

Supporting Information

Crystallographic Control of the Initial Electrochemical Reduction of Hematite

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S1 Computational details

To investigate the initial electrochemical reduction of hematite (α -Fe₂O₃) on the (0001), (10 $\bar{1}$ 0), and (1 $\bar{2}$ 10) facets under varying surface coverages, we performed density functional theory (DFT) using the Vienna *Ab initio* Simulation Package (VASP) ¹⁻³. The aqueous environment was represented using the implicit-solvation model VASPsol. ⁴ Analysis of magnetic configurations of hematite in the primitive unit cell are provided in the SI of our previous work. ⁵ The atomic structures were optimized using Gaussian smearing method with a smearing width of 0.05 eV. Convergence criteria for forces and total energy in the self-consistent field (SCF) cycle are set to 0.01 eV/Å and 10⁻⁶ eV, respectively. The plane-wave cutoff energy used for our calculations was 500 eV. A 3×3×1 k-point mesh was employed for surface calculations. The tetrahedron method with Blöchl corrections (ISMear = -5) and k-point mesh 9×9×1 was employed to calculate the density of states (DOS) and the Fe d-band center/O p-band center, and the sumo command-line tool was used for plotting the DOS. ⁶ Electronic self-consistency was accelerated using VASP's density mixing scheme with the charge and magnetization channels controlled by mixing parameters (AMIN = 0.01, AMIX = 0.8, BMIX = 1.5, AMIX_MAG = 3.2, and BMIX_MAG = 1.5). The density-mixing parameters were adjusted to achieve robust electronic convergence for the spin-polarized DFT + U calculations. The atomic structure and slab models were constructed and visualized using the Atomic Simulation Environment (ASE) ⁷ and Visualization for Electronic and STructural Analysis (VESTA) ⁸ software.

To assess the finite-temperature stability of representative surface configurations of hematite in an explicit aqueous environment, we performed *ab initio* molecular dynamics (AIMD) simulations using the CP2K 2025.2 ⁹/Quickstep software package¹⁰, which implements a hybrid Gaussian and plane-wave (GPW) approach. Periodic boundary conditions were applied in the x and y directions, while free boundary condition was imposed along the z-direction to prevent artificial interactions across the vacuum region. For the AIMD simulations, a lateral supercell four times larger than in the VASP calculations was used to allow Γ -point sampling; the 12*H_{sub} coverage therefore corresponds to 48 H atoms in the CP2K cell. Prior to the production AIMD run for finite-temperature stability analysis, the system was optimized using static DFT and then gradually heated from an initial temperature of 10 K to 300 K using an NVE annealing procedure. Subsequently, AIMD simulations were performed in the canonical (NVT) ensemble at 300 K using a time step of 0.5 fs. A total of 40,000 MD steps were carried

out. Temperature control was achieved using the canonical sampling through velocity rescaling (CSVR) thermostat, applied globally to the system with a thermostat time constant of 50 fs. The simulation box contained 784 atoms for the clean surface and 832 atoms for the $12^*\text{H}_{\text{sub}}$ -hydrogenated surface, including Fe, O, and H — from both the hematite slab and the surrounding water molecules. The number of surrounding water molecules was 128 for both surfaces.

S2 Modeling electrochemical processes on hematite

Electrochemical environments facilitate the adsorption of molecular and ionic species from the electrolyte onto the electrode surface through electrostatic interactions. To explain the surface structures that are thermodynamically stable at a given electrode potential (U), we apply an *ab initio* thermodynamics framework based on stability diagrams.¹¹ We focus on the thermodynamic stability of hydrogen adsorbed on lattice oxygen atoms under cathodic polarization, illustrated here for the (0001) facet.

To identify the energetically favored surface structures of hematite as a function of the applied electrode potential, we use a thermochemical model in combination with the computational hydrogen electrode (CHE) approach developed by Nørskov and coworkers.¹² This combined framework enables a thermodynamic-electrochemical evaluation of adsorption free energies for various surface adsorbate structures.^{13–18} In order to comprehend the surface structure of the hematite model electrode under different electrochemical conditions, it is necessary to determine the adsorption free energies for different $^*\text{H}$ coverage configurations under cathodic polarization. We then minimize the free energies of the different surface phases as a function of the applied electrode potential. The thermodynamically favored surface configurations are the one with the lowest free energy, and those are illustrated in the section of stability diagrams (cf. Section S2.4).

Surface stability diagrams provide a thermodynamic basis for identifying representative surface states under electrochemical conditions.^{19–24} In this study, we rely on the stability diagrams for reasonable comparison and to enhance our understanding of the reduction process. Consequently, we consider clean (bare), 8^*H_{sub} and $12^*\text{H}_{\text{sub}}$ surface coverages to study the reduction of hematite across three different crystallographic facets.

S2.1 Determination of adsorption free energies

We selected the stoichiometric $\alpha\text{-Fe}_2\text{O}_3(0001)$ surface in a (2×2) supercell, as shown in **Figure S1**, to illustrate how to determine the adsorption free energies using this clean (bare) surface.

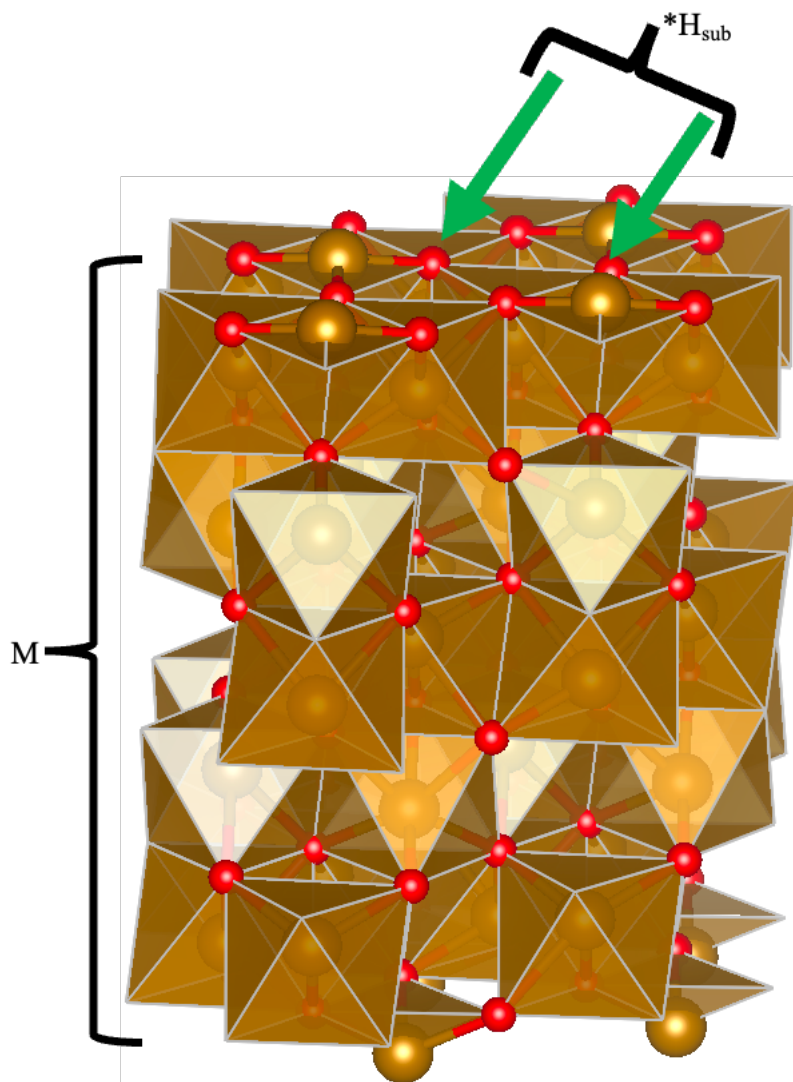


Figure S1. Slab model of (2×2) supercell $\alpha\text{-Fe}_2\text{O}_3$. The polyhedral representation of hematite shows Fe-O-Fe termination, where the outermost layer is partially octahedral, while the inner layer is fully octahedral. Atomic species are represented as follows: gold spheres for iron and red spheres for oxygen. The figure was created using the VESTA visualization software.⁸

For the formation of $^*\text{H}$ adsorbates on the lattice oxygen site, we consider the following process:



where M represents the remaining structure of hematite (cf. **Figure S1**).

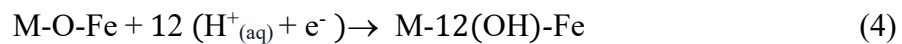
To calculate the free formation energy of liquid water using density functional theory (DFT), we consider gaseous water at a temperature of 298.15 K and adjust the pressure to the vapor pressure of water (0.035 bar). Since gaseous water at its vapor pressure is in equilibrium with liquid water, this adjustment converts the free energy of gaseous water into that of liquid water by accounting for the corresponding change in translational entropy. In this study, the chemical potential associated with proton-coupled electron transfer is evaluated using the CHE formalism. Accordingly, at $U = 0$ V vs. the standard hydrogen electrode (SHE), $\text{pH} = 0$, $T = 298.15$ K, and $P(\text{H}_2) = 1$ atm, the chemical potential of a proton–electron pair is defined by one-half the chemical potential of molecular hydrogen gas, as described by the equilibrium in equation (2):



Thus, it is sufficient to calculate the chemical potential of a hydrogen molecule using DFT by considering that the following relation holds under equilibrium conditions:

$$\mu_{\text{H}^+_{(\text{aq})}} + \mu_{\text{e}^-} = \frac{1}{2} \mu_{\text{H}_{2(\text{g})}} \quad (3)$$

The calculation of the Gibbs free-energy change (ΔG) for an adsorption process, as presented in equation (1), is crucial for constructing surface stability diagrams. In the case of multiple adsorbates in the (2×2) unit cell, we can apply a modified version of equation (1) by balancing the chemical equation. For example, for the adsorption of 12^*H on lattice oxygen sites (cf. **Figure S1**), we arrive at:



For simplicity, we replace M–O–Fe with $*$ to represent the remaining O site for hydrogen adsorption. Accordingly, equation (4) can be expressed as:



The corresponding ΔG value for this process is given by:

$$\Delta G(0,0) = G(*-12(\text{OH})) - G(*) - 6G(\text{H}_2) \quad (6)$$

The (0,0) in equation (6) indicates that this ΔG value refers to the Gibbs free energy at zero electrode potential and $pH = 0$. For all possible adsorbate structures, the $\Delta G(0,0)$ value is obtained through DFT calculations using the following relation:

$$\Delta G(0,0) = \Delta E_{tot} + \Delta E_{ZPE} - T\Delta S + \int_0^{T=298.15} c_P dT \quad (7)$$

Here, ΔE_{tot} denotes the difference in the electronic energy between the two thermodynamic states, as shown in equation (8):

$$\Delta E_{tot} = E(*-12(OH)) - E(*) - 6E(H_2) \quad (8)$$

ΔE_{ZPE} in equation (7) indicates the difference in zero-point energy between the adsorbate-covered surface and the stoichiometric hematite surface, including the respective reference states. These calculations are performed using VASPKIT²⁵. The vibrational frequency calculations in VASP were performed using the finite difference method (IBRION = 5), with atomic displacements of 0.015 Å (POTIM = 0.015) and NFREE=2. For the frequency calculations, H, Fe and O atoms on the outermost layer(s) are considered, assuming that the atoms relax due to vacancy formation during reduction process. We only account for the vibrational contribution to the total entropy for the adsorbates (term $T\Delta S$), as described by equation (9):²⁶

$$S_{vib} = k_B \sum_i^{modes} \left[\frac{x_i}{(e^{x_i} - 1)} - \ln(1 - e^{-x_i}) \right] \quad (9)$$

where $x_i = \frac{h\omega_i}{k_B T}$, h is Planck's constant, ω is the frequency, and k_B denotes Boltzmann's constant. The last term in equation (7) refers to the enthalpic temperature correction to translate the DFT-calculated energetics from 0 K to 298.15 K.

By counting the number of transferred protons, $\nu(H^+)$, and electrons, $\nu(e^-)$, in each electrochemical step, it is possible to convert the $\Delta G(0,0)$ values to potential-dependent free-energy changes:

$$\Delta G(pH, U) = \Delta G(0,0) + \nu(e^-)U_{SHE} + \nu(H^+)k_B T(\ln 10) pH \quad (10)$$

For example, under cathodic conditions, the formation of the $*-12(OH)$ phase in equation (4) results in the following relation for the potential-dependent free energy change:

$$\Delta G(pH, U) = \Delta G(0,0) + 12 k_B T (\ln 10) pH + 12 e U_{SHE} \quad (11)$$

where e is the elementary charge. Note that the term $k_B T (\ln 10)$ amounts to 0.059 eV at $T = 298.15$ K.

By minimizing the $\Delta G(pH, U)$ values for all possible adsorbate configurations on the hematite surface, we derive the energetically preferred surface phase as a function of ΔG and applied electrode potential U , which is illustrated in the surface stability diagram section (cf. Section S2.4).

S2.2 Relationship between SHE and RHE scale

We can rewrite equation (10) on the reversible hydrogen electrode (RHE) scale by considering the following correlation:

$$eU_{RHE} = eU_{SHE} + 0.059 pH \quad (12)$$

Therefore, by substituting equation (12) into equation (10) and assuming $\nu(e^-) = \nu(H^+)$, the free-energy change for the adsorption process on the RHE scale is:

$$\Delta G(U_{RHE}) = \Delta G(0,0) + \nu(e^-) e U_{RHE} \quad (13)$$

Note that this transformation is only valid if the redox reactions involve the same number of transferred protons, $\nu(H^+)$, and electrons, $\nu(e^-)$. This prerequisite is clearly satisfied for the hydrogenation of hematite surface for $*H$ adsorbate on lattice oxygen atoms. Consequently, we discuss the stability diagrams and the electrochemical reduction of hematite on different facets using RHE scale rather than the SHE scale.

S2.3 Free energies for hydrogenated hematite surfaces

The free energies of surface configurations containing $*H$ on hematite are calculated relative to the clean hematite surface in our model and are reported in **Table S1** for the three facets. The corresponding notations for each model are also provided in the table.

To investigate the electrochemical reduction of hematite, we considered the following surface configurations: clean, $8*H_{sub}$, and $12*H_{sub}$ surface coverages for the three facets. The stability of these surface coverages and their structures are presented in **Figures S2- S4** (cf. Section S2.4).

