac{\mu F}{cm^{2}}}{cm^{2}}$ , 2, and  $\frac{8.85 \times 10^{-8} \frac{\mu F}{cm}}{making} \frac{C_{H}}{\varepsilon_{r}\varepsilon_{0}} = 1.4121 \text{ Å}^{-1.8} \text{ We}$ note that the chosen values include an inherent uncertainty, we will discuss a variation of their magnitude in section 11. From this formalism  $\gamma$  can be defined directly as:

$$\gamma = \frac{\partial \Delta G}{\partial e U_{SHE}} = -\frac{1}{e} (\Delta \mu \frac{C_H}{\varepsilon_r \varepsilon_0} + \Delta \eta \left(\frac{C_H}{\varepsilon_r \varepsilon_0}\right)^2 (U_{SHE} - U_{PZC})) \#(2)$$

Thus, in this model,  $\gamma$  is linearly proportional to  $\Delta \mu$  of the respective adsorbate and changes with potential in the case of non-negligible  $\Delta \eta$ .

#### 5. Free energy changes including field effect

 $\Delta G_{avg,i*}(U_{RHE})$  including the field effect in terms of  $\Delta \mu$  and  $\Delta \eta$  is:

$$\Delta G_{avg,i*} (U_{RHE}) = \Delta G_{avg,i*} (DFT) - N_{pe} e U_{RHE} + \Delta \mu_{avg,i*} \left( -\frac{C_H}{\varepsilon_r \varepsilon_0} \left( U_{RHE} - \frac{k_B T}{e} \ln (10) p H - U_{PZC} \right) \right) + \frac{\Delta \eta_{avg,i*}}{2} \left( -\frac{C_H}{\varepsilon_r \varepsilon_0} \left( U_{RHE} - \frac{k_B T}{e} \ln (10) p H - U_{PZC} \right) \right)^2$$
(3)

Figure S2 b) contains the values of  $\Delta \mu_{avg,i*}$  and  $\Delta \eta_{avg,i*}$ .

Using equation (3), it is possible to observe the field effect on the potential vs. RHE ( $U_{RHE}$ ) where full OH\* coverage transitions to full O\* coverage at different pH, Figure S3. To obtain the potential vs. RHE at which the transition occurs as a function of the pH, the potential for each pH is calculated numerically by solving the equality  $\Delta G_{avg,OH*}(U_{RHE}) = \Delta G_{avg,O*}(U_{RHE})$ .



Figure S3 Field effect on the potential vs. RHE  $(U_{RHE})$  where full OH coverage transitions to full O coverage at different pH from **spin-polarized data** represented by black circles. Blue triangles are experimental data from ref<sup>9</sup>.

Similarly, equation (3) is the expression for the differential adsorption-free energies:

$$\Delta G_{diff,i@OH/O}(U_{RHE}) = \Delta G_{diff,i*@OH/O}(DFT) - N_{pe}eU_{RHE} + \Delta \mu_{diff,i*@OH/O}\left(-\frac{C_H}{\varepsilon_r\varepsilon_0}\left(U_{RHE} - \frac{k_BT}{e}\ln(10)pH - U_{PZC}\right)\right) + \frac{\Delta \eta_{diff,i*@OH/O}\left(-\frac{C_H}{\varepsilon_r\varepsilon_0}\left(U_{RHE} - \frac{k_BT}{e}\ln(10)pH - U_{PZC}\right)\right)^2$$
(4)

Data for  $\Delta G_{diff,i*@OH/O}(DFT)$  are in Tables S6 and S7 in the later section, and values for  $\Delta \mu_{diff,i*@OH/O}$  and  $\Delta \eta_{diff,i*@OH/O}$  in Figure 3 c).

The equations above can also be expressed in terms of  $\gamma$ . Below, we provide an example to demonstrate the equivalence of  $\Delta G_{diff,OH*@OH/O}(U_{RHE})$  as shown in 4) and in terms of  $\gamma$  for two cases: 1) when polarizabilities are negligible, and 2) when polarizabilities are included.

