Supporting Information for:

Strongly Facet-Dependent Activity of Iron-Doped β-Nickel Oxyhydroxide for the Oxygen Evolution Reaction

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S1. Additional details regarding the DFT calculations

All DFT calculations employed Gaussian smearing with a width of 0.01 eV to accelerate the convergence of the self-consistent energy. We applied dipole corrections[1] in each case in the direction perpendicular to the surface using the IDIPOL=3 option within VASP. These corrections were applied self-consistently to both the potential and forces using the LDIPOL=.TRUE. tag. We included a vacuum layer of approximately 15 Å in the direction perpendicular to the surface and modeled the same set of adsorbates on both exposed surfaces to minimize the inherent dipole moment of the system and thereby reduce spurious interactions with periodic images. For isolated molecules, we applied dipole corrections along all three coordinate directions using IDIPOL=4. The lateral periodic cell dimensions we employed were a = 5.8949 Å and b = 5.9844 Å, with the angle γ = 120.55° between the in-plane lattice vectors, for the (0001) surface. The corresponding values were a = 10.0085 Å, b = 5.9844 Å, and γ = 90.59° for the ($10\bar{1}0$) surface.

While we sampled the Fock exchange kernel for the hybrid DFT computations only at the gamma point (Γ) in a previous work on pure NiOOH,[2] we carried out the Fock k-point sampling using the same $3 \times 3 \times 1$ k-point mesh mentioned in the main text, in order to obtain 1 meV/atom accuracy in the present study. However, we were only able to optimize the structures using Γ-point sampling for the Fock exchange due to the extremely high computational cost of hybrid DFT calculations. We then followed these structural optimizations with single-point energy calculations using the more accurate $3 \times 3 \times 1$ k-point mesh for the Fock exchange to obtain the final hybrid DFT energy. Note that in the work involving the ($\bar{1}2\bar{1}1$) facet by Martirez and Carter, the in-plane lattice constants are greater than twice the short-range exchange screening length in the HSE06 XC functional ($1/\mu$ = $1/(0.2 \text{ Å}^{-1})$ = 5 Å), i.e., > 10 Å, justifying the Γ-point only Fock exchange energy evaluation (at $2/\mu$, the exact exchange decays to a negligible value, foregoing the need for periodicity within the exact exchange kernel). In the facets explored here, the in-plane lattice constants are less than or nearly equal to 10 Å, thus necessitating a denser Fock sampling mesh. All geometry optimizations, which relaxed all atoms, whether at the DFT-PBE+U or the DFT-HSE06(α=15%) level of theory, were carried out until the maximum absolute force on any atom was less than 0.01 eV/Å.

S2. Additional details regarding the ONIOM methodology and the vibrational frequency and free energy calculations

As mentioned in the main text, we used the "our own n-layered integrated molecular orbital and molecular mechanics (ONIOM)" formalism[3] to incorporate hybrid DFT using the Heyd-Scuseria-Ernzerhof (HSE06) XC functional[4–6] (with an α = 15% fraction of exact exchange), as a correction to the DFT-PBE+U energies. We performed this correction as follows:

$$\Delta G_{\text{ONIOM}}^{\text{DFT}-\text{HSE06}} = \Delta G_{NL}^{\text{DFT}-\text{PBE}+U} + \left(\Delta E_{ML}^{\text{DFT}-\text{HSE06}} - \Delta E_{ML}^{\text{DFT}-\text{PBE}+U} \right),$$

where $\Delta G_{\text{ONIOM}}^{\text{DFT}-\text{HSE06}}$ and $\Delta G_{NL}^{\text{DFT}-\text{PBE}+U}$ are the reaction Gibbs free energy changes calculated respectively using an ONIOM-like formalism and using the DFT-PBE+U level of theory. $\Delta E_{ML}^{\text{HSE06}}$ and $\Delta E_{ML}^{\text{DFT}-\text{PBE}+U}$ are the reaction DFT energies at respectively the DFT-HSE06(α=15%) and DFT-PBE+U levels of theory, while N and M denote the thickness of the surface slab, with $N >$ M.