Table S1. The free energies of adsorbed *H surface structures with respect to the clean surface of hematite in the (2×2) unit cell for the (0001), $(10\bar{1}0)$, and $(1\bar{2}10)$ facets. The corresponding notations for each model investigated in this study are also illustrated as follows: $(O_{12}H_p)$ refers to a hydrogenated lattice oxygen atom in the first/second layer of hematite, depends on the facet, where the subscript ‘p’ denotes the number of the corresponding adsorbed hydrogens. The symbol M denotes the remaining part of the slab.

facet	Hydrogenated surface coverages	$\Delta G / \text{eV}$
(0001)	M- O_{12} -4Fe (clean)	0.00
	M- $O_{12}H$ -4Fe	-0.29
	M- $O_{12}H_2$ -4Fe	-0.81
	M- $O_{12}H_3$ -4Fe	-1.20
	M- $O_{12}H_4$ -4Fe	-1.42
	M- $O_{12}H_5$ -4Fe	-1.43
	M- $O_{12}H_6$ -4Fe	-1.87
	M- $O_{12}H_7$ -4Fe	-1.32
	M- $O_{12}H_8$ -4Fe	-2.31
	M- $O_{12}H_{12}$ -4Fe	-3.12
$(10\bar{1}0)$	M- O_{12} -6Fe (clean)	0.00
	M- $O_{12}H$ -6Fe	-2.20
	M- $O_{12}H_2$ -6Fe	-4.13
	M- $O_{12}H_3$ -6Fe	-5.53
	M- $O_{12}H_4$ -6Fe	-6.45
	M- $O_{12}H_5$ -6Fe	-7.00
	M- $O_{12}H_6$ -6Fe	-7.55
	M- $O_{12}H_7$ -6Fe	-7.98
	M- $O_{12}H_8$ -6Fe	-8.01
	M- $O_{12}H_{12}$ -6Fe	-8.99
$(1\bar{2}10)$	M- O_{12} -8Fe (clean)	0.00
	M- $O_{12}H$ -8Fe	-0.96
	M- $O_{12}H_2$ -8Fe	-1.92
	M- $O_{12}H_3$ -8Fe	-2.61
	M- $O_{12}H_4$ -8Fe	-3.22
	M- $O_{12}H_5$ -8Fe	-3.82
	M- $O_{12}H_6$ -8Fe	-4.26
	M- $O_{12}H_7$ -8Fe	-4.66
	M- $O_{12}H_8$ -8Fe	-4.79
	M- $O_{12}H_{12}$ -8Fe	-4.59

S2.4 Stability diagram

DFT-based stability diagrams are constructed through a thermodynamic evaluation of reaction equations, using a well-defined reference state—namely the clean surface of the corresponding facet. Free-energy changes for various surface configurations, as derived from equation (13), are listed in **Table S1**. Based on these values, the stability diagram of hematite for the three facets is shown in **Figures S2 – S4**, along with the corresponding structures considered for the electrochemical reduction of hematite in this study. We did not include surface coverages of 9^*H_{sub} , $10^*\text{H}_{\text{sub}}$, and $11^*\text{H}_{\text{sub}}$ in the stability diagram analysis, as trends exhibited a smooth slope progression, and a maximum coverage of $12^*\text{H}_{\text{sub}}$ on the oxygen atoms of the first/second layer was selected following the 8^*H_{sub} coverage.

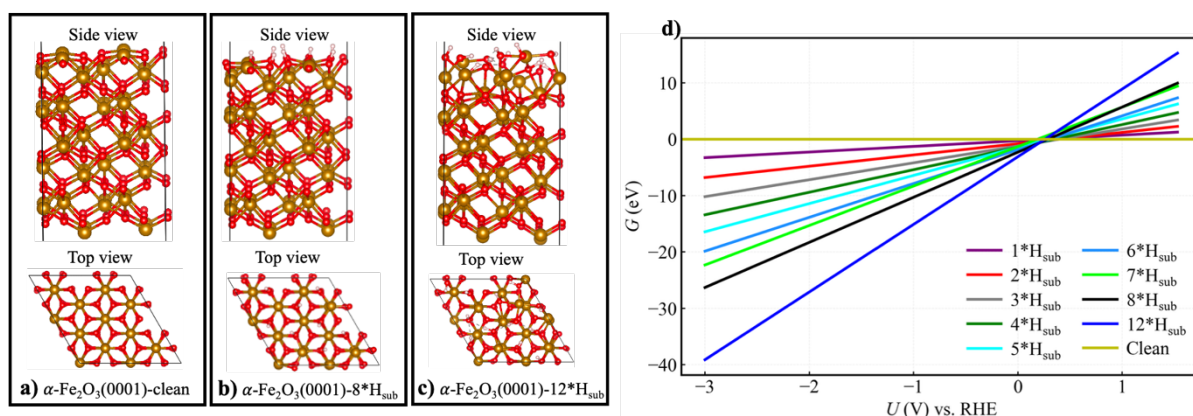


Figure S2. a), b), and c) show the (0001) facet configurations of hematite for clean, 8^*H_{sub} , and $12^*\text{H}_{\text{sub}}$ surface coverages, respectively. The scheme for atomic spheres: gold for iron, red for oxygen, and white for hydrogen. The figure was created using the VESTA visualization software.⁸ d) Stability diagram for the hydrogenation of the (0001) facet.

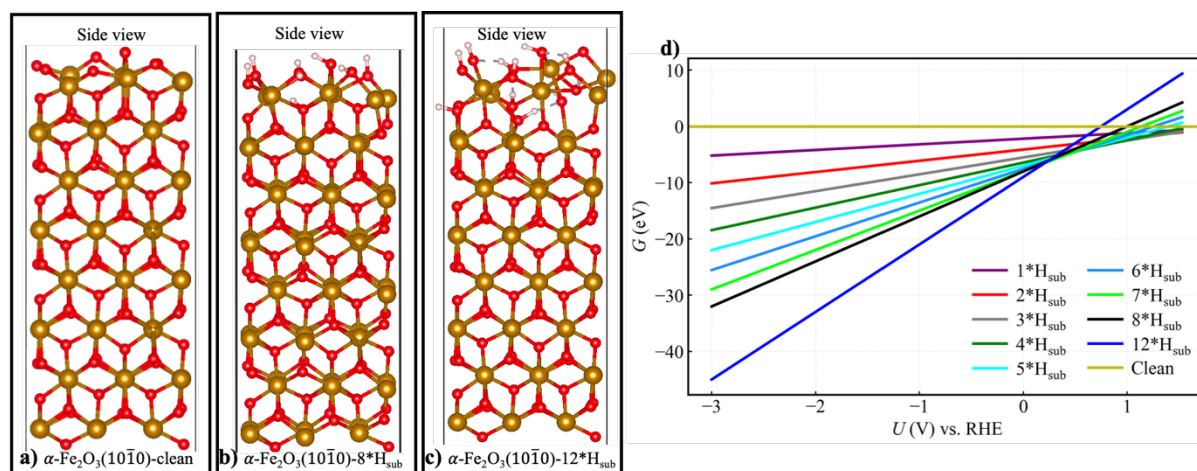


Figure S3. a), b) and c) show the (10 $\bar{1}$ 0) facet configurations of hematite for clean, 8^*H_{sub} , and $12^*\text{H}_{\text{sub}}$ surface coverages, respectively. The scheme for atomic spheres: gold for iron, red for oxygen, and white for hydrogen. The figure was created using the VESTA visualization software.⁸ d) Stability diagram for the hydrogenation of the (10 $\bar{1}$ 0) facet.

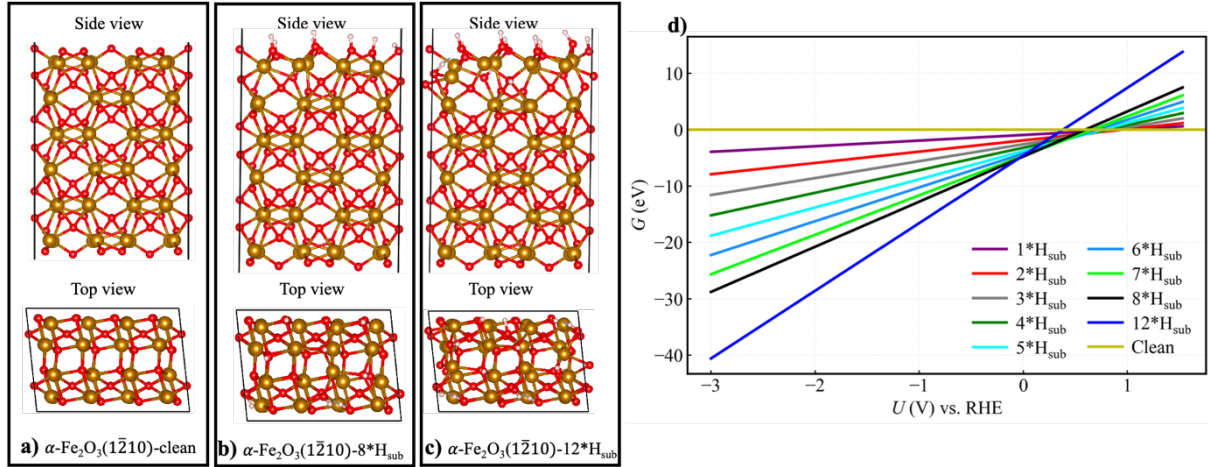
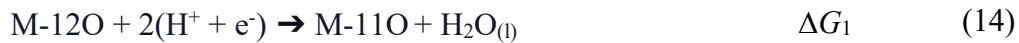
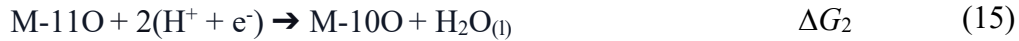


Figure S4. a), b) and c) show the (110) facet configurations of hematite for clean, 8*H_{sub}, and 12*H_{sub} surface coverages, respectively. The scheme for atomic spheres: gold for iron, red for oxygen, and white for hydrogen. The figure was created using the VESTA visualization software.⁸ d) Stability diagram for the hydrogenation of the (110) facet.

S3 Electrochemical reduction reactions of hematite

S3.1 Electrochemical reduction reactions of hematite–clean surface

To analyze the initial reduction of hematite surface, we start with a hematite surface without any surface coverage. To achieve a reduced hematite surface, where Fe atoms remain exposed in the first and/or second layers, the oxygen atoms are removed sequentially, step by step. Each oxygen removal occurs via two proton-coupled electron transfer steps, producing water as a byproduct. This process leads to the formation of oxygen vacancies on the surface and the release of water, as illustrated in equations (14) – (25).

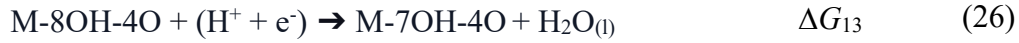
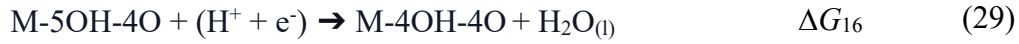
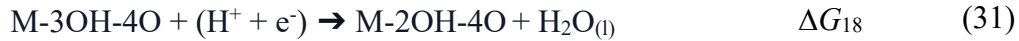




Note that M denotes the remaining slab after removal of the respective number of oxygen atoms from the near-surface region and does not represent a stoichiometric quantity. This definition applies to all instances of M in this study, unless otherwise specified. For instance, M-11O corresponds to a surface from which one oxygen atom has been removed, M-10O to a surface from which two oxygen atoms have been removed, and so forth. During the reduction, oxygen atoms from lower layers migrate into the outermost layers (cf. **Figure 3** of the main text).

S3.2 Electrochemical reduction reactions of hematite–8*H_{sub} surface (partial reduction)

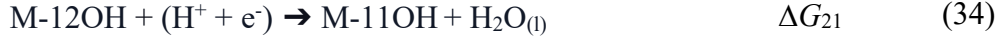
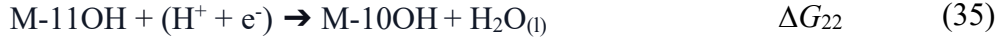
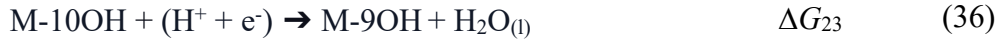
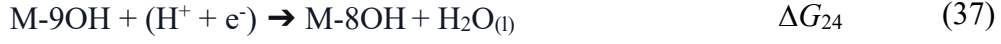
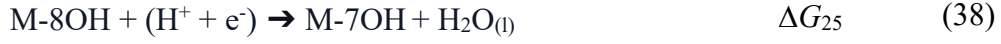
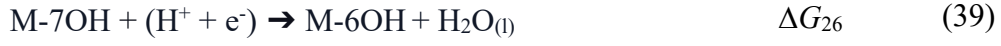
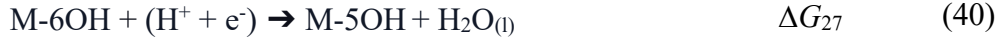
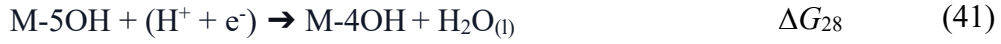
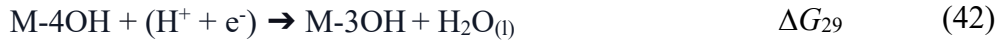
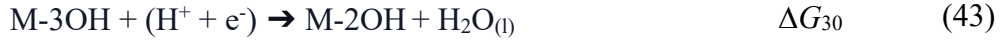
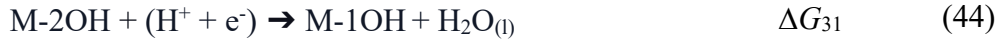
For the 8*H_{sub} hematite surface, the initial electrochemical reduction is modeled by sequential hydroxyl removal via a single proton-coupled electron transfer, producing water as a byproduct. This process creates hydroxyl vacancies on the surface and leads to the release of water, as illustrated in equations (26) – (33).



M-7OH-4O corresponds to a surface from which one hydroxyl group has been removed, M-6OH-4O to a surface from which two hydroxyl groups have been removed, and so on; the four non-hydroxylated oxygen atoms remain in the final state M-4O.

S3.3 Electrochemical reduction reactions of hematite–12*H_{sub} surface

For the 12*H_{sub} hematite surface, the initial electrochemical reduction is modeled by sequential hydroxyl removal via a single proton-coupled electron transfer, producing water as a byproduct. This process leads to the formation of hydroxyl vacancies on the surface and release of water, as shown in equations (34) – (45).



M-11OH corresponds to a surface with one hydroxyl vacancy, M-10OH corresponds to a surface with two hydroxyl vacancies, and so on.

The free-energy changes associated with $\Delta G_1 - \Delta G_{32}$ in equations (14) – (45) are provided in tabular form in Section S4 for all facets.

S4 Free-energy changes for the electrochemical reduction of hematite

S4.1 Free-energy changes for the (0001) facet

In Table S2, we have summarized the free-energy changes for the elementary reaction step of the electrochemical reduction of $\alpha\text{-Fe}_2\text{O}_3(0001)$ according to $(\Delta G_1) - (\Delta G_{32})$ in equations (14) – (45) of Section S3.

Table S2. Free-energy changes (ΔG) associated with (ΔG_1) – (ΔG_{32}) in equations (14) – (45) of Section S3 for all reactions investigated in the electrochemical reduction of the α -Fe₂O₃(0001) facet a function of different surface coverages at zero applied electrode potential. All values are given in eV.

Surface coverage	ΔG (eV)					
Clean	ΔG_1 : 0.38	ΔG_2 : -0.01	ΔG_3 : -0.30	ΔG_4 : -0.53	ΔG_5 : 0.21	ΔG_6 : -0.04
	ΔG_7 : -0.30	ΔG_8 : 0.13	ΔG_9 : 0.32	ΔG_{10} : 0.47	ΔG_{11} : 1.65	ΔG_{12} : 1.82
8*H _{sub}	ΔG_{13} : 0.82	ΔG_{14} : -0.90	ΔG_{15} : 0.12	ΔG_{16} : 0.61	ΔG_{17} : 0.17	ΔG_{18} : 0.31
	ΔG_{19} : 0.58	ΔG_{20} : 0.30				
12*H _{sub}	ΔG_{21} : -0.03	ΔG_{22} : -0.02	ΔG_{23} : 0.63	ΔG_{24} : -0.04	ΔG_{25} : 0.46	ΔG_{26} : 0.81
	ΔG_{27} : 0.94	ΔG_{28} : -0.07	ΔG_{29} : 0.52	ΔG_{30} : -0.06	ΔG_{31} : 0.16	ΔG_{32} : 1.31
Clean as a function of 4*H on the outermost Fe atoms	ΔG_1 : -2.59	ΔG_2 : -1.20	ΔG_3 : -0.04	ΔG_4 : 0.70	ΔG_5 : -0.55	ΔG_6 : 0.59
	ΔG_7 : -0.94	ΔG_8 : 0.31	ΔG_9 : -0.84	ΔG_{10} : 0.28	ΔG_{11} : -0.83	ΔG_{12} : 0.99
8*H _{sub} as a function of 4*H on the outermost Fe atoms	ΔG_{13} : -1.00	ΔG_{14} : 0.14	ΔG_{15} : 0.31	ΔG_{16} : 0.26	ΔG_{17} : 0.29	ΔG_{18} : 0.18
	ΔG_{19} : -0.15	ΔG_{20} : 1.75				
12*H _{sub} as a function of 4*H on the outermost Fe atoms	ΔG_{21} : -0.32	ΔG_{22} : 0.56	ΔG_{23} : -0.31	ΔG_{24} : 0.55	ΔG_{25} : 0.25	ΔG_{26} : -0.15
	ΔG_{27} : 0.05	ΔG_{28} : -0.25	ΔG_{29} : 0.49	ΔG_{30} : 1.14	ΔG_{31} : 0.12	ΔG_{32} : -0.13
Benchmark gas phase DFT calculation for 8*H _{sub}	ΔG_{13} : 0.23	ΔG_{14} : -0.20	ΔG_{15} : 0.55	ΔG_{16} : 0.13	ΔG_{17} : 0.16	ΔG_{18} : 0.55
	ΔG_{19} : 0.84	ΔG_{20} : 0.35				

S4.2 Free-energy changes for the (10 $\bar{1}$ 0) facet

In **Table S3**, we have summarized the free-energy changes for the elementary reaction step of the electrochemical reduction of α -Fe₂O₃(10 $\bar{1}$ 0) according to (ΔG_1) – (ΔG_{32}) in equations (14)-(45) of Section S3.