#### 5.1 Gamma and $\Delta G$ if polarizabilities are negligible

The expression for  $\gamma$  considering only the dipole term is:

$$\gamma = \frac{\partial \Delta G}{\partial e U_{SHE}} = \frac{\partial \Delta G}{\partial (e U_{RHE} - k_B T \ln (10) pH)} = -\frac{1}{e} \Delta \mu \frac{C_H}{\varepsilon_r \varepsilon_0}$$
(5)

#### **Example for OH:**

From equations (4) considering only dipole terms:

$$\Delta G_{OH*} \left( U_{RHE} \right) = \Delta G_{OH*} \left( DFT \right) - N_{pe} (*OH) e U_{RHE} + \Delta \mu_{OH*} \left( -\frac{C_H}{\varepsilon_r \varepsilon_0} \left( U_{RHE} - \frac{k_B T}{e} \ln (10) p H - U_{PZC} \right) \right)$$
(6)

To get an equivalent equation in terms of  $\gamma$ , we first define  $\Delta G_{OH*}$  at 0 V vs. RHE and pH 0.  $\Delta G_{OH*} (U_{RHE} = 0, pH = 0) = \Delta G_{OH*} (DFT) - \Delta \mu_{OH*} \left( -\frac{C_H}{\varepsilon_r \varepsilon_0} \right) U_{PZC} = \Delta G_{OH*} (DFT) - e\gamma U_{PZC}$ 

Then,  $\Delta G_{OH*}(U_{RHE})$  in terms of gamma is:

$$\Delta G_{OH *} (U_{RHE}) = \Delta G_{OH *} (U_{RHE} = 0, pH = 0) - N_{pe} (*OH)eU_{RHE} + e \int_{U_{RHE}}^{U_{RHE}} \gamma_{OH *} dU_{RHE} - k_{B}T \ln (10) \int_{pH = 0}^{pH} \gamma_{OH *} d(pH)$$
(7)

After solving the integrals in equation (7), the expression  $\Delta G_{OH*}(U_{RHE})$  in terms of gamma, when only dipole terms are considered, looks like this:

$$\Delta G_{OH*}(U_{RHE}) = \Delta G_{OH*}(U_{RHE} = 0, pH = 0) - N_{pe}(*OH)eU_{RHE} + \gamma_{OH*}(eU_{RHE} - k_BT\ln(10)pH)$$
(8)

Thus, if we want to calculate where the Pourbaix lines of OH\* and O\* cross in Figure 4 b), we look for  $\Delta G_{OH*}(U_{RHE},pH) = \Delta G_{O*}(U_{RHE},pH)$  (both average free energies) and solve for  $U_{RHE}$ :

$$\frac{\Delta G_{O*} (U_{RHE} = 0, pH = 0) - \Delta G_{OH*} (U_{RHE} = 0, pH = 0)}{N_{pe} (* O) - N_{pe} (* OH) + \gamma_{OH*} - \gamma_{*O}} + k_B T \ln (10) pH}$$
  
$$eU_{RHE=}^{x} \frac{(\gamma_{*OH} - \gamma_{*O})}{N_{pe} (* O) - N_{pe} (* OH) + \gamma_{OH*} - \gamma_{*O}}$$

In order to get the crossing potential dependence on pH, we look at

$$\frac{\partial U_{RHE}^{x}}{\partial pH} = \frac{k_{B} T \ln (10)}{e} \frac{(\gamma_{*OH} - \gamma_{*O})}{N_{pe}(*O) - N_{pe}(*OH) + \gamma_{*OH} - \gamma_{*O}} = 59 m V \frac{(\gamma_{*OH} - \gamma_{*O})}{1 + \gamma_{*OH} - \gamma_{*O}}$$

Using only the polarizability-free dipole moments shown in Figure S4 to define gamma, this leads to a change of crossing potential of  $\sim$ -13 mV/pH.



Figure S4 Potential vs. RHE ( $U_{RHE}$ ) where full \*OH coverage transitions to full \*O coverage at different pH from **non-spin-polarized data** when polarizabilities are negligible.

#### 5.2 Gamma and $\Delta G$ if polarizabilities are not negligible

The expression for  $\gamma$  considering both the dipole and polarizability terms is:

$$\gamma = \frac{\partial \Delta G}{\partial e U_{SHE}} = \frac{1}{e} \left( \Delta \mu \left( -\frac{C_H}{\varepsilon_r \varepsilon_0} \right) + \Delta \eta \left( -\frac{C_H}{\varepsilon_r \varepsilon_0} \right)^2 (U_{SHE} - U_{PZC}) \right)$$
(9)

#### **Example for OH:**

according to the equations (4):

$$\Delta G_{OH*} \left( U_{RHE} \right) = \Delta G_{OH*} \left( DFT \right) - N_{pe} (*OH)eU_{RHE} + \Delta \mu_{OH*} \left( -\frac{C_H}{\varepsilon_r \varepsilon_0} \left( U_{RHE} - \frac{k_B T}{e} \ln (10)pH - U_{PZC} \right) \right) + \frac{\Delta \eta_{OH} *}{2} \left( -\frac{C_H}{\varepsilon_r \varepsilon_0} \left( U_{RHE} - \frac{k_B T}{e} \ln (10)pH - U_{PZC} \right) \right)^2$$
(10)

