Supplementary Information

The Ir–OOOO–Ir Transition State and the Mechanism of the Oxygen Evolution Reaction on $IrO_2(110)$

Tobias $\operatorname{Binninger}^{1,*}$ and $\operatorname{Marie-Liesse}$ $\operatorname{Doublet}^1$

¹ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France ^{*}Email: tobias.binninger.science@gmx.de



Figure S1: Computed density of states (DOS) of bulk IrO_2 at an electronic temperature of $kT = 0.05 \,\mathrm{eV}$ with thermal peak broadening as derived in Ref. [1]



Figure S2: Stoichiometric $IrO_2(110)$ surface with rows of unsaturated Ir cations (left) and surface configuration with one unsaturated Ir cation per simulation cell (right). Color coding: Oxygen atoms: red; Iridium atoms: pale golden. Naming scheme: Occupations of adsorbate sites per simulation cell; t: top oxygen site; b: bridge oxygen site; V: oxygen vacancy at top site.



Figure S3: Relevant adsorbate configurations at the $IrO_2(110)$ surface in an aqueous environment. The first set corresponds to a complete O-coverage with different degrees of protonation. The second set contains single or double OO motifs. Color coding: Oxygen atoms: red; Hydrogen atoms: white; Iridium atoms: pale golden. Naming scheme: Occupations of adsorbate sites per simulation cell; t: top oxygen site; b: bridge oxygen site.



Figure S4: Computed grand-canonical stability diagram restricted to the (100/0)%, (75/25)%, (50/50)%, (25/75)%, and (0/100)% (*OH/*O)-covered IrO₂(110) surface with the fully *OH-covered surface as reference system. The equilibrium potentials for the transition between lowest-energy adsorbate states are indicated by dotted vertical lines.



Figure S5: Computed grand-canonical stability diagram for the relevant adsorbate configurations on the $IrO_2(110)$ surface including an energy correction of +0.408 eV per OO motif present at the surface.



Figure S6: Computed grand-canonical stability diagram for all investigated adsorbate configurations on the $IrO_2(110)$ surface with the fully *O-covered surface as reference system. The equilibrium potentials for the transition between lowest-energy adsorbate states are indicated by dotted vertical lines.



Figure S7: Comparison between the conventionally considered OER mechanism (golden color) and the novel mechanism (blue color) at pH = 0 and a potential of $1.53 V_{NHE}$ (a) and $1.23 V_{NHE}$ (b). An energy correction of +0.408 eV was added per O₂ molecule only. The intermediate adsorbate configurations are denoted by the occupation of the two top oxygen sites per surface cell. If not otherwise indicated, the bridge oxygen sites are occupied by O + O. The zero energy reference was chosen at the respective lowest-energy surface configuration involving only *O and *OH. Reaction barriers of dissociative water adsorption (H₂O \downarrow) and oxygen evolution (O₂ \uparrow) steps were estimated from climbing-image NEB calculations for the neutral systems. No O₂ energy correction was used for the NEB-derived barriers of oxygen evolution steps because of the unknown distribution of the O₂ DFT error along the barriers.



Figure S8: Comparison between the conventionally considered OER mechanism (golden color) and the novel mechanism (blue color) at pH = 0 and a potential of $1.53 V_{\text{NHE}}$ (a) and $1.23 V_{\text{NHE}}$ (b). An energy correction of +0.408 eV was added per O₂ molecule and per OO motif present at the surface. The intermediate adsorbate configurations are denoted by the occupation of the two top oxygen sites per surface cell. If not otherwise indicated, the bridge oxygen sites are occupied by O + O. The zero energy reference was chosen at the respective lowest-energy surface configuration involving only *O and *OH. Reaction barriers of dissociative water adsorption (H₂O \downarrow) and oxygen evolution (O₂ \uparrow) steps were estimated from climbing-image NEB calculations for the neutral systems. No O₂/OO energy correction was used for the NEB-derived barriers of oxygen evolution steps because of the unknown distribution of the O₂ DFT error along the barriers.