Table S3. Free-energy changes (ΔG) associated with (ΔG_1) – (ΔG_{32}) in equations (14) – (45) of Section S3 for all reactions investigated in the electrochemical reduction of the α -Fe₂O₃(10 $\bar{1}$ 0) facet as a function of different surface coverages at zero applied electrode potential. All values are given in eV.

Surface coverage	ΔG (eV)					
Clean	ΔG_1 : -2.86	ΔG_2 : -2.21	ΔG_3 : -1.02	ΔG_4 : -0.89	ΔG_5 : -0.67	ΔG_6 : -0.49
	ΔG_7 : 0.20	ΔG_8 : 1.23	ΔG_9 : 1.79	ΔG_{10} : 1.63	ΔG_{11} : 1.80	ΔG_{12} : -0.20
Clean as a function of 6*H on the outermost Fe atoms	ΔG_1 : 1.18	ΔG_2 : -4.80	ΔG_3 : 1.26	ΔG_4 : 0.93	ΔG_5 : 1.64	ΔG_6 : -0.69
	ΔG_7 : -0.17	ΔG_8 : 3.05	ΔG_9 : -1.86	ΔG_{10} : -0.60	ΔG_{11} : 2.47	ΔG_{12} : -0.15
8*H _{sub}	ΔG_{13} : -0.60	ΔG_{14} : -0.57	ΔG_{15} : -0.13	ΔG_{16} : -0.08	ΔG_{17} : 0.30	ΔG_{18} : 0.63
	ΔG_{19} : 1.29	ΔG_{20} : -0.26				
12*H _{sub}	ΔG_{21} : -0.42	ΔG_{22} : 0.05	ΔG_{23} : -0.10	ΔG_{24} : -0.16	ΔG_{25} : -1.25	ΔG_{26} : -0.03
	ΔG_{27} : 0.19	ΔG_{28} : 0.02	ΔG_{29} : 1.43	ΔG_{30} : 0.50	ΔG_{31} : 1.22	ΔG_{32} : 0.71

S4.3 Free-energy changes for the (1 $\bar{2}$ 10) facet

In Table S4, we have summarized the free-energy changes for the elementary reaction step of the electrochemical reduction of α -Fe₂O₃(1 $\bar{2}$ 10) according to (ΔG_1) – (ΔG_{32}) in equations (14) – (45) of Section S3.

Table S4. Free-energy changes (ΔG) associated with (ΔG_1) – (ΔG_{32}) in equations (14) – (45) of Section S3 for all reactions investigated in the electrochemical reduction of the α -Fe₂O₃(1 $\bar{2}$ 10) facet as a function of different surface coverages at zero applied electrode potential. All values are given in eV.

Surface coverage	ΔG (eV)					
Clean	ΔG_1 : -0.73	ΔG_2 : -0.72	ΔG_3 : -0.42	ΔG_4 : -0.40	ΔG_5 : 0.18	ΔG_6 : 0.17
	ΔG_7 : 0.68	ΔG_8 : 0.49	ΔG_9 : 1.67	ΔG_{10} : 1.92	ΔG_{11} : -0.48	ΔG_{12} : 1.55
Clean as a function of 8*H on the outermost Fe atoms	ΔG_1 : -2.31	ΔG_2 : 0.72	ΔG_3 : 1.84	ΔG_4 : -0.41	ΔG_5 : -0.22	ΔG_6 : 1.12
	ΔG_7 : -0.27	ΔG_8 : 0.59	ΔG_9 : -0.14	ΔG_{10} : -0.09	ΔG_{11} : 0.34	ΔG_{12} : 1.20
8*H _{sub}	ΔG_{13} : 0.29	ΔG_{14} : 0.38	ΔG_{15} : 0.42	ΔG_{16} : 1.48	ΔG_{17} : 0.69	ΔG_{18} : 0.60
	ΔG_{19} : 0.58	ΔG_{20} : -0.08				
12*H _{sub}	ΔG_{21} : -0.38	ΔG_{22} : 0.33	ΔG_{23} : 0.44	ΔG_{24} : -0.18	ΔG_{25} : 0.57	ΔG_{26} : 0.83
	ΔG_{27} : 0.48	ΔG_{28} : 0.88	ΔG_{29} : 0.90	ΔG_{30} : 1.42	ΔG_{31} : 1.77	ΔG_{32} : 0.48

Since each intermediate is obtained by relaxing the preceding structure, the reduced states depend on the reduction sequence: during the removal of *O and *OH species, the geometry and the magnetic configuration evolve differently, so that final states of identical composition reached from different initial surfaces can differ in structure and free energy.

S5 Free-energy span model of $G_{\max}(U)$

Tables S5, S6, and S7 summarize all possible spans for the electrochemical reduction of hematite on the surface. The descriptor $G_{\max}(U)$ is determined by extracting the largest free-energy span for each surface coverage reactions in dependence of U .^{12,27}

Table S5. Possible free-energy spans for the electrochemical reduction starts from clean surface and clean surface as a function of hydrogen on the outermost Fe atoms. The indicated spans refer to a difference in free-energy.

Spans for clean and clean as a function of hydrogen on the outermost Fe atoms					
Span(1)	M12O → M11O	Span(27)	M10O → M6O	Span(53)	M7O → M4O
Span(2)	M12O → M10O	Span(28)	M10O → M5O	Span(54)	M7O → M3O
Span(3)	M12O → M9O	Span(29)	M10O → M4O	Span(55)	M7O → M2O
Span(4)	M12O → M8O	Span(30)	M10O → M3O	Span(56)	M7O → M1O
Span(5)	M12O → M7O	Span(31)	M10O → M2O	Span(57)	M7O → M
Span(6)	M12O → M6O	Span(32)	M10O → M1O	Span(58)	M6O → M5O
Span(7)	M12O → M5O	Span(33)	M10O → M	Span(59)	M6O → M4O
Span(8)	M12O → M4O	Span(34)	M9O → M8O	Span(60)	M6O → M3O
Span(9)	M12O → M3O	Span(35)	M9O → M7O	Span(61)	M6O → M2O
Span(10)	M12O → M2O	Span(36)	M9O → M6O	Span(62)	M6O → M1O
Span(11)	M12O → M1O	Span(37)	M9O → M5O	Span(63)	M6O → M
Span(12)	M12O → M	Span(38)	M9O → M4O	Span(64)	M5O → M4O
Span(13)	M11O → M10O	Span(39)	M9O → M3O	Span(65)	M5O → M3O
Span(14)	M11O → M9O	Span(40)	M9O → M2O	Span(66)	M5O → M2O
Span(15)	M11O → M8O	Span(41)	M9O → M1O	Span(67)	M5O → M1O
Span(16)	M11O → M7O	Span(42)	M9O → M	Span(68)	M5O → M
Span(17)	M11O → M6O	Span(43)	M8O → M7O	Span(69)	M4O → M3O
Span(18)	M11O → M5O	Span(44)	M8O → M6O	Span(70)	M4O → M2O
Span(19)	M11O → M4O	Span(45)	M8O → M5O	Span(71)	M4O → M1O
Span(20)	M11O → M3O	Span(46)	M8O → M4O	Span(72)	M4O → M
Span(21)	M11O → M2O	Span(47)	M8O → M3O	Span(73)	M3O → M2O
Span(22)	M11O → M1O	Span(48)	M8O → M2O	Span(74)	M3O → M1O
Span(23)	M11O → M	Span(49)	M8O → M1O	Span(75)	M3O → M
Span(24)	M10O → M9O	Span(50)	M8O → M	Span(76)	M2O → M1O
Span(25)	M10O → M8O	Span(51)	M7O → M6O	Span(77)	M2O → M
Span(26)	M10O → M7O	Span(52)	M7O → M5O	Span(78)	M1O → M

Table S6. Possible free-energy spans for the electrochemical reduction starts from 8*H_{sub} surface. The indicated spans refer to a difference in free-energy.

Spans for 8*H _{sub} surface (partial reduction on the reactive layer(s))					
Span(1)	M8OH4O → M7OH4O	Span(13)	M7OH4O → M2OH4O	Span(25)	M5OH4O → M1OH4O
Span(2)	M8OH4O → M6OH4O	Span(14)	M7OH4O → M1OH4O	Span(26)	M5OH4O → M4O
Span(3)	M8OH4O → M5OH4O	Span(15)	M7OH4O → M4O	Span(27)	M4OH4O → M3OH4O
Span(4)	M8OH4O → M4OH4O	Span(16)	M6OH4O → M5OH4O	Span(28)	M4OH4O → M2OH4O
Span(5)	M8OH4O → M3OH4O	Span(17)	M6OH4O → M4OH4O	Span(29)	M4OH4O → M1OH4O
Span(6)	M8OH4O → M2OH4O	Span(18)	M6OH4O → M3OH4O	Span(30)	M4OH4O → M4O
Span(7)	M8OH4O → M1OH4O	Span(19)	M6OH4O → M2OH4O	Span(31)	M3OH4O → M2OH4O
Span(8)	M8OH4O → M4O	Span(20)	M6OH4O → M1OH4O	Span(32)	M3OH4O → M1OH4O
Span(9)	M7OH4O → M6OH4O	Span(21)	M6OH4O → M4O	Span(33)	M3OH4O → M4O
Span(10)	M7OH4O → M5OH4O	Span(22)	M5OH4O → M4OH4O	Span(34)	M2OH4O → M1OH4O
Span(11)	M7OH4O → M4OH4O	Span(23)	M5OH4O → M3OH4O	Span(35)	M2OH4O → M4O
Span(12)	M7OH4O → M3OH4O	Span(24)	M5OH4O → M2OH4O	Span(36)	M1OH4O → M4O

Table S7. Possible free-energy spans for the electrochemical reduction starts from 12*H_{sub} surface. The indicated spans refer to a difference in free-energy.

Spans for 12*H _{sub} surface					
Span(1)	M12OH → M11OH	Span(27)	M10OH → M6OH	Span(53)	M7OH → M4OH
Span(2)	M12OH → M10OH	Span(28)	M10OH → M5OH	Span(54)	M7OH → M3OH
Span(3)	M12OH → M9OH	Span(29)	M10OH → M4OH	Span(55)	M7OH → M2OH
Span(4)	M12OH → M8OH	Span(30)	M10OH → M3OH	Span(56)	M7OH → M1OH
Span(5)	M12OH → M7OH	Span(31)	M10OH → M2OH	Span(57)	M7OH → M
Span(6)	M12OH → M6OH	Span(32)	M10OH → M1OH	Span(58)	M6OH → M5OH
Span(7)	M12OH → M5OH	Span(33)	M10OH → M	Span(59)	M6OH → M4OH
Span(8)	M12OH → M4OH	Span(34)	M9OH → M8OH	Span(60)	M6OH → M3OH
Span(9)	M12OH → M3OH	Span(35)	M9OH → M7OH	Span(61)	M6OH → M2OH
Span(10)	M12OH → M2OH	Span(36)	M9OH → M6OH	Span(62)	M6OH → M1OH
Span(11)	M12OH → M1OH	Span(37)	M9OH → M5OH	Span(63)	M6OH → M
Span(12)	M12OH → M	Span(38)	M9OH → M4OH	Span(64)	M5OH → M4OH
Span(13)	M11OH → M10OH	Span(39)	M9OH → M3OH	Span(65)	M5OH → M3OH
Span(14)	M11OH → M9OH	Span(40)	M9OH → M2OH	Span(66)	M5OH → M2OH
Span(15)	M11OH → M8OH	Span(41)	M9OH → M1OH	Span(67)	M5OH → M1OH
Span(16)	M11OH → M7OH	Span(42)	M9OH → M	Span(68)	M5OH → M
Span(17)	M11OH → M6OH	Span(43)	M8OH → M7OH	Span(69)	M4OH → M3OH
Span(18)	M11OH → M5OH	Span(44)	M8OH → M6OH	Span(70)	M4OH → M2OH
Span(19)	M11OH → M4OH	Span(45)	M8OH → M5OH	Span(71)	M4OH → M1OH
Span(20)	M11OH → M3OH	Span(46)	M8OH → M4OH	Span(72)	M4OH → M
Span(21)	M11OH → M2OH	Span(47)	M8OH → M3OH	Span(73)	M3OH → M2OH
Span(22)	M11OH → M1OH	Span(48)	M8OH → M2OH	Span(74)	M3OH → M1OH
Span(23)	M11OH → M	Span(49)	M8OH → M1OH	Span(75)	M3OH → M
Span(24)	M10OH → M9OH	Span(50)	M8OH → M	Span(76)	M2OH → M1OH
Span(25)	M10OH → M8OH	Span(51)	M7OH → M6OH	Span(77)	M2OH → M
Span(26)	M10OH → M7OH	Span(52)	M7OH → M5OH	Span(78)	M1OH → M

S6 Free-energy diagrams for the electrochemical reduction of hematite

S6.1 Clean surface

In this section, we present potential-dependent free-energy landscapes for the electrochemical reduction of the (0001), (10 $\bar{1}$ 0), and (1 $\bar{2}$ 10) facets starting from the clean surface. The free-energy changes associated with the reaction steps outlined in $\Delta G_1 - \Delta G_{12}$ or equations (14) – (25) of Section S3 are compiled in **Tables S2–S4** (cf. Section S4). Knowledge of these free-

energy changes enables the construction of free-energy diagrams along the reaction coordinate, which are analyzed at $U = -0.7$ V vs. RHE (cf. **Figures S5–S7**). All possible free-energy spans are summarized in **Table S5** (cf. Section S5). The limiting free-energy span for each facet is shown by vertical green arrow which is uphill in free-energy. The inset images on the left and right depict the surface structures before and after reduction, respectively.