Within the ONIOM framework, we used five-layered ($N = 5$) and three-layered ($M = 3$) slabs of β-NiOOH to model the (0001) surface while carrying out both DFT-PBE+U and hybrid DFT calculations as prescribed by the equation above. Similarly, we used seven-layered ($N = 7$) and five-layered ($M = 5$) slabs of β-NiOOH to model the ($10\bar{1}0$) surface.[2] The use of five and seven layers of the material reproduced the bulk density of states of electrons in the middle layer within DFT-PBE+U for the (0001) and ($10\bar{1}0$) facets, respectively, of β-NiOOH.[7,8] Note that we evaluated the vibrational frequencies, and hence the free energies, only within DFT-PBE+U using the thicker NL models. We included in the vibrational frequency calculations all atoms in and on the surface, i.e., the topmost layer of the slab, the adsorbed OER intermediates, as well as all other co-adsorbed species. We assumed that the vibrational modes of the surface species are uncoupled from the bulk and bulk-like phonon modes. Although we have identical surface species on the top and bottom surfaces, we did not perform frequency calculations for the bottom surface because the top and bottom terminations should yield the same vibrational spectrum (the reaction free energies are calculated per active site). Note that because the reactions are occurring on solid surfaces, there are no rotational or translational energies to contribute to the free energies. Moreover, the Gibbs free energies are approximated as per convention as Helmholtz free energies, namely absent the pressure-volume term, which is expected to largely cancel for free energy differences between states involving solid surfaces.

S3. Atom-projected magnetic moments for the surface atoms on the (0001) and ($10\bar{1}0$) facets of Fe-doped β-NiOOH and their assigned oxidation states

We found the low-spin and high-spin configurations, respectively, of Ni and Fe, to be most stable in our calculations. Tables S1 and S2 summarize the atom-projected magnetic moments of the Ni and Fe ions, respectively, on the (0001) and the ($10\bar{1}0$) surfaces of β-NiOOH.

Table S1. Range of atom-projected magnetic moments (M_z) for the surface Ni and Fe cations in the various intermediates considered on β-NiOOH(0001) using the DFT-HSE06(α=15%) level of theory.

Ion	M_z (μ_B)
Ni^{2+}	1.6-1.7
Ni^{3+}	0.8-0.9
Ni^{4+}	0.0-0.1
Fe^{3+}	4.0-4.1

Table S2. Range of atom-projected magnetic moments (M_z) for the surface Ni and Fe cations in the various intermediates considered on β-NiOOH($10\bar{1}0$) using the DFT-HSE06(α=15%) level of theory.

Ion[a]	M_z (μ_B)
Ni^{2+}	1.7
Ni^{3+}	0.8-0.9[a]
Fe^{3+}	3.9-4.1
Fe^{4+}	3.4

[a]The Ni^{3+} ion attached to an adsorbed H_2O molecule has a higher magnetic moment of around 1.4, indicating some charge donation from the adsorbed water into an empty d-orbital.

S4. Reaction Gibbs free energies of the alternative, higher-free-energy mechanisms for the OER on various Fe-doped active sites at the ONIOM-DFT-HSE06(α=15%) level of theory

Table S3. Reaction Gibbs free energies for the alternative steps for the OER (via mechanism M2[a]) on the Fe-doped *O site (▲) on β-NiOOH(0001), calculated using ONIOM-DFT-HSE06(α=15%). Mechanism M2 is unlikely at room temperature due to the highly endergonic non-electrochemical step R1a. Note that mechanism M3 is not possible at this active site as the initial catalyst state is *O, which cannot be eliminated from the mechanism.

Mechanism	Step	Reaction	ΔG_r^0 (eV)
M2	R1a	▲O + H_2O → ▲O(OH)H	2.22
	R1b	▲O(OH)H → ▲OOH + (H^++e^-)	0.08

[a]To obtain mechanism M2, step R1 in Table 1 of the main text splits into steps R1a and R1b.

Table S4. Reaction Gibbs free energies for the alternative steps for the OER (via mechanisms M2[a] and M3[b]) on the Fe-doped *OH site (▪) on β-NiOOH(0001), calculated using ONIOM-DFT-HSE06(α=15%). Mechanism M2 is unlikely at room temperature due to the highly endergonic non-electrochemical step R1a, while mechanism M3 has a higher overpotential of 1.88 V compared to 0.59 V via mechanism M1 reported in the main text.