To get an equivalent equation in terms of  $\gamma$ ,

$$\Delta G_{OH*} \left( U_{RHE} = 0, pH = 0 \right) = \Delta G_{OH*} \left( DFT \right) + \Delta \mu_{OH*} \left( -\frac{C_H}{\varepsilon_r \varepsilon_0} \left( -U_{PZC} \right) \right) + \frac{\Delta \eta_{OH} *}{2} \left( -\frac{C_H}{\varepsilon_r \varepsilon_0} \left( -U_{PZC} \right) \right)^2$$

 $\Delta G_{OH*}(U_{RHE})$  in terms of gamma, assuming pH does not change:

$$\Delta G_{OH}(U_{RHE}) = \Delta G_{OH*}(U_{RHE} = 0, pH = 0) - N_{pe}(*OH)eU_{RHE} +$$

$$e \int_{U_{RHE}}^{U_{RHE}} \gamma_{OH*} d\left( U_{RHE} - \frac{k_B T}{e} \ln (10) pH \right)$$
(11)

Since gamma in equation (9) depends on the applied potential in the term related to the polarizabilities, to solve the integral in equation (11), gamma from equation (9) is replaced. The expression  $\Delta G_{OH*}(U_{RHE})$  after solving the integrals looks like this:

$$\Delta G_{OH*}(U_{RHE}) = \Delta G_{OH*}(U_{RHE} = 0, pH = 0) - N_{pe}(*OH)eU_{RHE} + \Delta \mu_{OH*}\left(-\frac{C_H}{\varepsilon_r \varepsilon_0}\right)(U_{RHE} - \frac{k_B T}{e}\ln(10)pH) + \frac{1}{2}\Delta \eta_{OH*}\left(-\frac{C_H}{\varepsilon_r \varepsilon_0}\right)^2 \left((U_{RHE} - \frac{k_B T}{e}\ln(10)pH)^2 - \frac{2}{2}\Delta \eta_{OH*}\left(-\frac{C_H}{\varepsilon_r \varepsilon_0}\right)^2 \left((U_{RHE} - \frac{k_B T}{e}\ln(10)pH - U_{PZC}\right)\right)$$
(12)

# 6. Thermodynamic data without field effect

1. Calculation of the average Gibbs free energy, for example, for full OH coverage on 4 Ir<sub>CUS</sub> sites:

 $4H_2O(l) + 4 * - IrO_2(110) \rightarrow 4OH - IrO_2(110) + N_{pe}(H^+ + e^-); N_{pe} = 4$ 

$$\Delta G_{avg,OH*}(DFT) = \frac{1}{N_s} \left( G_{4OH-IrO_2(110)} + \frac{N_{pe}}{2} G_{H_2(g)} - G_{IrO_2(110)} - 4G_{H_2O(l)} \right)$$
(13)

Where:

$$G_{40H-IrO_2(110)} = E_{40H-IrO_2(110)} + E_{40H-IrO_2(110)}^{ZPE} - TS_{40H-IrO_2(110)}^{harm},$$

$$G_{40H-IrO_{2}(110)}^{correction} = E_{40H-IrO_{2}(110)}^{ZPE} + \int C_{P,40H-IrO_{2}(110)} dT - TS_{40H-IrO_{2}(110)}^{harm}$$

For  ${}^{G_{H_2(g)}}$  and  ${}^{G_{H_2O(l)}}$  the equations are analogous to  ${}^{G_{OH-IrO_2(110)}}$ .

 $\Delta G_{avg,OH*}(DFT)$  can be expressed in terms of  $\Delta E_{OH*}$  and  $\Delta G_{OH*}^{correction}$ :

$$\Delta G_{avg,OH*}(DFT) = \frac{1}{N_S} \left( \Delta E_{OH*} + \Delta G_{OH*}^{correction} \right)$$
(14)

Where:

$$\Delta E_{OH*} = E_{4OH-IrO_2(110)} + \frac{N_{pe}}{2} E_{H_2(g)} - E_{IrO_2(110)} - 4E_{H_2O(l)},$$

$$\Delta G_{OH*}^{correction} = G_{40H-IrO_2(110)}^{correction} + \frac{N_{pe}}{2} G_{H_2(g)}^{correction} - 4 G_{H_2O(l)}^{correction}, \text{ and}$$

 $N_s = total number of sites$ , we used 4  $Ir_{CUs}$  sites.