S6.1.1 Free-energy diagram for $\alpha\text{-Fe}_2\text{O}_3(0001)$ -clean reduction: VASPsol

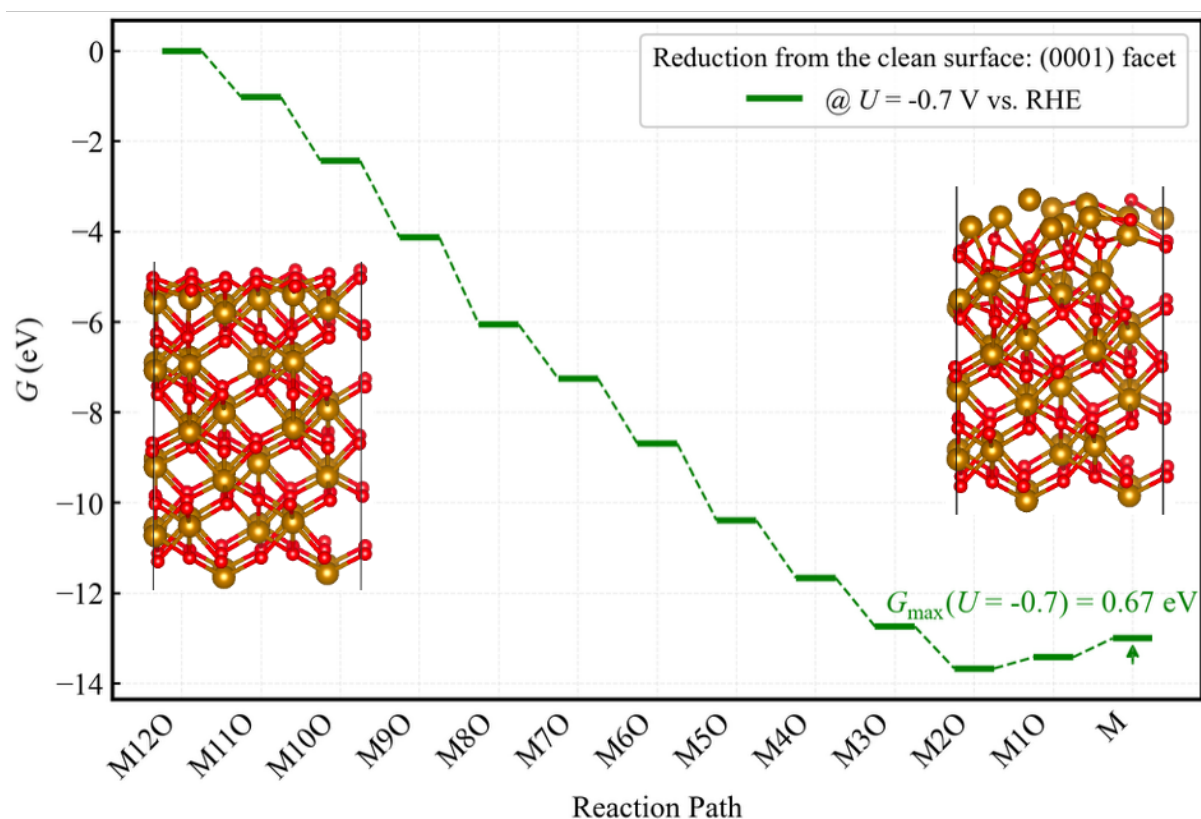


Figure S5. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(0001)$ -clean surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

S6.1.2 Free-energy diagram for $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)$ -clean reduction: VASPsol

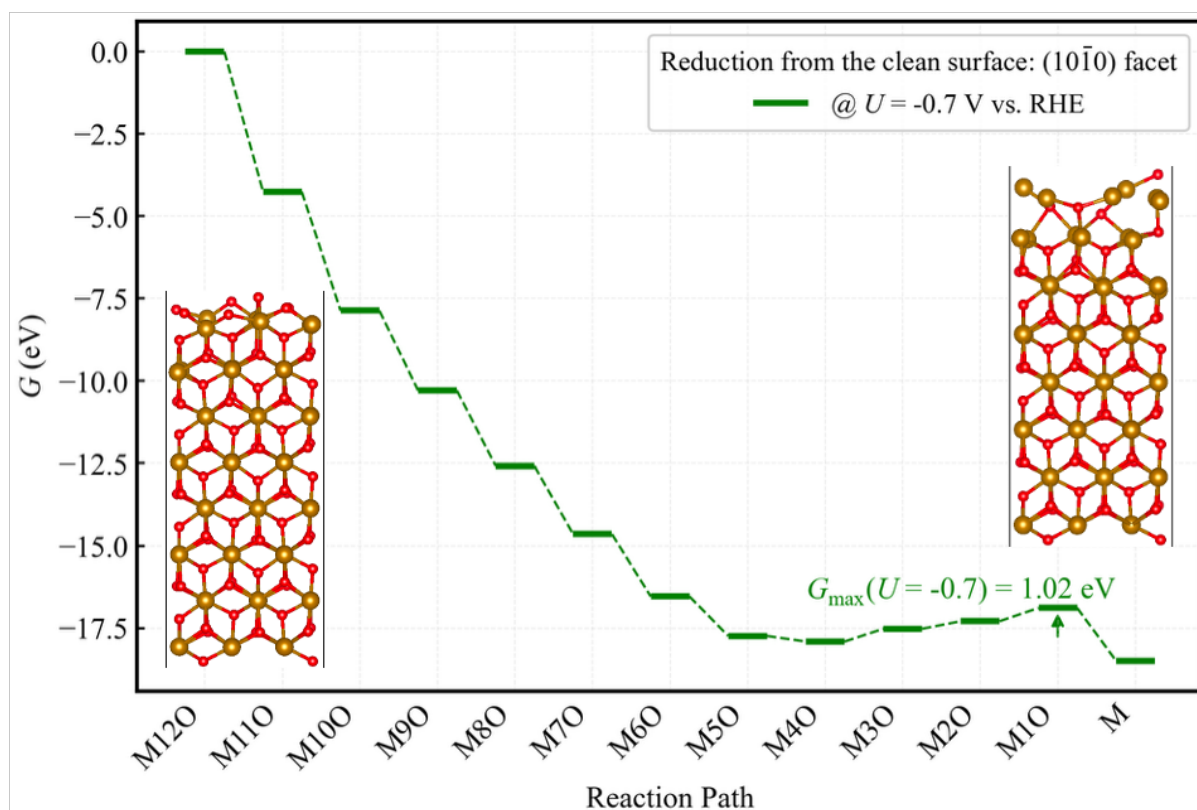


Figure S6. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)$ -clean surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

S6.1.3 Free-energy diagram for $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ -clean reduction: VASPsol

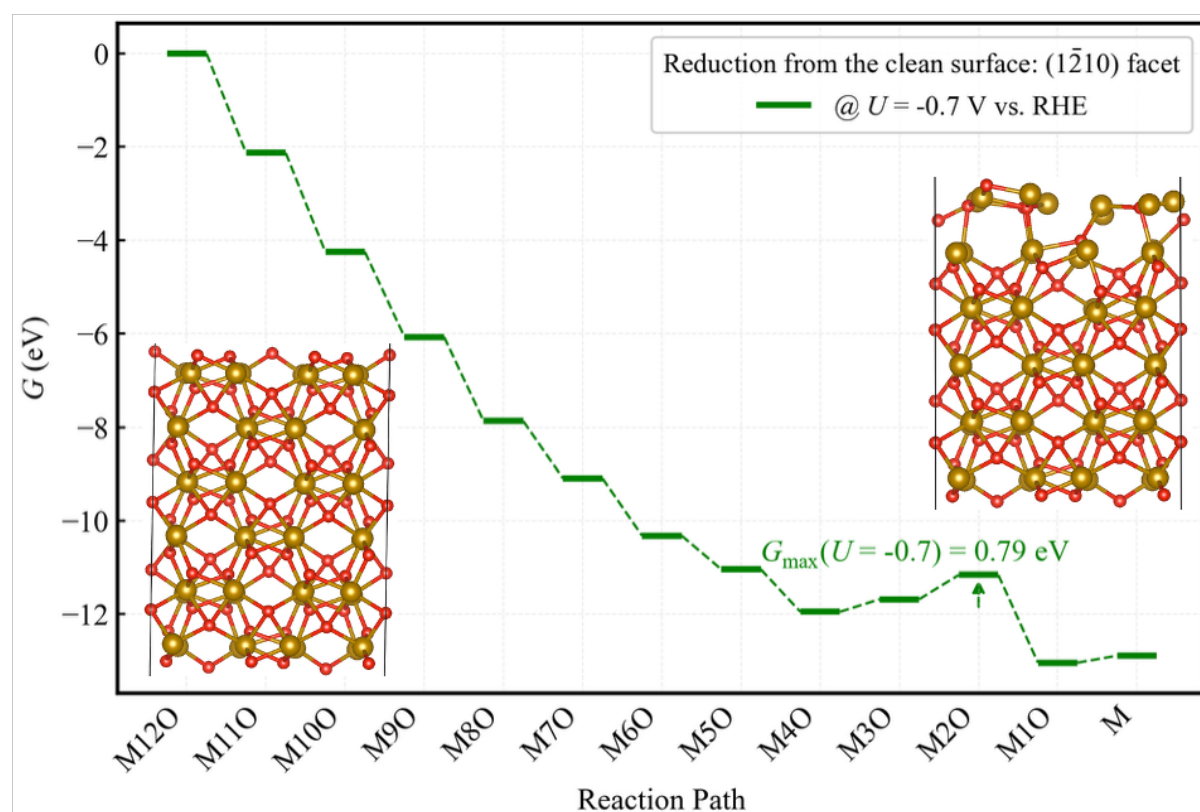


Figure S7. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ -clean surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

S6.2 Hydrogenated hematite surfaces

In this section, we present potential-dependent free-energy landscapes for the electrochemical reduction of the (0001), ($10\bar{1}0$), and ($1\bar{2}10$) facets starting from hydrogenated hematite surfaces. The free-energy changes associated with the reaction steps outlined in $(\Delta G_{13}) - (\Delta G_{32})$ or equations (26) – (45) of Section S3 are compiled in **Tables S2–S4** (cf. section S4). Knowledge of these free-energy changes enables the construction of free-energy diagrams along the reaction coordinate, which are analyzed at $U = -0.7$ V vs. RHE (cf. **Figures S8–S19**). All possible free-energy spans are summarized in **Tables S6** and **S7** (cf. Section S5). The limiting free-energy span for each facet is shown by vertical green arrow which is uphill in free-energy. The inset images on the left and right depict the surface structures before and after reduction, respectively.

S6.2.1 Free-energy diagram for the α -Fe₂O₃(0001)

Free-energy diagram for the α -Fe₂O₃(0001)-4*H & clean reduction: VASPsol

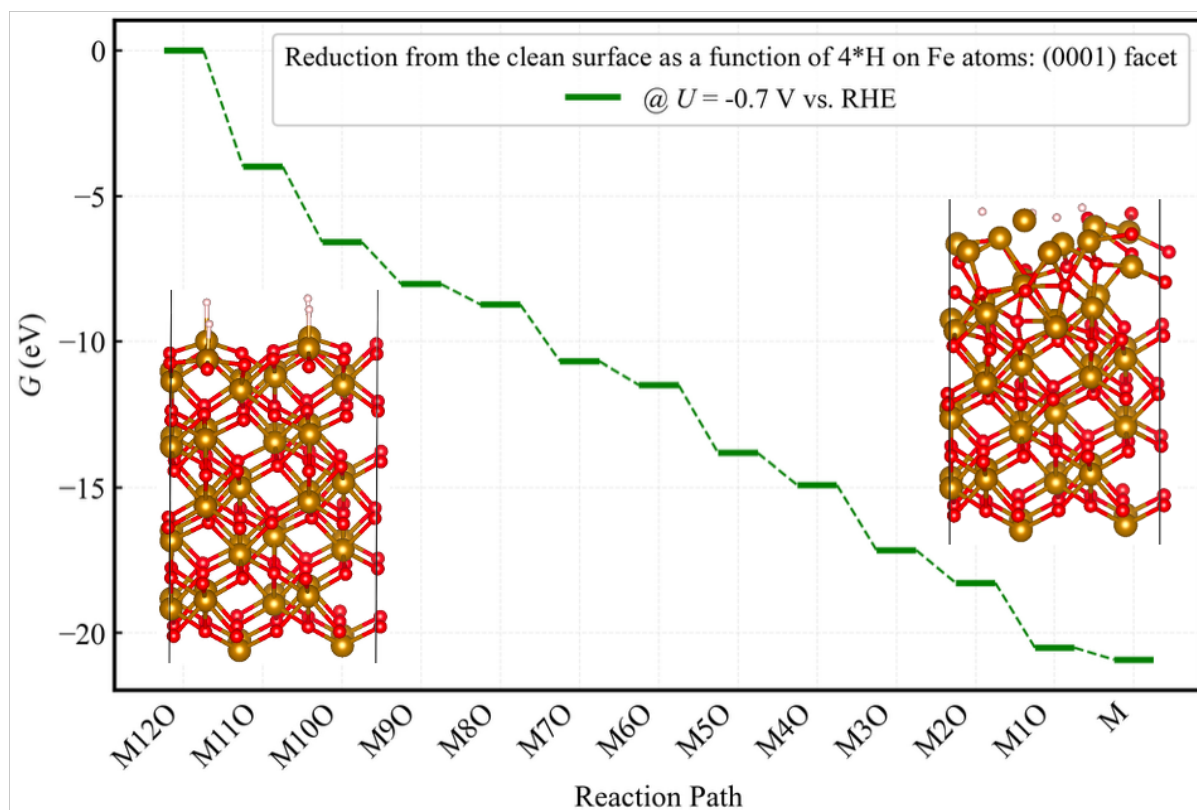


Figure S8. Potential-dependent free-energy diagram for the electrochemical reduction of the α -Fe₂O₃(0001)-4*H & clean surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

Free-energy diagram for the $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}8^*\text{H}_{\text{sub}}$ reduction: Gas phase DFT

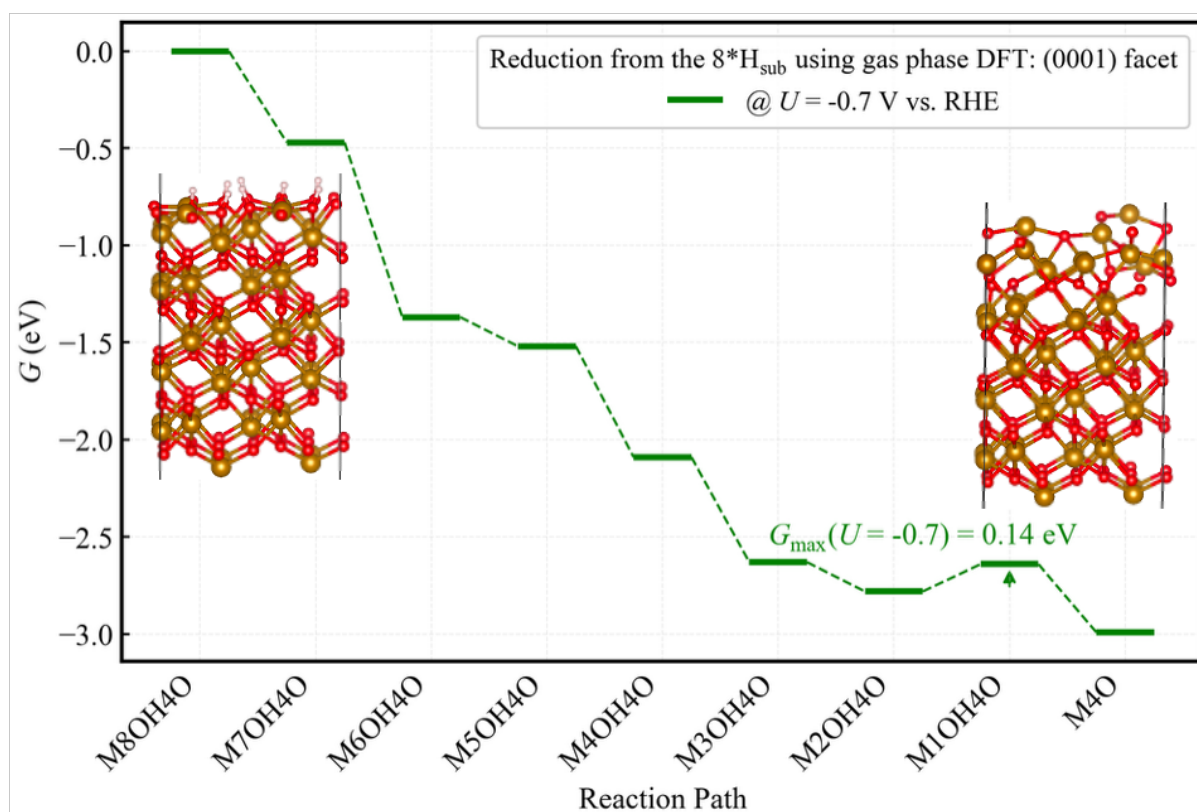


Figure S9. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}8^*\text{H}_{\text{sub}}$ surface using gas phase DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

Free-energy diagram for the $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}8^*\text{H}_{\text{sub}}$ reduction: VASPsol