Mechanism	Step	Reaction	ΔG_r^0 (eV)
M2	R1a	▪O + H_2O → ▪O(OH)H	1.48
	R1b	▪O(OH)H → ▪OOH + (H^++e^-)	0.34
M3	R6′	▪OH + H_2O → ▪O(OH)H + (H^++e^-)	3.11 (η=1.88 V)
	R1b	▪O(OH)H → ▪OOH + (H^++e^-)	0.34

[a]To obtain mechanism M2, step R1 in Table 2 of the main text splits into steps R1a and R1b.
[b]To obtain mechanism M3, steps R6 and R1 in Table 2 of the main text are replaced respectively with steps R6′ and R1b.

Table S5. Reaction Gibbs free energies for the alternative steps for the OER (via non-lattice oxygen mechanisms M1[a], M2[b], and M3[c]; "non-lattice-oxygen" refers to the lack of involvement of the ♣OO[l] intermediate in the mechanism) on the Fe-doped *OH₂ site (♣) on β-NiOOH(10$\bar{1}$0), calculated using ONIOM-DFT-HSE06(α=15%). Mechanisms M1 (non-lattice-oxygen), M2, and M3 all have higher overpotentials (of 0.64 V, 0.64 V, 0.67 V, respectively) than the lattice-oxygen mechanism M1[l], which has an overpotential of 0.43 V, as reported in the main text. Note that mechanisms M2 and M3 do not have lattice-oxygen counterparts, as the formation of ♣O(OH)H from ♣O requires the participation of a water molecule due to the extra hydrogen atoms.

Mechanism	Step	Reaction	ΔG_r^0 (eV)
Non-lattice-oxygen	R6	♣OH → ♣O + (H^+ + e^-)	1.87 (η=0.64 V)

Mechanism	Step	Reaction	ΔG
M1	R1[d]	$H_2O + {}^{\bullet}O + O^{l'}H^{l} + O^{r} \rightarrow {}^{\bullet}O_2 + O^{l'}H + O^{r}H^{l} + (H^+ + e^-)$	0.00
M2	R6	${}^{\bullet}OH \rightarrow {}^{\bullet}O + (H^+ + e^-)$	1.87 (η=0.64 V)
M2	R1a	${}^{\bullet}O + H_2O \rightarrow {}^{\bullet}O(OH)H$	0.03
	R1b[d]	${}^{\bullet}O(OH)H + O^{l'}H^{l} + O^{r} \rightarrow {}^{\bullet}O_2 + O^{l'}H + O^{r}H^{l} + (H^++e^-)$	-0.03
M3	R6′	${}^{\bullet}OH + H_2O \rightarrow {}^{\bullet}O(OH)H + (H^++e^-)$	1.90 (η=0.67 V)
M3	R1b[d]	${}^{\bullet}O(OH)H + O^{l'}H^{l} + O^{r} \rightarrow {}^{\bullet}O_2 + O^{l'}H + O^{r}H^{l} + (H^++e^-)$	-0.03

[a]To obtain the non-lattice-oxygen mechanism M1, steps R6[l] and R1[l] in Table 3 of the main text are replaced respectively with steps R6 and R1.

[b]To obtain mechanism M2, steps R6[l] and R1[l] in Table 3 of the main text are replaced respectively with steps R6 and collectively, R1a and R1b.

[c]To obtain mechanism M3, steps R6[l] and R1[l] in Table 3 of the main text are replaced respectively with steps R6′ and R1b.

[d]Note that the steps R1 and R1b shown here differ from what is mentioned in the section "Reaction intermediates and plausible mechanisms involved in the OER" of the main text, i.e., $*O + H_2O \rightarrow *OOH + (H^++e^-)$ and $*O(OH)H \rightarrow *OOH + (H^++e^-)$, respectively. This is because the ${}^{\bullet}OOH$ intermediate relaxes upon geometry optimization to ${}^{\bullet}O_2$ plus a protonated lattice oxygen in the same catalyst layer and a protonated lattice oxygen in the adjacent catalyst layer, i.e., ${}^{\bullet}O_2 + O^{l'}H + O^{r}H^{l}$.