2. Changes of  $\Delta G_{avg}$  for coverage i with potential vs. RHE ( $U_{RHE}$ ):

$$\Delta G_{avg,i*}(U_{RHE}) = \Delta G_{avg,i*}(DFT) - \frac{N_{pe}}{N_s}eU_{RHE}$$
(15)

Where:

 $U_{RHE} = U_{SHE} + \frac{k_B T}{e} \ln (10) p H.$ 

Tables S3, S4, and S5 contain the relevant values of  $\Delta E_i$  and  $\Delta G^{correction}_i$ .

Table S3: Zero-point energy correction,  $E_{i}^{ZPE}$ , enthalpic temperature correction,  $\int C_{p,i} dT$ , entropy,  $TS_{i}^{harm}$ , and Gibbs free energy correction,  $G_{i}^{correction}$ . Values are obtained at T 298.15 K for all systems. The pressure used for hydrogen  $(H_2)$  and water  $(H_2^0)$  are 101325 Pa and 3166 Pa, respectively. For surface-adsorbate systems, \* represents empty Ir<sub>CUS</sub> sites and  $O_b$  are oxygens bound to Ir<sub>b</sub>, see Figure S5c.

System <i>i</i>	$E^{ZPE}_{i}$	$\int C_{ni} dT$	$TS^{harm}_{i}$	$G^{correction}_{i}$
	(eV)	(eV)	(eV)	(eV)
$H_2(g)$	0.27	0.09	0.40	-0.04
$H_2O(l)$	0.56	0.10	0.67	-0.01
$4 * + 4H - O_b$	1.25	0.02	0.03	1.24
$4H_2O * + 4H - O_b$	4.04	0.24	0.41	3.87
$4OH * + 4H - O_b$	2.78	0.19	0.38	2.59
$40H * + O_b$	1.50	0.17	0.30	1.37
$10 * + 30H * + 0_b$	1.19	0.17	0.29	1.07
$10H *+ 30 * + 0_b$	0.57	0.16	0.29	0.44
$40 * + 0_b$	0.28	0.14	0.25	0.17
$100H * + 30 * + 0_b$	0.67	0.16	0.29	0.54
$400H * + O_b$	1.78	0.28	0.50	1.56

Table S4: Number of proton-electron couples consumed (-) and produced (+),  $N_{pe}$ , total energies difference for the reaction using **non-spin-polarized data**,  $\Delta E_{i*}$ , change in the Gibbs free energy correction,  $\Delta G^{correction}_{i*}$ , and average change of Gibbs free energies,  $\Delta G_{avg,i*}(DFT)$ . \* represents empty Ir<sub>CUS</sub> sites and  $O_b$  are oxygens bound to Ir<sub>b</sub>, see Figure S5c.

Reaction	N <sub>pe</sub>	$\frac{\Delta E_{i*}}{(eV)}$	$\Delta G^{correction}_{i*}$ (eV)	Δ <i>G<sub>avg,i *</sub></i> (DFT) (eV)
$4 *+ 4O_b + 4(H^+ + e^-) \rightarrow * + 4H - O_b$	- 4	- 3.93	1.33	- 0.65
$4H_20 + 4 *+ 4O_b + 4(H^+ + e^-) \rightarrow 4H_20 * + 4H - 0$	- 4	- 6.32	3.75	- 0.64
$4H_20 + 4 * + 4O_b + 4(H^+ + e^-) \rightarrow 40H * + 4(H^+ + e^-)$	- 4+ 4	- 5.84	2.63	- 0.80

$4H_2O + 4 *+ 4O_b \rightarrow 4OH * + 4(H^+ + e^-) + 4O_b$	4	- 0.67	1.34	0.17
$4H_20 + 4 *+ 40_b \rightarrow 40 * + 8(H^+ + e^-) + 40_b$	8	6.70	0.05	1.69
$8H_20 + 4 * + 40_b \rightarrow 400H * + 12(H^+ + e^-) + 40_b$	12	12.17	1.40	3.39

Table S5: Number of proton-electron couples consumed (-) and produced (+),  $N_{pe}$ , total energies difference for the reaction using **spin-polarized data**,  $\Delta E_{i*}$ , change in the Gibbs free energy correction,  $\Delta G_{i*}^{correction}$ , and average change of Gibbs free energies,  $\Delta G_{avg,i*}(DFT)$ . \* represents empty Ir<sub>CUS</sub> sites and  $O_b$  are oxygens bound to Ir<sub>b</sub>, see Figure S5c.