OER intermediate state	w/o corr.	with O_2 corr.	with OO corr.
$\mathbf{t:} \mathbf{O} + \mathbf{O} \mathbf{b:} \mathbf{O} + \mathbf{O}$	0	0	0
$\mathbf{t:} \mathbf{OH} + \mathbf{OOH} \mathbf{b:} \mathbf{O} + \mathbf{O}$	0.000	0.000	0.408
$\mathbf{t:} \mathbf{OH} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	-0.474	-0.474	-0.066
$\mathbf{t:} \mathbf{O} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	-0.474	-0.474	-0.066
$\mathbf{t:} \mathbf{O} + \mathbf{V} \mathbf{b:} \mathbf{O} + \mathbf{O} (+ \mathbf{O_2})$	-0.017	0.391	0.391
t: $O + OH$ b: $O + O (+ O_2)$	-1.487	-1.079	-1.079
t: OO + OO b: O + OH	-0.727	-0.727	0.089
$\mathbf{t:} \mathbf{OO} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	-0.947	-0.947	-0.131
t: $O + O$ b: $O + O$ (+ O_2)	-1.612	-1.204	-1.204

Table S1: Grand-canonical free energies $\Delta\Omega$ [eV] of OER intermediate states at pH = 0 and a potential of $1.53 V_{\text{NHE}}$ without (w/o corr.) and with the energy correction of +0.408 eV, once applied for O₂ molecules only (O₂ corr.) as commonly done, and once applied for any OO motif present (OO corr.) incl. O₂ molecules. The (**t**: O + O **b**: O + O) state is the zero-energy reference.

OER intermediate state	w/o corr.	with O_2 corr.	with OO corr.
$\mathbf{t:} \mathbf{O} + \mathbf{O} \mathbf{b:} \mathbf{O} + \mathbf{O}$	0.463	0.463	0.463
$\mathbf{t:} \mathbf{OH} + \mathbf{OOH} \mathbf{b:} \mathbf{O} + \mathbf{O}$	0.587	0.587	0.995
$\mathbf{t:} \mathbf{OH} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	0.313	0.313	0.721
$\mathbf{t:} \mathbf{O} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	0.605	0.605	1.013
$\mathbf{t}: \mathbf{O} + \mathbf{V} \mathbf{b}: \mathbf{O} + \mathbf{O} (+ \mathbf{O_2})$	1.138	1.546	1.546
t: $O + OH$ b: $O + O (+ O_2)$	-0.094	0.313	0.313
t: OO + OO b: O + OH	0.702	0.702	1.518
$\mathbf{t:} \mathbf{OO} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	0.739	0.739	1.555
t: $O + O$ b: $O + O$ (+ O_2)	0.051	0.459	0.459

Table S2: Grand-canonical free energies $\Delta\Omega$ [eV] of OER intermediate states at pH = 0 and a potential of $1.23 V_{\text{NHE}}$ without (w/o corr.) and with the energy correction of +0.408 eV, once applied for O₂ molecules only (O₂ corr.) as commonly done, and once applied for any OO motif present (OO corr.) incl. O₂ molecules. The (**t**: OH + OH **b**: O + O) state is the zero-energy reference.

Comparison of the free energy steps for the conventional OER mechanism with previous literature

In the following, we discuss the agreement between our computational results for the free energies of OER intermediate states with previous reports by Ping et al. [2], Gauthier et al. [3], and González et al. [4] for the conventional mechanism.

Table S3 presents the comparison with results from Ref. [2]. We used a very similar computational framework and (implicit) electrolyte model, and, accordingly, our results show a very good agreement within approx. $0.05 \,\mathrm{eV}$. The only intermediate state with a larger deviation of approx. $0.25 \,\mathrm{eV}$ is (t: O + V b: O + O (+ O₂)) with a vacant top oxygen site. In agreement with other studies [3], we treated this state in the same way as all the other intermediates. In contrast, the authors of Ref. [2] obtained this state as a transition state by climbing-image nudged elastic band (CI-NEB) calculations, which might explain the slight difference of the corresponding free energy. However, even an uncertainty of the order of 0.25 eV around the free energy of the (t: O + V b: O + O (+ O₂)) intermediate state would *not* qualitatively alter the OER pathway (see Figure 2 of the main article), and thus have no effect on our conclusions regarding the non-feasibility of the conventional pathway in comparison to the novel one.