Table S6. Reaction Gibbs free energies for the alternative steps for the OER (via mechanisms M1[a] and M3[b]) on the Fe-doped $*OH$ site (${}^{\bullet}$) on β-NiOOH($10\bar{1}0$), calculated using ONIOM-DFT-HSE06(α=15%). Mechanisms M1 and M3 both have higher overpotentials of 0.74 V and 0.82 V, which is higher than that 0.54 V for mechanism M2, as reported in the main text.

Mechanism	Step	Reaction	ΔG_{r}^{0} (eV)
M1	R1	${}^{\bullet}O + H_2O \rightarrow {}^{\bullet}OOH + (H^+ + e^-)$	1.97 (η=0.74 V)
M3	R6′[c]	${}^{\bullet}OH + H_2O + O^{r} \rightarrow {}^{\bullet}OOH + O^{r}H + (H^+ + e^-)$	2.05 (η=0.82 V)

[a]To obtain mechanism M1, steps R1a and R1b for the Fe-doped case in Table 4 of the main text are replaced with a single step R1.

[b]To obtain mechanism M3, steps R6 and R1a for the Fe-doped case in Table 4 of the main text are replaced with a single step R6′.

[c]Note that step R6′ shown here differs from what is mentioned in the section "Reaction intermediates and plausible mechanisms involved in the OER" of the main text, i.e., $*OH + H_2O \rightarrow *O(OH)H + (H^++e^-)$. This is because ${}^{\bullet}O(OH)H$ relaxes upon geometry optimization to ${}^{\bullet}OOH$ plus a protonated lattice oxygen in the adjacent catalyst layer, i.e., ${}^{\bullet}OOH + O^{r}H$.

S5. Reaction Gibbs free energies at the DFT-PBE+U level of theory of the elementary steps in the OER mechanism with the lowest overpotential (according to the ONIOM-DFT-HSE06(α=15%) level of theory) on various Fe-doped active sites

Table S7. Reaction Gibbs free energies for the steps comprising the OER on the Fe-doped *O site ($\blacktriangle$) on β-NiOOH(0001), calculated using the DFT-PBE+U level of theory on the 5L slab model. See Table 1 in the main text for the corresponding ONIOM-DFT-HSE06(α=15%) free energies and reaction species nomenclature. The PDS is shown in red.

Step	Reaction	ΔG_r^0 (eV)
R1	$^{\blacktriangle}O + H_2O \rightarrow {}^{\blacktriangle}OOH + (H^+ + e^-)$	1.91 (η=0.68 V)[a]
R2	$^{\blacktriangle}OOH \rightarrow {}^{\blacktriangle}O_2 + (H^+ + e^-)$	0.78
R3	$^{\blacktriangle}O_2 \rightarrow O_2 + {}^{\blacktriangle}$	0.36
R4	$H_2O + {}^{\blacktriangle} \rightarrow {}^{\blacktriangle}OH_2$	0.00
R5	$^{\blacktriangle}OH_2 \rightarrow {}^{\blacktriangle}OH + (H^+ + e^-)$	0.41
R6	$^{\blacktriangle}OH \rightarrow {}^{\blacktriangle}O + (H^+ + e^-)$	1.46

[a]η is the overpotential defined as (max PCET ΔG_r^0 − 1.23 eV)/e.

Table S8. Reaction Gibbs free energies for the steps comprising the OER on the Fe-doped *OH site ($\blacksquare$) on β-NiOOH(0001), calculated using the DFT-PBE+U level of theory on the 5L slab model. See Table 2 in the main text for the corresponding ONIOM-DFT-HSE06(α=15%) free energies and reaction species nomenclature. The PDS is shown in red; note that the PDS is different here than predicted by ONIOM (see Table 2 in the main text).