Reaction	N <sub>pe</sub>	$\Delta E_{i*}$	$\Delta G^{correction}_{i*}$	$\Delta G_{avg,i*}$
		(eV)	(eV)	(DFT) (eV)
$4 *+ 4O_b + 4(H^+ + e^-) \rightarrow * + 4H - O_b$	- 4	- 3.99	1.33	- 0.66
$4H_20 + 4 *+ 40_b + 4(H^+ + e^-) \rightarrow 4H_20 * + 4H - 0$	- 4	- 6.32	3.75	- 0.64
$4H_2O + 4 *+ 4O_b + 4(H^+ + e^-) \rightarrow 4OH * + 4(H^+ + 4(H^+ + e^-) \rightarrow 4(H^+ + 4(H^+ + e^-) \rightarrow 4(H^+ + 4(H^+ + e^-) \rightarrow 4(H^+ + (H^+ + e^-) \rightarrow 4(H^+ + (H^+ + H^+ + H^+) \rightarrow 4(H^+ + H^+ + (H^+ + H^+) \rightarrow 4(H^+ + H^+ + H^+) \rightarrow 4(H^+ + H^+ + H^+) \rightarrow 4(H^+ + H^+ + H^+) \rightarrow 4(H^+ + H^$	- 4+ 4	- 5.84	2.63	- 0.80
$4H_20 + 4 *+ 40_b \rightarrow 40H * + 4(H^+ + e^-) + 40_b$	4	- 0.69	1.34	0.16
$4H_2O + 4 * + 4O_b \rightarrow 1O * + 3OH * + 5(H^+ + e^-) + 4O$	5	1.04	1.01	0.51
$4H_20 + 4 *+ 40_b \rightarrow 10H *+ 30 *+ 7(H^+ + e^-) + 40$	7	4.43	0.34	1.19
$4H_20 + 4 *+ 40_b \rightarrow 40 * + 8(H^+ + e^-) + 40_b$	8	5.80	0.05	1.46
$5H_20 + 4 *+ 40_b \rightarrow 100H * + 30 *+ 9(H^+ + e^-) +$	9	7.36	0.41	1.94
$8H_20 + 4 * + 40_b \rightarrow 400H * + 12(H^+ + e^-) + 40_b$	12	12.14	1.40	3.38

Table S6: Differential adsorption energies at T = 298.15 K from non-spin-polarized data for each adsorbate when the surface is covered with OH (@OH) and O (@O).

Non-spin polarized data								
i * @OH								
Adsorbate (i	Coverage on	Coverage on	$\Delta E_{i*@OH}^{diff}$	$\Delta G^{correction}_{i * @OH}$	$\Delta G_{i * @OH}^{diff}$			
) on $Ir_{CUS}$	other Ir <sub>cus</sub>	0 <sub>b</sub>	(eV)	(eV)	(DFT) (eV)			
$H_2^{0} *$	<i>OH</i> *	-	- 1.43	0.67	- 0.76			
<i>OH</i> *	<i>OH</i> *	-	- 0.22	0.34	0.12			
0 *	<i>OH</i> *	-	1.63	0.02	1.65			
0 – 0H <sup>‡</sup>	<i>OH</i> *	-			3.32			
00H *	<i>OH</i> *	-	3.19	0.35	3.54			
0-0‡	<i>OH</i> *	-			4.15			
02*	<i>OH</i> *	-	4.26	0.04	4.30			
		i *	@0					
Adsorbate (i	Coverage on	Coverage on	$\Delta E_{i*@0}^{diff}$	$\Delta G^{correction}_{i * @0}$	$\Delta G_{i * @0}^{diff}$			
) on $Ir_{CUS}$	other <i>Ir<sub>cus</sub></i>	0 <sub>b</sub>		(eV)	(DFT) (eV)			
$H_20 *$	0 *	-	- 1.40	0.66	- 0.74			
ОН *	0 *	-	- 0.01	0.34	0.33			

0 *	0 *	-	1.84	0.01	1.85
0 – 0H <sup>‡</sup>	0 *	-			3.53
00H *	0 *	-	3.00	0.35	3.35
0-0‡	0 *	-			4.53
02*	0 *	-	4.04	0.07	4.11

Table S7: Differential adsorption energies at T = 298.15 K from spin-polarized data for each adsorbate when the surface is covered with OH (@OH) and O (@O).