Table S4 presents the comparison with results from Ref. [3], which were extracted by digitizing the data plotted in Figure 7 therein. The same ($\mathbf{t}: O + V \mathbf{b}: O + O$) reference state with one vacant top oxygen site was chosen, and our results, computed at 1.53 V_{NHE}, were extrapolated to the same potential of $0.0 V_{NHE}$ by adding a shift of 1.53 eV *per* electron/oxidation step. Our results are in agreement with those from Ref. [3] up to approx. 0.15 eV, which we consider satisfactory given the different electrolyte models employed: We employed an implicit water model and included electrode–electrolyte interface charging in our calculations, whereas in Ref. [3] an explicit water model was used, but without including interface charging. Such minor differences in free energies would have no effect on the conclusions from our work. The main difference between our work and the study of Ref. [3] is the treatment of the *OOH intermediate. In agreement with the previous findings by Ping et al. [2], we found that the conventional pathway does not go through the ($\mathbf{t}: O + OOH$) state, but it rather directly passes from the ($\mathbf{t}: OH + OOH$) state (obtained after water dissociation) to an ($\mathbf{t}: OH + OO$) intermediate, which was not considered in Ref. [3]. The ($\mathbf{t}: OH + OO$) state is significantly more stable than ($\mathbf{t}: O + OOH$).

Finally, Table S5 presents the comparison with results from Ref. [4]. Also here, our results agree very well within around 0.1 eV or less. The free energy of the state (t: O + V b: O + O (+ O_2)) with a vacant top oxygen site was not reported in Ref. [4].

OER intermediate state	This work	Ref. [2]
$\mathbf{t:} \mathbf{O} + \mathbf{O} \mathbf{b:} \mathbf{O} + \mathbf{O}$	0	0
t: $OH + OOH$ b: $O + O$	0.000	0.067
$\mathbf{t:} \mathbf{OH} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	-0.474	-0.436
$\mathbf{t:} \mathbf{O} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	-0.474	-0.415
t: $O + V$ b: $O + O$ (+ O_2)	0.391	0.145^{*}
t: $O + OH$ b: $O + O (+ O_2)$	-1.079	-1.064
t: $O + O$ b: $O + O$ (+ O_2)	-1.204	-1.198

Table S3: Literature comparison: Grand-canonical free energies $\Delta\Omega$ [eV] of OER intermediate states for the conventional mechanism at pH = 0 and a potential of 1.53 V_{NHE} including the energy correction of +0.408 eV for the O₂-molecule *only*. The (**t**: O + O **b**: O + O) state is the zero-energy reference. Results of this work are compared with those reported by Ping et al. [2]. *The authors of Ref. [2] obtained this state as a transition state by climbing-image nudged elastic band (CI-NEB) calculations including an additional H₂O molecule that interacts through a hydrogen bond with an adjacent top surface oxygen. This additional hydrogen bond can explain the slight lowering of the corresponding free energy in comparison to our result.

OER intermediate state	This work	Ref. $[3]^{\dagger}$
$\mathbf{t:} \mathbf{O} + \mathbf{V} \mathbf{b:} \mathbf{O} + \mathbf{O}$	0	0
$\mathbf{t:} \mathbf{O} + \mathbf{OH} \mathbf{b:} \mathbf{O} + \mathbf{O}$	0.06	0.20
$\mathbf{t:} \mathbf{O} + \mathbf{O} \mathbf{b:} \mathbf{O} + \mathbf{O}$	1.465	1.60
$\mathbf{t:} \mathbf{OH} + \mathbf{OOH} \mathbf{b:} \mathbf{O} + \mathbf{O}$	1.465	
$\mathbf{t:} \mathbf{OH} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	2.521	
$\mathbf{t:} \mathbf{O} + \mathbf{OOH} \mathbf{b:} \mathbf{O} + \mathbf{O}$		3.14
$\mathbf{t:} \mathbf{O} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	4.051	4.22
$\mathbf{t}: \mathbf{O} + \mathbf{V} \mathbf{b}: \mathbf{O} + \mathbf{O} (+ \mathbf{O_2})$	4.916	4.92