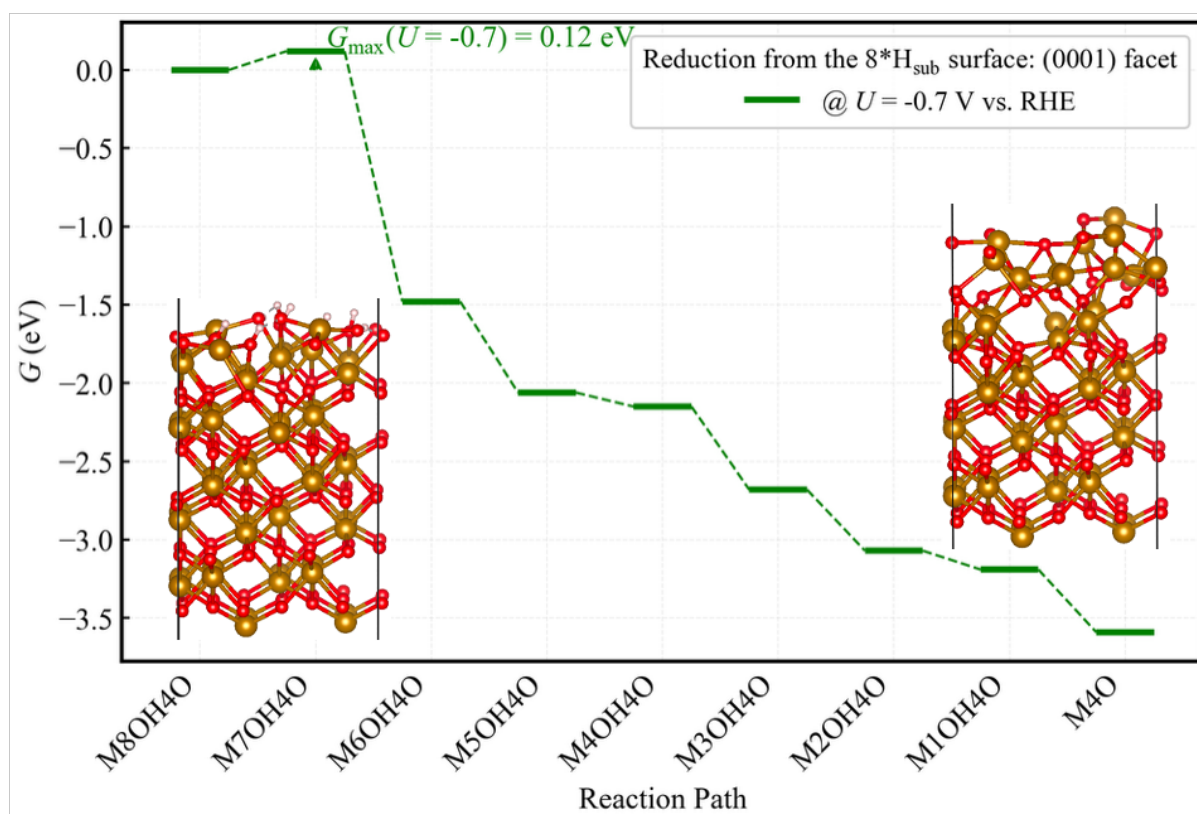


Figure S10. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}8^*\text{H}_{\text{sub}}$ surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

Free-energy diagram for the $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}4^*\text{H}$ & 8^*H_{sub} reduction: VASPsol

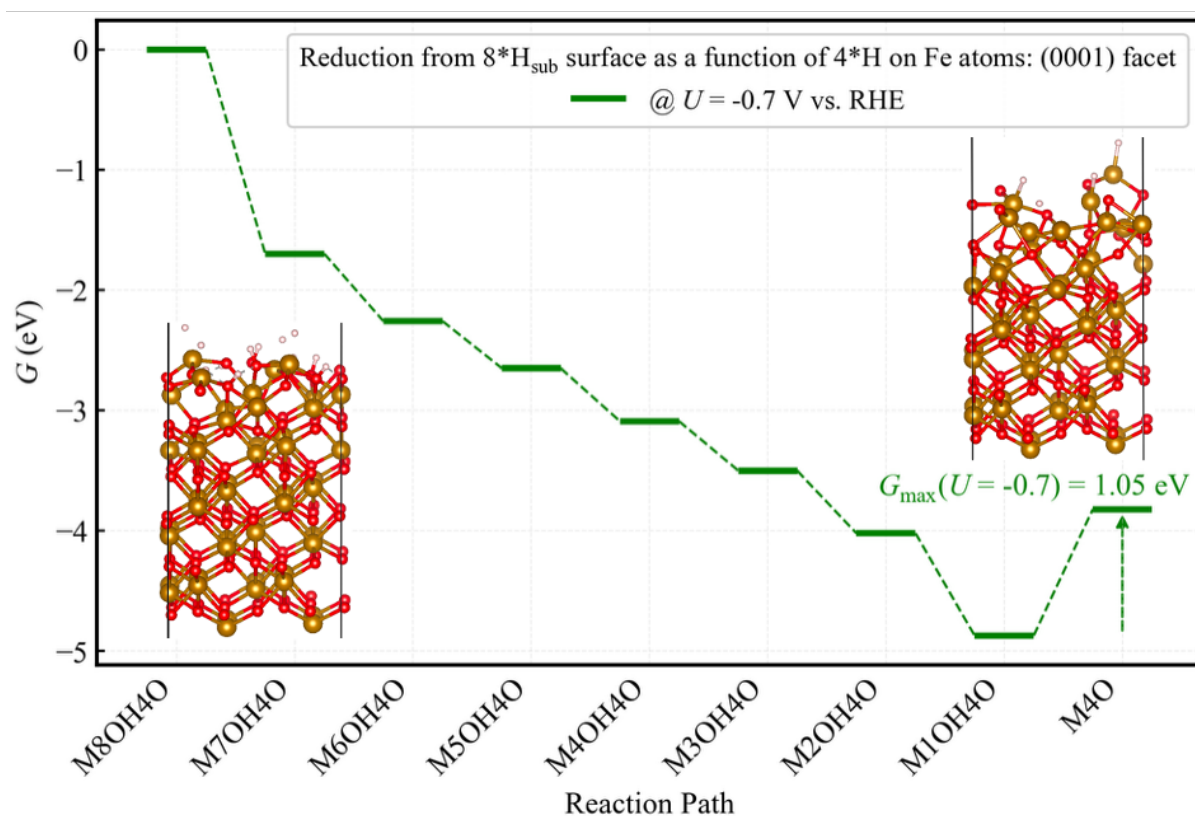


Figure S11. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}4^*\text{H}$ & 8^*H_{sub} surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

Free-energy diagram for the $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}12^*\text{H}_{\text{sub}}$ reduction: VASPsol

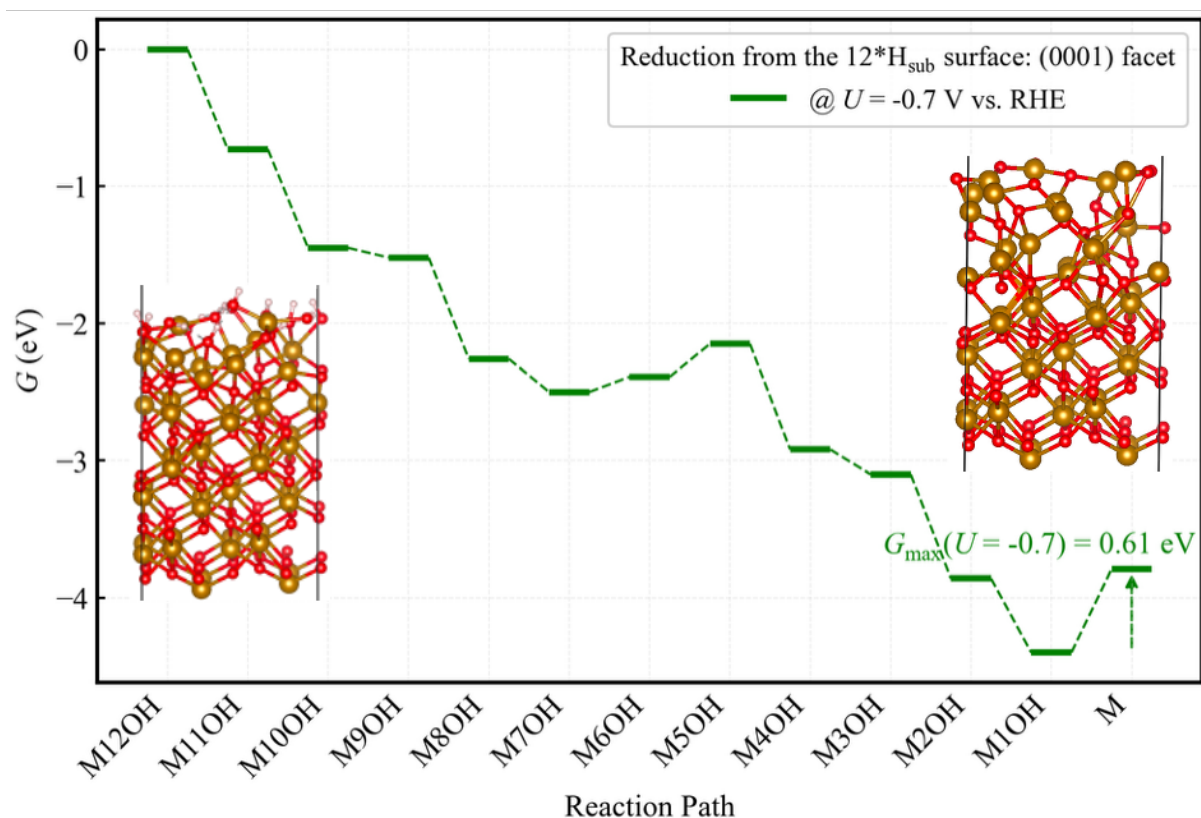


Figure S12. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}12^*\text{H}_{\text{sub}}$ surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

Free-energy diagram for the $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}4^*\text{H}$ & $12^*\text{H}_{\text{sub}}$ reduction: VASPsol

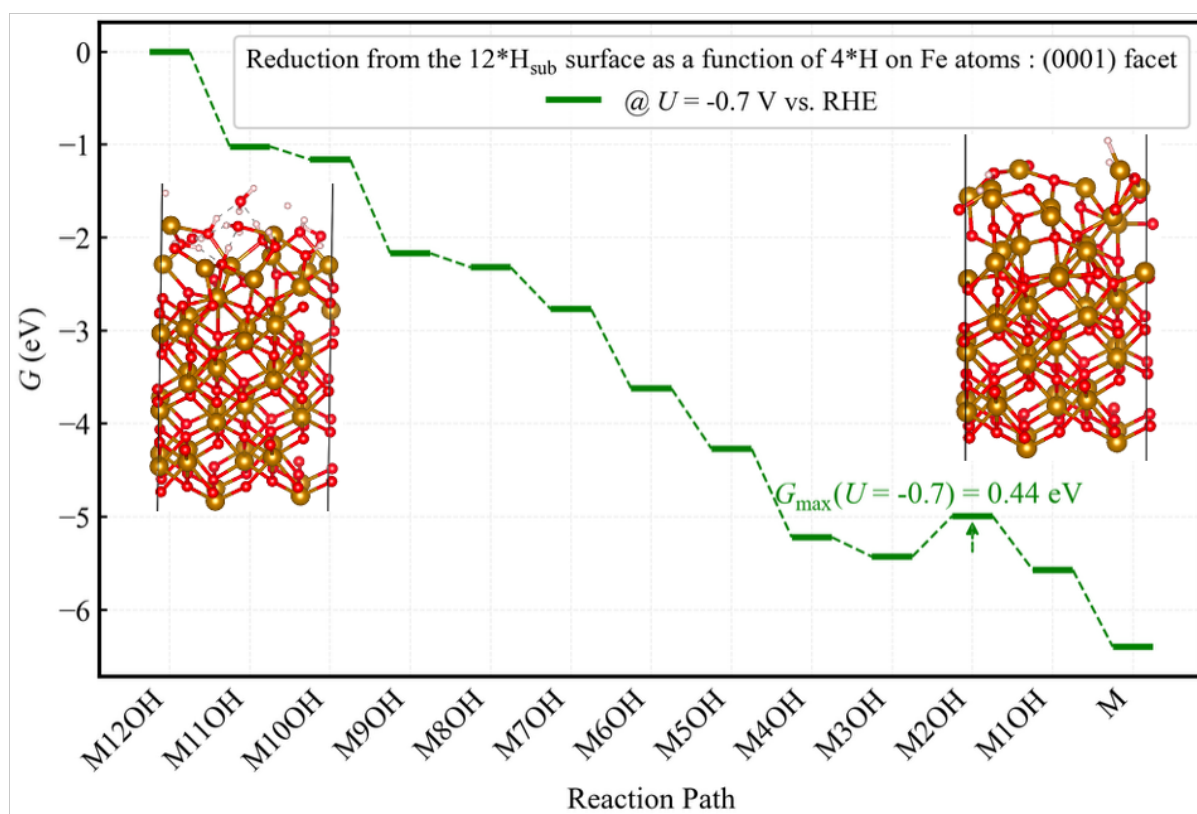


Figure S13. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}4^*\text{H}$ & $12^*\text{H}_{\text{sub}}$ surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

S6.2.2 Free-energy diagram for the $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)$

Free-energy diagram for $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)\text{-}6^*\text{H}$ & clean reduction: VASPsol

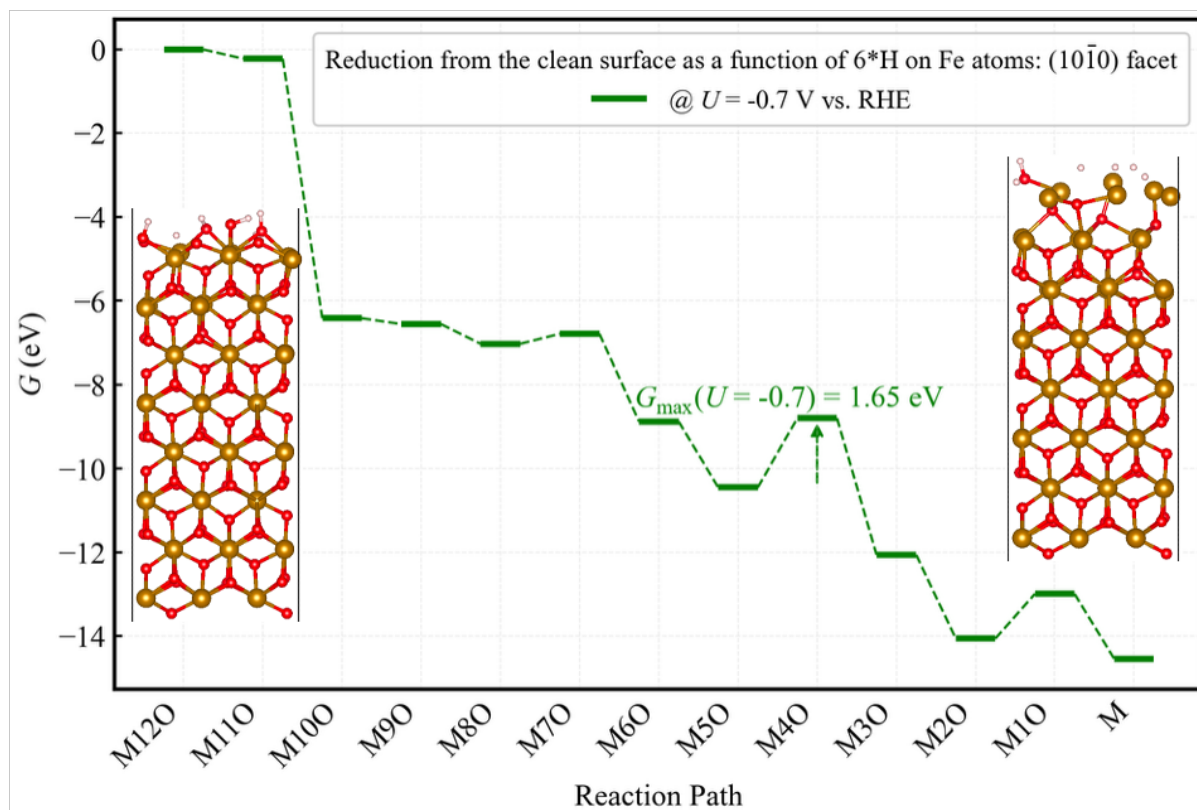


Figure S14. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)\text{-}6^*\text{H}$ & clean surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