	Spin-polarized data							
		i * (	@OH					
Adsorbate (i	Coverage on	Coverage on	$\Delta E_{i*@OH}^{diff}$	$\Delta G^{correction}_{i * @OH}$	$\Delta G_{i*@OH}^{diff}$			
) on $Ir_{CUS}$	other Ir <sub>cus</sub>	<i>O</i> <sub>b</sub>	(eV)	(eV)	) (eV)			
H <sub>2</sub> 0 *	<i>OH</i> *	-	- 1.42	0.68	- 0.74			
<i>OH</i> *	<i>OH</i> *	_	- 0.22	0.32	0.10			
0 *	<i>OH</i> *	-	1.51	0.03	1.54			
0 – ОН <sup>‡</sup>	<i>OH</i> *	-			3.26			
00Н *	<i>OH</i> *	-	3.19	0.32	3.51			
0-0‡	<i>OH</i> *	-			3.91			
02*	<i>OH</i> *	-	4.21	0.05	4.26			
		i *	@0					
Adsorbate (i	Coverage on	Coverage on	$\Delta E_{i*@0}^{diff}$	$\Delta G^{correction}_{i * @0}$	$\Delta G_{i*@0}^{diff}$			
) on $lr_{CUS}$	other <i>Ircus</i>	0 <sub>b</sub>		(eV)	(DFT)(eV)			
H <sub>2</sub> 0 *	0 *	-	- 1.37	0.65	- 0.72			
<i>OH</i> *	0 *	-	- 0.02	0.33	0.31			
0 *	0 *	-	1.47	0.02	1.49			
0 – ОН <sup>‡</sup>	0 *	-			3.33			
00Н *	0 *	-	3.04	0.35	3.39			
0-0‡	0 *	-			3.81			
02*	0 *	-	4.15	0.02	4.17			

#### Spin-polarized data Non-spin-polarized data b) $Ir_{CUS}$ sites = 4 $Ir_{CUS}$ sites = 4 Pristine IrO<sub>2</sub>(110) T = 298.15 Ka) Pristine IrO<sub>2</sub>(110) T = 298.15 KpH = 0pH = 0- - Clean IrO<sub>2</sub> (110) -- Clean IrO<sub>2</sub> (110) H-O<sub>b</sub> + \* Ir<sub>CUS</sub> $\text{H-O}_{b} + * \text{Ir}_{\text{CUS}}$ 1.0 $H-O_b + 1H_2O-Ir_{CUS}$ $H-O_b + 1OH-Ir_{CUS}$ $H-O_b + 1H_2O-Ir_{CUS}$ 1.0 $H-O_{h} + 10H-Ir_{CUS}$ 10H-Ir<sub>CUS</sub> (0.750H+0.250)-Ir<sub>CUS</sub> 10H-Ir<sub>CUS</sub> 0.0 10-Ir<sub>CUS</sub> 100H-Ir<sub>CUS</sub> (0.50H+0.50)-Ir<sub>CUS</sub> 0.0 (0.25OH + 0.75O)-Ir<sub>CUS</sub> $\Delta G_{avg}/eV$ $\Delta G_{avg}/eV$ 10-Ir<sub>CUS</sub> (0.2500H + 0.750)-Ir<sub>C</sub> -0.15 100H-Ir<sub>cus</sub> -1.0 -1.0 1.3 H-O<sub>b</sub> + OH-Ir<sub>CUS</sub> $\text{H-O}_{b} + \text{OH-Ir}_{\text{CUS}}$ +\* Ir<sub>cus</sub> -2.0 OH-Ir<sub>CUS</sub> OH-Ir<sub>CUS</sub> -2.0 O-Ir<sub>CUS</sub> O-Ir<sub>CUS</sub> ЧО-Н I-HOO HOO--3.0 -3.0 $V^{\perp}_{V}$ 0.5 1.0 -0.5 0.0 0.5 1.0 1.5 2.0 0.0 2.0 -0.5 Potential vs. RHE / Potential vs. RHE / V c) ∘н ●О Ir

# 7. Pourbaix diagrams without field effects

Figure S5 Phase diagram using average Gibbs free energies,  $\Delta G_{avg,i}(U_{RHE})$  for different coverage conditions on the pristine IrO<sub>2</sub>(110) surface at the full coverage limit and **without field effects**. The reference systems are clean IrO<sub>2</sub> with 4 Ir<sub>CUS</sub> sites (1x4 slab) and H<sub>2</sub>O(l), with spin-polarized calculations data in a) and with non-spin-polarized calculations data in b). Representation of the most stable coverages in c). \* represents empty Ir<sub>CUS</sub> sites, and coverage # i

is expressed in terms of the number of adsorbates (#*i*) per total sites ( $N_s = 4$ ):  $\overline{N_s}$ .