Table S4: Literature comparison: Grand-canonical free energies $\Delta\Omega$ [eV] of OER intermediate states for the conventional mechanism at pH = 0 and a potential of $0.0 V_{\text{NHE}}$ (extrapolated from $1.53 V_{\text{NHE}}$) including the energy correction of +0.408 eV for the O₂molecule *only*. Results of this work are compared with those reported by Gauthier et al. [3]. Note: Unlike in Tables S3 and S5, the (**t**: O + V **b**: O + O) state is the zeroenergy reference for reasons of comparability with Ref. [3]. [†] The free energies of Ref. [3] were obtained by digitizing the data plotted in Figure 7 therein, where the results including explicit solvent were chosen.

OER intermediate state	This work	Ref. [4]
$\mathbf{t:} \mathbf{O} + \mathbf{O} \mathbf{b:} \mathbf{O} + \mathbf{O}$	0	0
t: $OH + OOH$ b: $O + O$	0.000	-0.12
$\mathbf{t:} \mathbf{OH} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	1.056	0.99
$\mathbf{t:} \mathbf{O} + \mathbf{OO} \mathbf{b:} \mathbf{O} + \mathbf{O}$	2.586	2.52
t: $O + V$ b: $O + O$ (+ O_2)	3.451	not reported
t: $O + OH$ b: $O + O (+ O_2)$	3.511	3.56
t: $O + O$ b: $O + O$ (+ O_2)	4.916	4.92

Table S5: Literature comparison: Grand-canonical free energies $\Delta\Omega$ [eV] of OER intermediate states for the conventional mechanism at pH = 0 and a potential of $0.0 V_{\text{NHE}}$ (extrapolated from $1.53 V_{\text{NHE}}$) including the energy correction of +0.408 eV for the O₂molecule *only*. The (**t**: O + O **b**: O + O) state is the zero-energy reference. Results of this work are compared with those reported by González et al. [4].

Surface adsorbate state	$1.23V_{\rm NHE}$	$1.53V_{\rm NHE}$
$\mathbf{t}: \mathbf{V} + \mathbf{V} \mathbf{b}: \mathbf{O} + \mathbf{O}$	0	0
$\mathbf{t}: \mathbf{OH} + \mathbf{OH} \mathbf{b}: \mathbf{OH} + \mathbf{OH}$	-2.487	-2.459
$\mathbf{t:} \mathbf{OH} + \mathbf{OH} \mathbf{b:} \mathbf{O} + \mathbf{O}$	-2.643	-3.114
$\mathbf{t}: \mathbf{O} + \mathbf{O} \mathbf{b}: \mathbf{O} + \mathbf{O}$	-2.180	-3.177

Table S6: Grand-canonical free energies $\Delta \Omega$ [eV] of different adsorbate states of the IrO₂ (110) surface versus the "clean" stoichiometric surface state (**t**: V + V **b**: O + O). This table aids in the conversion between the different reference states for the OER pathways at potentials 1.23 V_{NHE} and 1.53 V_{NHE}, see tables S2 and S1.

References

- [1] T. Binninger. Piecewise nonlinearity and capacitance in the joint density functional theory of extended interfaces. *Physical Review B*, 103:L161403, 2021.
- [2] Y. Ping, R. J. Nielsen, and W. A. Goddard. The reaction mechanism with free energy barriers at constant potentials for the oxygen evolution reaction at the IrO₂ (110) surface. *Journal of the American Chemical Society*, 139(1):149–155, 2017.
- [3] J. A. Gauthier, C. F. Dickens, L. D. Chen, A. D. Doyle, and J. K. Nørskov. Solvation effects for oxygen evolution reaction catalysis on IrO₂(110). *The Journal of Physical Chemistry C*, 121(21):11455–11463, 2017.
- [4] D. González, J. Heras-Domingo, M. Sodupe, L. Rodríguez-Santiago, and X. Solans-Monfort. Importance of the oxyl character on the IrO₂ surface dependent catalytic activity for the oxygen evolution reaction. *Journal of Catalysis*, 396:192–201, 2021.