Step	Reaction	ΔG_r^0 (eV)
R6	$^{\blacksquare}OH \rightarrow {}^{\blacksquare}O + (H^+ + e^-)$	1.86 (η=0.63 V)[a]
R1	$^{\blacksquare}O + H_2O \rightarrow {}^{\blacksquare}OOH + (H^+ + e^-)$	1.43
R2	$^{\blacksquare}OOH \rightarrow {}^{\blacksquare}O_2 + (H^+ + e^-)$	0.97
R3	$^{\blacksquare}O_2 \rightarrow O_2 + {}^{\blacksquare}$	0.10
R4	$H_2O + {}^{\blacksquare} \rightarrow {}^{\blacksquare}OH_2$	-0.07
R5	$^{\blacksquare}OH_2 \rightarrow {}^{\blacksquare}OH + (H^+ + e^-)$	0.63

[a]η is the overpotential defined as (max PCET ΔG_r^0 − 1.23 eV)/e.

Table S9. Reaction Gibbs free energies for the steps comprising the OER on the Fe-doped *OH$_2$ site ($\bullet$) on β-NiOOH(10$\bar{1}$0), calculated using the DFT-PBE+U level of theory on the 7L slab model. See Table 3 in the main text for the corresponding ONIOM-DFT-HSE06(α=15%) free energies and reaction species nomenclature. The PDS is shown in red; note that the PDS is different here than predicted by ONIOM.

Step	Reaction	ΔG_r^0 (eV)
R5	$^{\bullet}OH_2 \rightarrow {}^{\bullet}OH + (H^+ + e^-)$	1.69 (η=0.46 V)[a]
R6^l	$^{\bullet}OH + O^l \rightarrow {}^{\bullet}OO^l + (H^+ + e^-)$	1.08
R1^l	$H_2O + {}^{\bullet}OO^l + O^{l'}H^l + O^r \rightarrow {}^{\bullet}O_2 + O^l + O^{l'}H + O^rH^l + (H^+ + e^-)$	0.45
R2	$^{\bullet}O_2 + O^{l'}H + O^rH^l \rightarrow {}^{\bullet}O_2 + O^{l'}H^l + O^r + (H^+ + e^-)$	1.55

R3	$^\bullet O_2 \to O_2 + {}^\bullet$	0.09
R4	$H_2O + {}^\bullet \to {}^\bullet OH_2$	0.05

$^a\eta$ is the overpotential defined as $(\max \text{PCET}\,\Delta G_\mathrm{r}^0 - 1.23\ \text{eV})/e$.

Table S10. Reaction Gibbs free energies for the steps comprising the OER on the Fe-doped *OH site ($^\bullet$) on β-NiOOH($10\bar{1}0$), calculated using the DFT-PBE+U level of theory on the $7L$ slab model. See Table 4 in the main text for the corresponding ONIOM-DFT-HSE06(α=15%) free energies and reaction species nomenclature. The PDS is shown in red.

Step	Reaction	ΔG_r^0 (eV)
R6	$^\bullet OH \to {}^\bullet O + (H^+ + e^-)$	2.12 (η=0.89 V)^a
R1a^b	$^\bullet O + H_2O + O^rH \to {}^\bullet OOH + O^rH$	-0.33
R1b^b	$^\bullet OOH + O^rH \to {}^\bullet OOH + O^r + (H^+ + e^-)$	1.92
R2	$^\bullet OOH \to {}^\bullet O_2 + (H^+ + e^-)$	0.69
R3	$^\bullet O_2 + {}^\bullet OH_2 + O^r \to O_2 + {}^\bullet OH + O^rH + {}^\bullet$	-1.21
R4	$H_2O + {}^\bullet \to {}^\bullet OH_2$	0.31
R5	$^\bullet OH + O^rH \to {}^\bullet OH + O^r + (H^+ + e^-)$	1.42

$^a\eta$ is the overpotential defined as $(\max \text{PCET}\,\Delta G_\mathrm{r}^0 - 1.23\ \text{eV})/e$.
^{b}Note that steps R1a and R1b shown here differ from what is mentioned in the section "Reaction intermediates and plausible mechanisms involved in the OER" of the main text, i.e., *OH + H$_2$O → *O(OH)H + (H$^+$+e$^-$). This is because $^\bullet$O(OH)H relaxes upon geometry optimization to $^\bullet$OOH plus a protonated lattice oxygen in the adjacent catalyst layer, i.e., $^\bullet$OOH + O^{r}H.

S6. Supplementary References

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