Free-energy diagram for $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)\text{-}8^*\text{H}_{\text{sub}}$ reduction: VASPsol

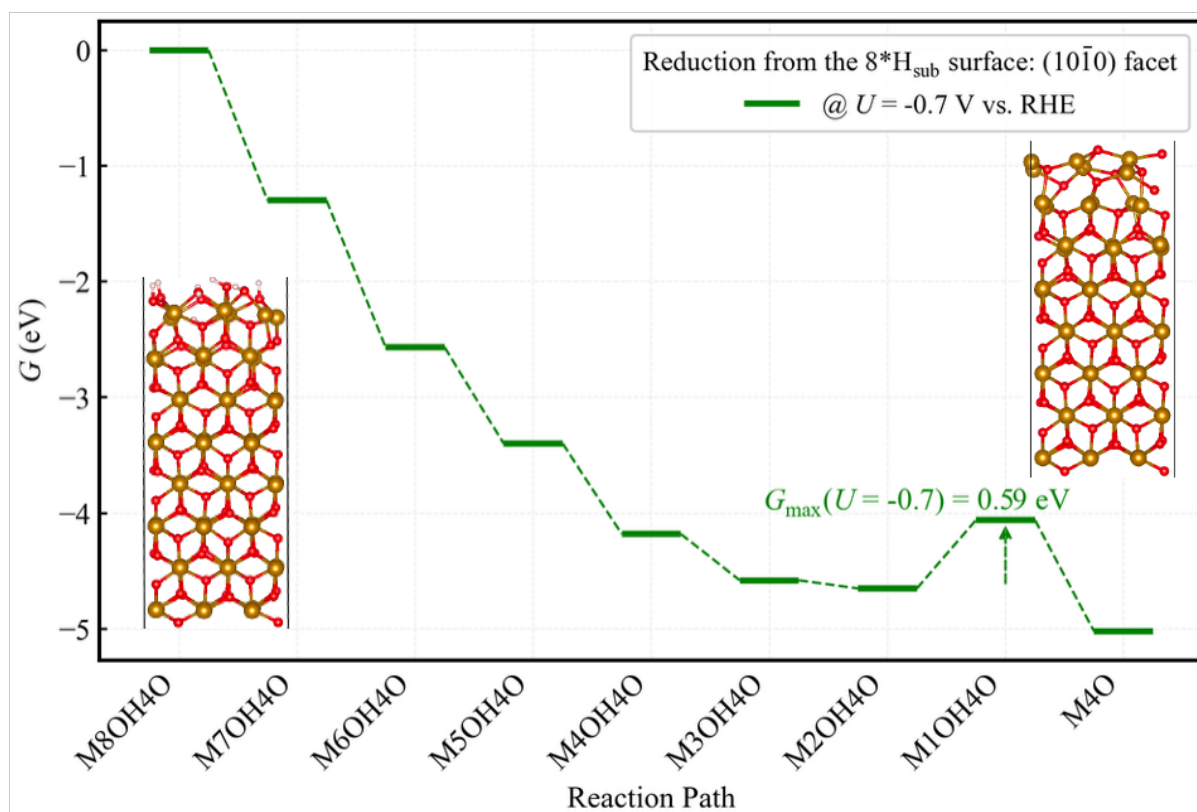


Figure S15. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)\text{-}8^*\text{H}_{\text{sub}}$ surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

Free-energy diagram for $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)\text{-}12^*\text{H}_{\text{sub}}$ reduction: VASPsol

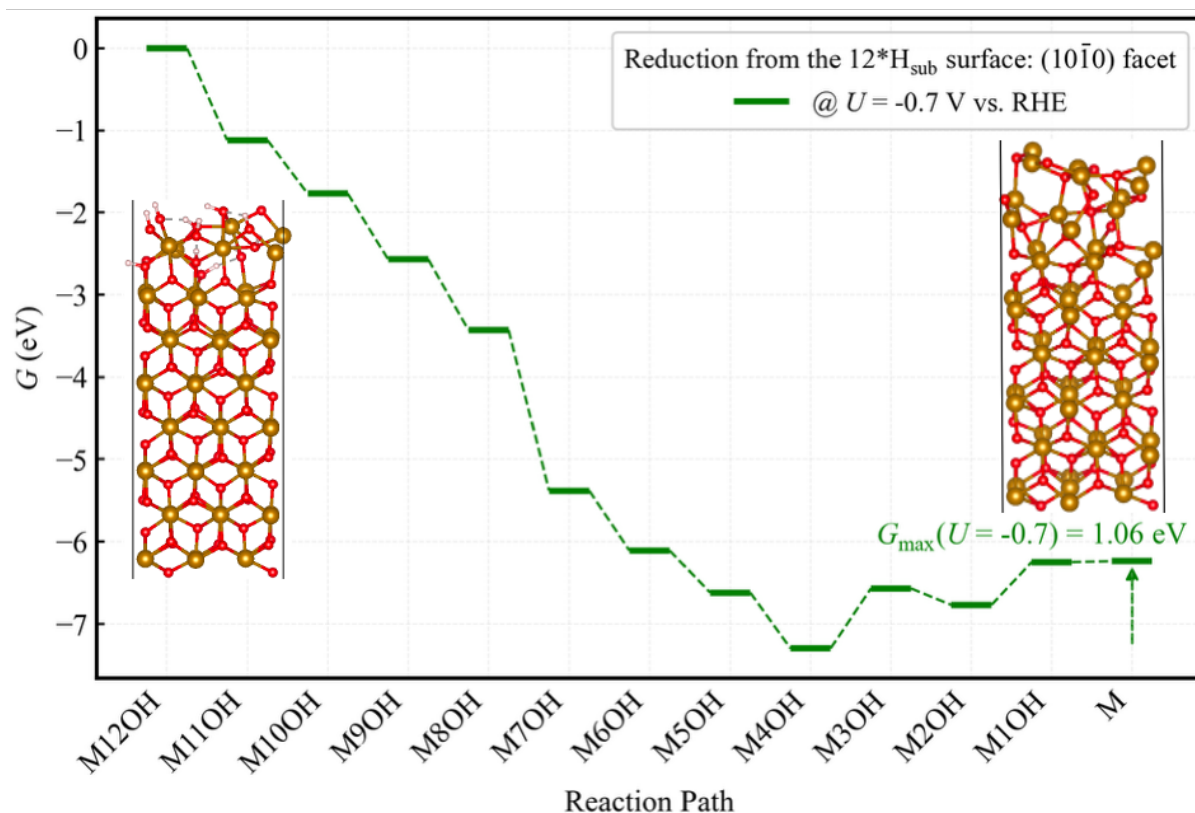


Figure S16. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)\text{-}12^*\text{H}_{\text{sub}}$ surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

S6.2.3 Free-energy diagram for the $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$

Free-energy diagram for $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ - 8^*H & clean reduction: VASPsol

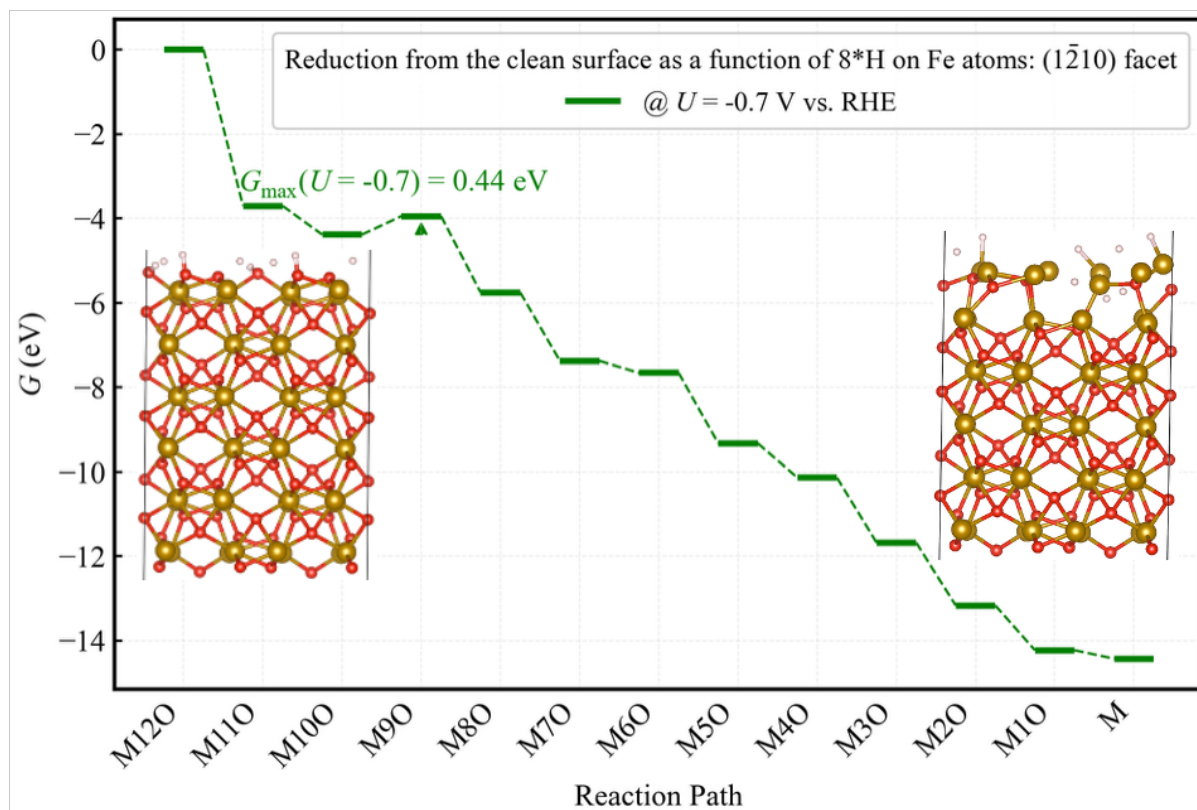


Figure S17. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ - 8^*H & clean surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

Free-energy diagram for $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)\text{-}8^*\text{H}_{\text{sub}}$ reduction: VASPsol

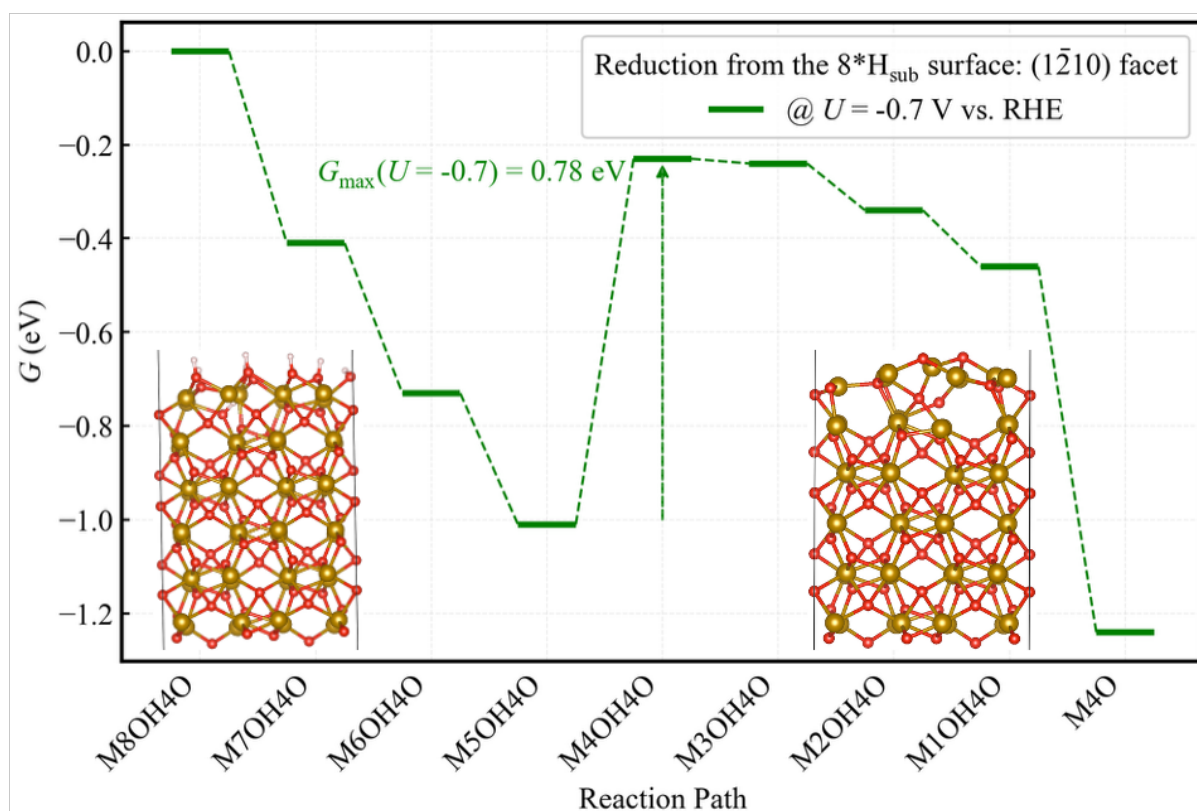


Figure S18. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)\text{-}8^*\text{H}_{\text{sub}}$ surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

Free-energy diagram for $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ - $12^*\text{H}_{\text{sub}}$ reduction: VASPsol

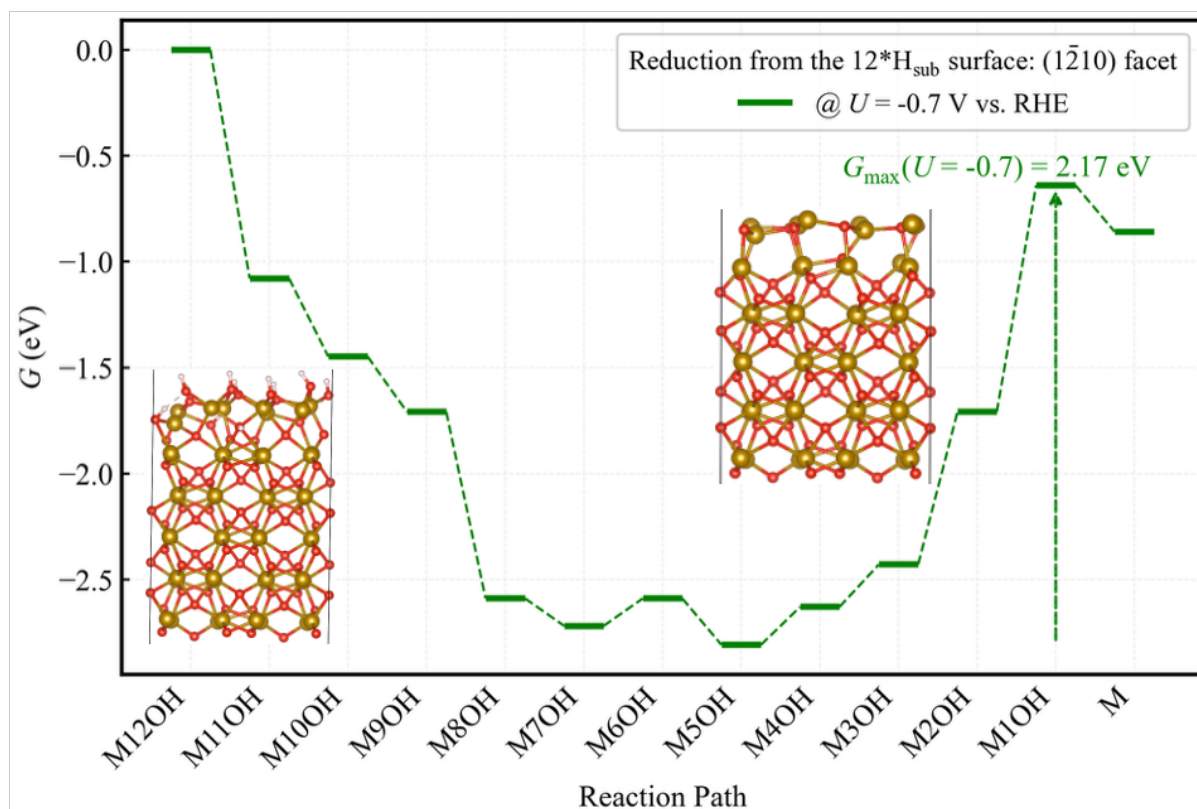


Figure S19. Potential-dependent free-energy diagram for the electrochemical reduction of the $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ - $12^*\text{H}_{\text{sub}}$ surface using VASPsol DFT. The inset images on the left and right depict the surface structures before and after reduction, respectively.