#### 8. Microkinetic model (MKM)

Microkinetic modeling was carried out using CatMAP<sup>10</sup> software package which uses steady state approximation to determine rates and coverages. The rate equation can be determined by,

$$rate = \frac{k_B T}{h} exp^{(n)} \left(\frac{-G_a}{k_B T}\right)$$

 $k_B T$ 

 $\overline{h}$  represents prefactor equal to  $10^{13}$  s<sup>-1</sup> were used for all the reaction step.  $k_B$  represents the Boltzmann constant and T represents the reaction temperature (298.15 K). Two mechanisms for the formation of the O-O bond formation are tested namely, the Langmuir Hinshelwood (LH) mechanism (via chemical O-O coupling) and the Eley-Rideal (ER) mechanism (via a coupled proton-electron transfer). In the LH mechanism, the O-O coupling from two adsorbed oxygen on the surface (2O\*  $\rightarrow$  O<sub>2</sub>\*) is considered a rate-limiting step (RLS), and the activation barrier calculated via CI-NEB is included.

In the ER mechanism, the O-OH formation  $(O^* + H_2O(aq) \rightarrow OOH^* + H^+ + e^-)$  is the RLS. On rutile (110) surfaces, the activation barrier for this step scales linearly with the difference between the adsorption energies of O<sup>\*</sup> and OH<sup>\*</sup>,  $\Delta G_{O^*} - \Delta G_{OH^*}$ , and the electrode potential, as previously discussed.<sup>11</sup> Then, the following equation is used to include the energy of the transition state relative to the O<sup>\*</sup> + H<sub>2</sub>O(aq),  $\Delta G_a$ :

$$\Delta G_{a}(\Delta G_{O*} - \Delta G_{OH*}, U_{SHE}) = -0.48 (\Delta G_{O*} - \Delta G_{OH*}) + \beta_{O-OH}U_{SHE} + 2.41$$

The field dipole interaction was included based on the theory mentioned in the previous section. Dipole moment  $(\Delta \mu)$  and polarizability  $(\Delta \eta)$  of each adsorbate were included as initial parameter as given in Figure 3c (main manuscript). A shift in the rate-limiting step is represented by Degree of rate control (DRC) analysis. A Degree of rate control analysis was carried out as follows,<sup>12</sup>

 $DRC = \frac{d(\log{(TOF)})}{dG_i}$ 

where  $G_i$  is the free energy of each reaction intermediate and the rate is determined by theoretical turnover frequencies (TOF). Due to uncertainty in the value of Capacitance (C<sub>H</sub>) and potential zero charge (U<sub>pzc</sub>), we have also done the sensitivity analysis for these parameters at pH = 0 and  $\beta$  = -0.58.



Figure S6: Free Energy Diagram for OER including effects of electric field on  $IrO_2(110)$ . (*a*) shows the free energy diagram for ER mechanism under OH coverage. (b) shows free energy diagram for LH mechanism under OH coverage at varying potentials and at pH = 0. Mean value of effective charge transfer ( $\alpha$ ) is mentioned for each step.

# 9. O<sub>2</sub> desorption energy correction



Figure S7 Experimental O<sub>2</sub> temperature-programmed desorption (TPD) profile on IrO<sub>2</sub>(110) reproduced using data from ref.<sup>13</sup>. The solid purple line indicates the temperature at which the desorption rate reaches its maximum  $\binom{T_p}{p}$  based on the experimental data. The Redhead equation analysis is applied to correlate  $T_p$  with the activation energy of the desorption of O<sub>2</sub> ( $\Delta G_{O_2^{r,des}}^{TPD}$ ). Similarly, the dashed line represents the expected  $T_p$  when the desorption energy is obtained from DFT calculations ( $\Delta G_{O_2^{r,des}}^{DFT}$ ).

The Redhead equation analysis is applied to correlate the temperature at which the desorption rate reaches its maximum  ${T_p}$  with the activation energy of the desorption of O<sub>2</sub>  ${\Delta G_{O_2}^{TPD}}$ . We employed the linearized form of the Redhead equation for a first-order desorption reaction, derived under the assumptions that  ${\Delta G_{O_2}^{TPD}}$  is independent of the coverage and a temperature-independent pre-exponential factor  $(\nu)$  <sup>14</sup>:

$$\Delta G_{O_{2},des} = k_B T_p \ln\left(\frac{\nu T_p}{\beta} - 3.64\right),$$

Where:  $v = \frac{k_B}{h}$ , and  $\beta = 1 K s^{-1}$ , which is the rate of heating in the experimental TPD in Figure S7.