S7 D-band and p-band center as an electronic structure descriptor

S7.1 D-band center

As further descriptor for the electrochemical reduction of hematite, we calculated the d-band center of the top three reactive layers for the surfaces before and after reduction. The results are presented in **Table S8**.

Table S8. D-band center before and after the electrochemical reduction of α -Fe₂O₃(0001), α -Fe₂O₃(10 $\bar{1}$ 0), and α -Fe₂O₃(1 $\bar{2}$ 10) facets for the surface coverages considering the top three reactive layers, within the energy interval of -10 to 4 eV.

Facet	Surfaces	D-band center/ eV		Change in d-band center / eV
		Before reduction (B)	After reduction (A)	D-band (A)-D-band(B)
(0001)	α -Fe ₂ O ₃ -clean	0.09	-1.47	-1.56
	α -Fe ₂ O ₃ -4*H & clean	0.08	-1.19	-1.27
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	-0.51	-1.43	-0.92
	α -Fe ₂ O ₃ -12*H _{sub}	-1.25	-1.50	-0.25
(10 $\bar{1}$ 0)	α -Fe ₂ O ₃ -clean	0.38	-1.44	-1.82
	α -Fe ₂ O ₃ -6*H & clean	0.92	-1.33	-2.26
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	-0.03	-1.00	-0.97
	α -Fe ₂ O ₃ -12*H _{sub}	-0.61	-1.44	-0.83
(1 $\bar{2}$ 10)	α -Fe ₂ O ₃ -clean	0.41	-1.64	-2.05
	α -Fe ₂ O ₃ -8*H & clean	0.00	-1.45	-1.45
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	-0.43	-1.37	-0.94
	α -Fe ₂ O ₃ -12*H _{sub}	-0.76	-1.58	-0.82

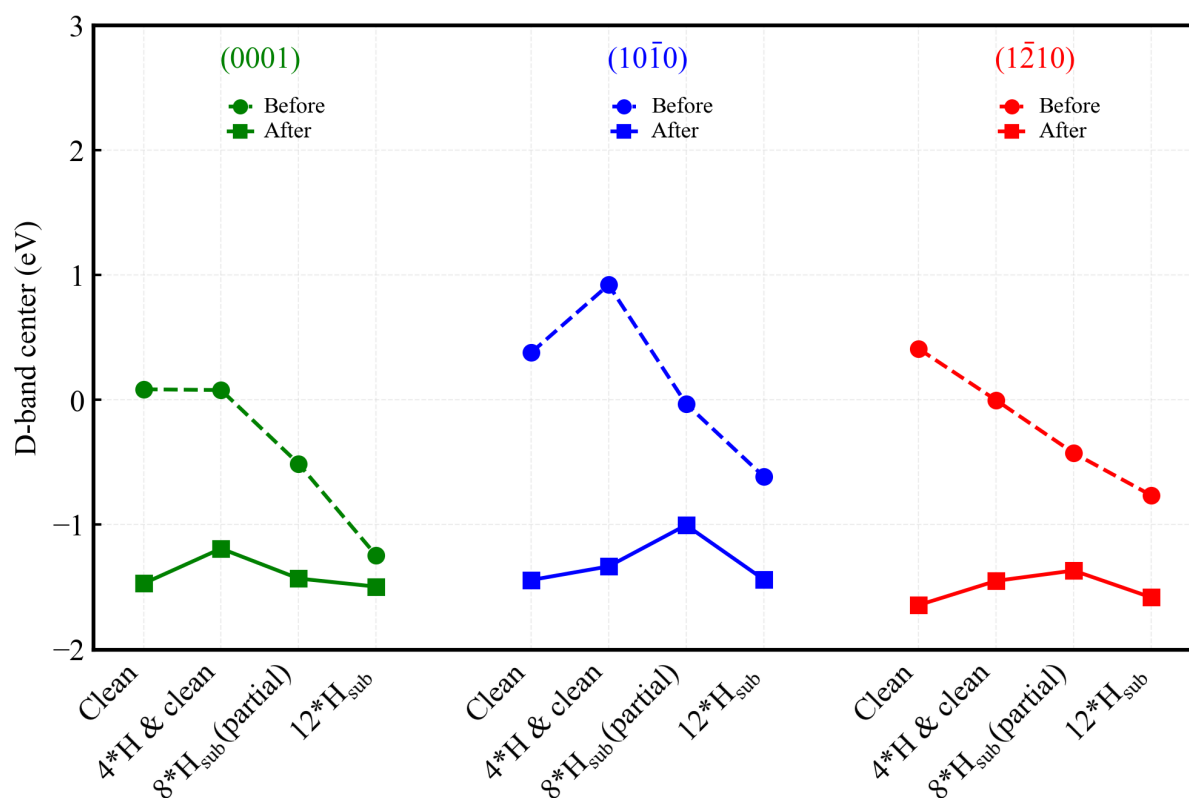


Figure S20. D-band center values before and after the electrochemical reduction of α -Fe₂O₃(0001), α -Fe₂O₃(10 $\bar{1}$ 0), and α -Fe₂O₃(1 $\bar{2}$ 10) facets for the selected surface coverages for reactive layers, within the energy interval -10 to 4 eV. The green plot represents the (0001), the blue plot corresponds to the (10 $\bar{1}$ 0), and the red plot is for the (1 $\bar{2}$ 10) facet.

Table S9. D-band center before and after the electrochemical reduction of α -Fe₂O₃(0001), α -Fe₂O₃(10 $\bar{1}$ 0), and α -Fe₂O₃(1 $\bar{2}$ 10) facets for the surface coverages considering the non-reactive layers, within the energy interval of -10 to 4 eV.

Facet	Surfaces	D-band center/ eV		Change in d-band center / eV
		Before reduction (B)	After reduction (A)	D-band (A)-D-band(B)
(0001)	α -Fe ₂ O ₃ -clean	0.46	0.14	-0.32
	α -Fe ₂ O ₃ -4*H & clean	0.85	0.65	-0.20
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	0.81	-0.39	-1.20
	α -Fe ₂ O ₃ -12*H _{sub}	-0.27	-0.39	-0.13
(10 $\bar{1}$ 0)	α -Fe ₂ O ₃ -clean	0.11	-0.33	-0.45
	α -Fe ₂ O ₃ -6*H & clean	0.00	-0.32	-0.32
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	0.16	0.04	-0.12
	α -Fe ₂ O ₃ -12*H _{sub}	0.08	-0.39	-0.47
(1 $\bar{2}$ 10)	α -Fe ₂ O ₃ -clean	0.51	-0.39	-0.90
	α -Fe ₂ O ₃ -8*H & clean	0.26	0.33	0.07
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	0.12	0.10	-0.01
	α -Fe ₂ O ₃ -12*H _{sub}	0.04	-0.17	-0.21

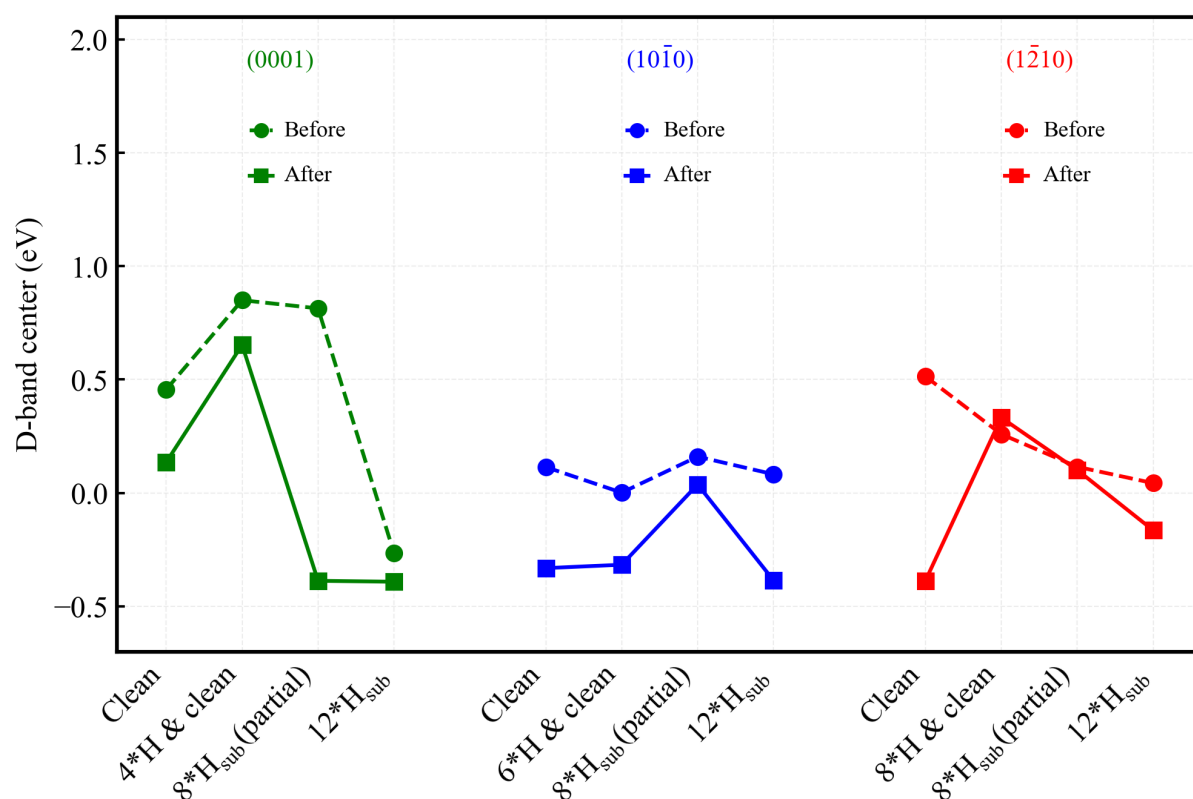


Figure S21. D-band center values before and after the electrochemical reduction of α -Fe₂O₃(0001), α -Fe₂O₃(10 $\bar{1}$ 0), and α -Fe₂O₃(1 $\bar{2}$ 10) facets for the selected surface coverages for non-reactive layers, within the energy interval -10 to 4 eV. The green plot represents the (0001), the blue plot corresponds to the (10 $\bar{1}$ 0), and the red plot is for the (1 $\bar{2}$ 10) facet.

Table S10. D-band center before and after the electrochemical reduction of α -Fe₂O₃(0001), α -Fe₂O₃(10 $\bar{1}$ 0), and α -Fe₂O₃(1 $\bar{2}$ 10) facets for the surface coverages considering all Fe atoms in the supercell, within the energy interval of -10 to 4 eV.

Facet	Surfaces	D-band center/ eV		Change in d-band center / eV
		Before reduction (B)	After reduction (A)	D-band (A)-D-band(B)
(0001)	α -Fe ₂ O ₃ -clean	0.27	-0.57	-0.84
	α -Fe ₂ O ₃ -4*H & clean	0.51	-0.18	-0.69
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	0.25	-0.80	-1.05
	α -Fe ₂ O ₃ -12*H _{sub}	-0.64	-0.85	-0.21
(10 $\bar{1}$ 0)	α -Fe ₂ O ₃ -clean	0.17	-0.71	-0.88
	α -Fe ₂ O ₃ -6*H & clean	0.01	-0.66	-0.66
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	0.09	-0.29	-0.38
	α -Fe ₂ O ₃ -12*H _{sub}	-0.19	-0.80	-0.61
(1 $\bar{2}$ 10)	α -Fe ₂ O ₃ -clean	0.38	-0.79	-1.17
	α -Fe ₂ O ₃ -8*H & clean	0.13	-0.42	-0.54
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	-0.12	-0.43	-0.32
	α -Fe ₂ O ₃ -12*H _{sub}	-0.28	-0.70	-0.42

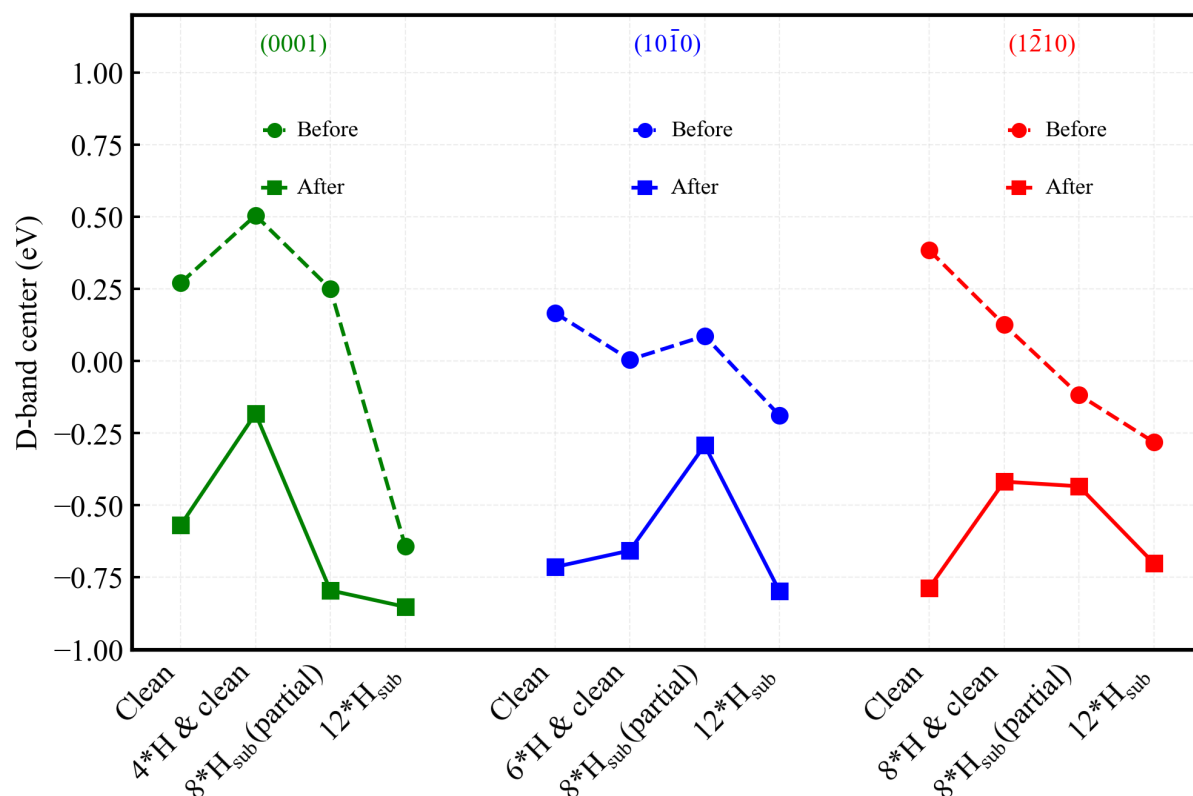


Figure S22. D-band center values before and after the electrochemical reduction of α -Fe₂O₃(0001), α -Fe₂O₃(10 $\bar{1}$ 0), and α -Fe₂O₃(1 $\bar{2}$ 10) facets for the selected surface coverages for all Fe atoms in the supercell, within the energy interval -10 to 4 eV. The green plot represents the (0001), the blue plot corresponds to the (10 $\bar{1}$ 0), and the red plot is for the (1 $\bar{2}$ 10) facet.