To calculate the activation desorption energy of O<sub>2</sub> from DFT, we assume that the process does not have a barrier as discussed in our previous work.<sup>15</sup> The correction is applied to  $\Delta G_{O_2} * @OH/O = MOHO}$  (DFT) from Tables S5 and S6.

 $\Delta G_{O_2,des}^{DFT}$  is calculated by the difference between 4.92 eV and  $\Delta G_{O_2}^{diff} \stackrel{diff}{*@OH/O}$  (DFT).

Non-spin polarized							
Adsorbate $(i *)$ on $Ir_{CUS}$	Coverage	$\Delta G_{0} \stackrel{diff}{* @0H/0}$	$\Delta G_{O_2, des}^{DFT}$	$T_p$	$\Delta G_{0_2 * @OH/0}^{diff}$		
	on other Ir <sub>cus</sub>	T) (eV)	(eV)	(K)	(TPD) (eV)		
$O_2$	30	4.11	0.81	320	4.61		
Spin polarized							
$O_2$	30	4.17	0.75	295	4.61		
$O_2$	3OH	4.16	0.66	26	4.61		
Gas reference							
O <sub>2</sub> (g) 4.92							
$\Delta G_{O_{2},des}$							
		From TPD	0.31	126			

Table S8: Data to correct desorption free energies of O<sub>2</sub> based on experimental TPD.

# **10.Degree of rate-control analysis**

Figure S8 shows DRC analysis for change in  $O_2(g)$  production with change in binding energies of the species involved in the reaction with pH. At very low potential, the rate is largely influenced by OH\* binding energies which can be increased by increasing the Gibbs free energy of OH\* (i.e. destabilizing). However, at more positive oxidative potentials, the rate is majorly influenced by O\* on the surface. The rate will increase by decreasing the barrier energy of O-OH formation over the whole potential range.

Figure S9 shows that the barrier of O-O coupling is insensitive to the change in potential, the rate is not influenced over the whole potential range.



Figure S8: Degree of rate control (DRC) analysis on IrO<sub>2</sub> (110) considering ER Mechanism.



Figure S9: Degree of rate control (DRC) analysis on IrO<sub>2</sub>(110) considering LH Mechanism.

### 11. Sensitivity analysis

To simulate the polarization curve, we chose a constant value of Helmholtz Capacitance ( $C_H$ ) = 25  $\mu$ F/cm<sup>2</sup> and the potential of zero charge ( $U_{pzc}$ ) = 1.5 V in the microkinetic model. In Figures S10- S12, we estimated the sensitivity of simulated current density and Tafel slopes to different values of  $C_H$  and  $U_{pzc}$ . Results indicate that the overall activity trend will not change with these parameters. However, the magnitude of current density and Tafel slope slightly depend on the choice of  $C_H$  and  $U_{pzc}$ . At low  $C_H$  and  $U_{pzc}$ , field effects will be larger which stabilizes the reaction intermediates. Conversely, at high  $C_H$ , field effects will be lower which destabilizes the reaction species and improves the OER performance,



Figure S10: The sensitivity analysis of the effect of Helmholtz capacitance ( $C_H$ ) on the activity (left panel) and Tafel slope (right panel) of OER reaction on  $IrO_2(110)$  under full O coverage while keeping the potential of zero charge (Upzc) = 1.5 V<sub>SHE</sub> at pH = 0.



Figure S11: The sensitivity analysis of the effect of potential of zero charge ( $U_{pzc}$ ) on the activity (left panel) and Tafel slope (right panel) of OER reaction on IrO<sub>2</sub>(110) under full O coverage **including the polarizability** of reaction intermediates while keeping the Helmholtz capacitance ( $C_H$ ) = 25 µF/cm<sup>2</sup> at pH = 0.



Figure S12: The sensitivity analysis of the effect of potential of zero charge ( $U_{pzc}$ ) on the activity (left panel) and Tafel slope (right panel) of OER reaction on  $IrO_2(110)$  under full O coverage **without including the polarizability** of reaction intermediates and keeping the Helmholtz capacitance ( $C_H$ ) = 25  $\mu$ F/cm<sup>2</sup> at pH = 0.

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