The d-band center descriptor does not reveal a clear correlation with the electrochemical reduction activity of the three investigated facets.

S7.2 P-band center

Table S11. P-band center before and after the electrochemical reduction of α -Fe₂O₃(0001), α -Fe₂O₃(10 $\bar{1}$ 0), and α -Fe₂O₃(1 $\bar{2}$ 10) facets for the surface coverages considering non-reactive layers for O atoms, within the energy interval of -10 to 4 eV.

Facet	Surfaces	P-band center/ eV		Change in p-band center / eV
		Before reduction (B)	After reduction (A)	P-band (A)-P-band(B)
(0001)	α -Fe ₂ O ₃ -clean	-2.32	-2.73	-0.41
	α -Fe ₂ O ₃ -4*H & clean	-1.69	-2.24	-0.55
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	-2.05	-3.17	-1.12
	α -Fe ₂ O ₃ -12*H _{sub}	-3.08	-3.73	-0.64
(10 $\bar{1}$ 0)	α -Fe ₂ O ₃ -clean	-2.41	-2.72	-0.31
	α -Fe ₂ O ₃ -6*H & clean	-2.43	-2.73	-0.30
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	-2.25	-2.41	-0.16
	α -Fe ₂ O ₃ -12*H _{sub}	-2.37	-2.79	-0.41
(1 $\bar{2}$ 10)	α -Fe ₂ O ₃ -clean	-2.40	-2.88	-0.48
	α -Fe ₂ O ₃ -8*H & clean	-2.58	-2.51	0.07
	α -Fe ₂ O ₃ -8*H _{sub} (partial)	-2.65	-2.55	0.10
	α -Fe ₂ O ₃ -12*H _{sub}	-2.64	-2.72	-0.08

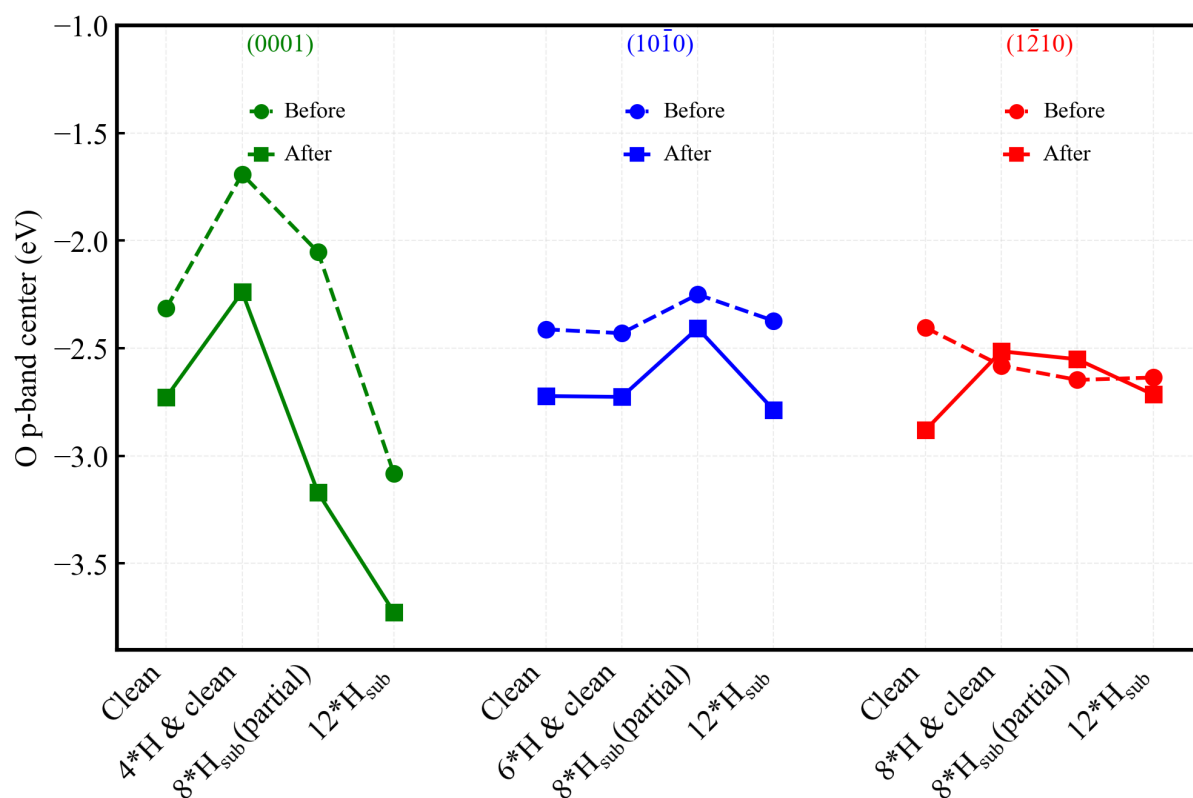


Figure S23. P-band center values before and after the electrochemical reduction of α -Fe₂O₃(0001), α -Fe₂O₃(10 $\bar{1}$ 0), and α -Fe₂O₃(1 $\bar{2}$ 10) facets for the selected surface coverages for non-reactive layers of O atoms within the energy interval -10 to 4 eV. The green plot represents the (0001), the blue plot corresponds to the (10 $\bar{1}$ 0), and the red plot is for the (1 $\bar{2}$ 10) facet.

Upon reduction, the O p-band center shifts most strongly on the (0001) facet, both on average over the complete reduction sequences and for the hydrogen-covered states, which qualitatively parallels its highest reducibility. However, the O p-band center does not reproduce the ordering of the two non-basal facets and shows no systematic correlation with $G_{\max}(U)$; it therefore serves as a qualitative indicator rather than as a quantitative descriptor of reducibility.

Table S12. P-band center before and after the electrochemical reduction of $\alpha\text{-Fe}_2\text{O}_3(0001)$, $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)$, and $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ facets for the surface coverages considering all O atoms in the supercell, within the energy interval of -10 to 4 eV.

Facet	Surfaces	P-band center/ eV		Change in p-band center / eV
		Before reduction (B)	After reduction (A)	P-band (A)-P-band(B)
(0001)	$\alpha\text{-Fe}_2\text{O}_3\text{-clean}$	-2.46	-2.79	-0.33
	$\alpha\text{-Fe}_2\text{O}_3\text{-4*H \& clean}$	-1.72	-2.36	-0.64
	$\alpha\text{-Fe}_2\text{O}_3\text{-8*H}_{\text{sub}}(\text{partial})$	-2.26	-3.23	-0.97
	$\alpha\text{-Fe}_2\text{O}_3\text{-12*H}_{\text{sub}}$	-3.26	-3.03	0.23
(10 $\bar{1}0$)	$\alpha\text{-Fe}_2\text{O}_3\text{-clean}$	-2.33	-2.78	-0.45
	$\alpha\text{-Fe}_2\text{O}_3\text{-6*H \& clean}$	-2.52	-2.79	-0.27
	$\alpha\text{-Fe}_2\text{O}_3\text{-8*H}_{\text{sub}}(\text{partial})$	-2.35	-2.51	-0.16
	$\alpha\text{-Fe}_2\text{O}_3\text{-12*H}_{\text{sub}}$	-2.51	-2.89	-0.37
(1 $\bar{2}10$)	$\alpha\text{-Fe}_2\text{O}_3\text{-clean}$	-2.39	-2.96	-0.57
	$\alpha\text{-Fe}_2\text{O}_3\text{-8*H \& clean}$	-2.63	-2.60	0.03
	$\alpha\text{-Fe}_2\text{O}_3\text{-8*H}_{\text{sub}}(\text{partial})$	-2.65	-2.63	0.02
	$\alpha\text{-Fe}_2\text{O}_3\text{-12*H}_{\text{sub}}$	-2.79	-2.81	-0.03

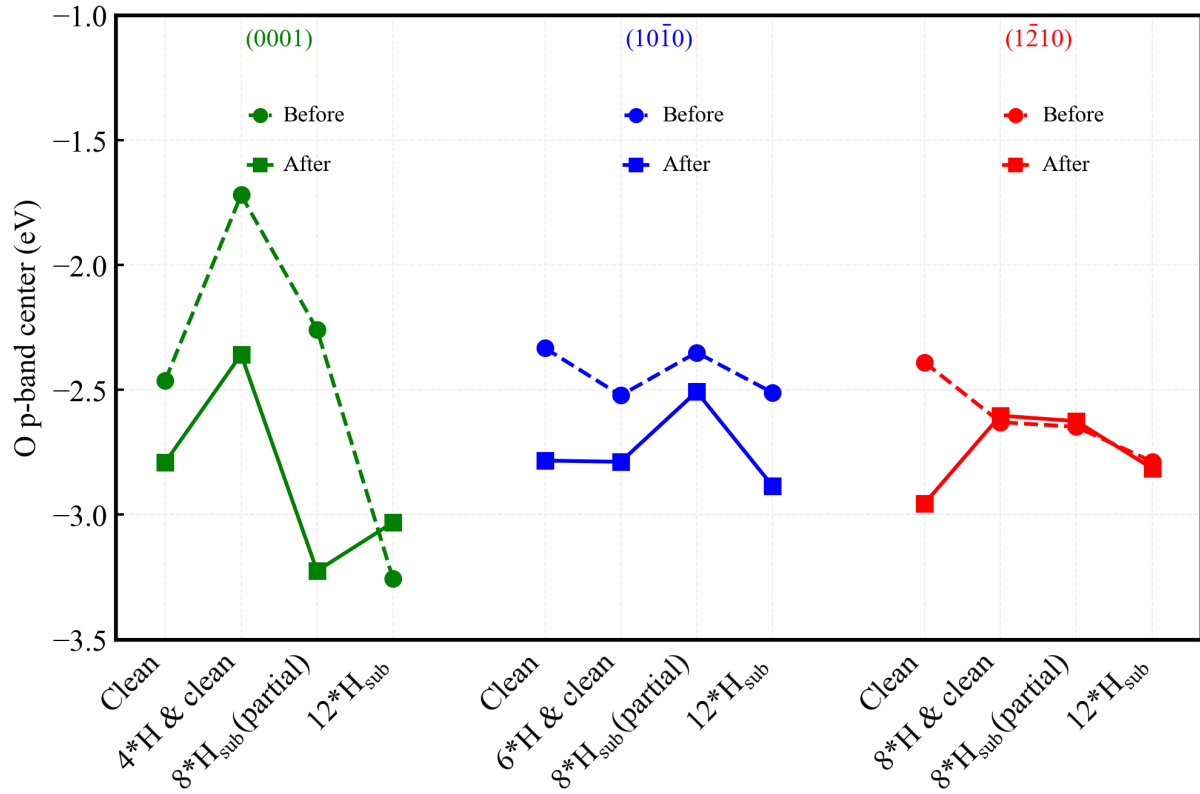


Figure S24. P-band center values before and after the electrochemical reduction of $\alpha\text{-Fe}_2\text{O}_3(0001)$, $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)$, and $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ facets for the selected surface coverages for all O atoms in the supercell, within the energy interval -10 to 4 eV. The green plot represents the (0001), the blue plot corresponds to the (10 $\bar{1}$ 0), and the red plot is for the (1 $\bar{2}$ 10) facet.

S8 Density of states (DOS)

In this section, we present the density of states before and after the electrochemical reduction.

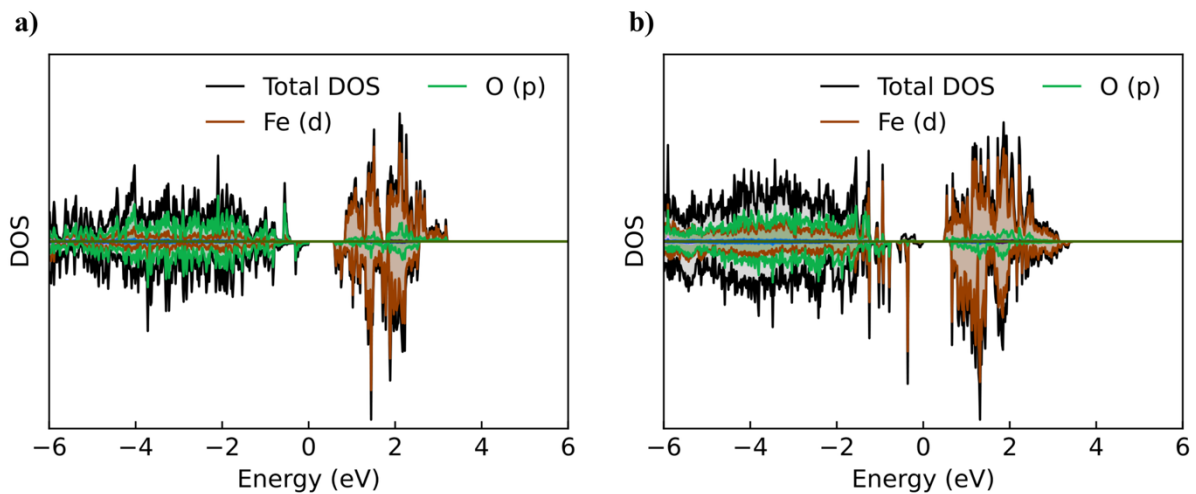


Figure S25. DOS of $\alpha\text{-Fe}_2\text{O}_3(0001)$ -clean surface. **a)** before the electrochemical reduction, and **b)** after the electrochemical reduction using VASPsol.

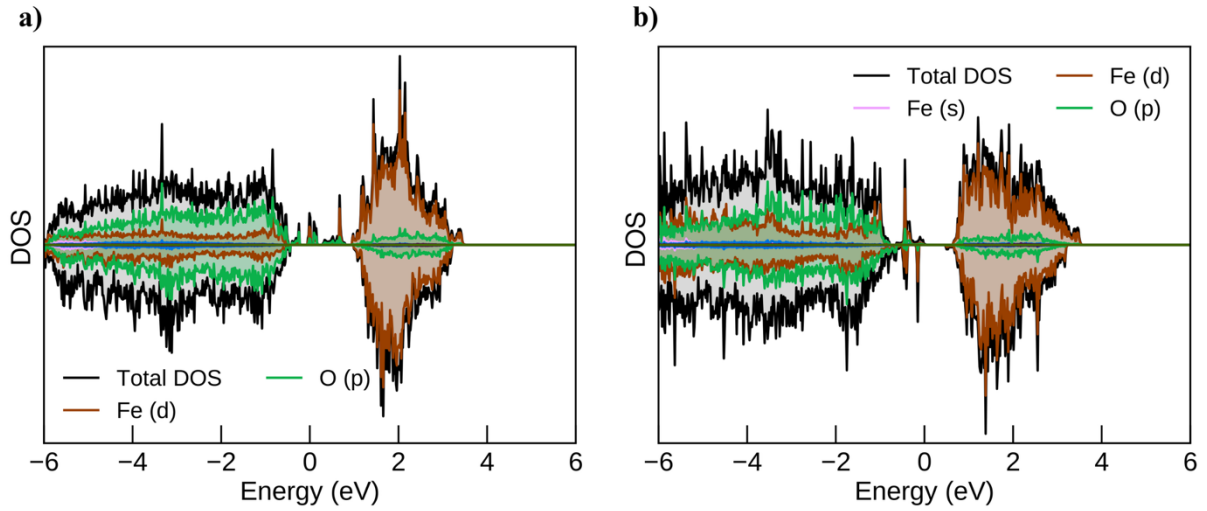


Figure S26. DOS of $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)$ -clean surface. **a)** Before electrochemical reduction, and **b)** after electrochemical reduction using VASPsol.

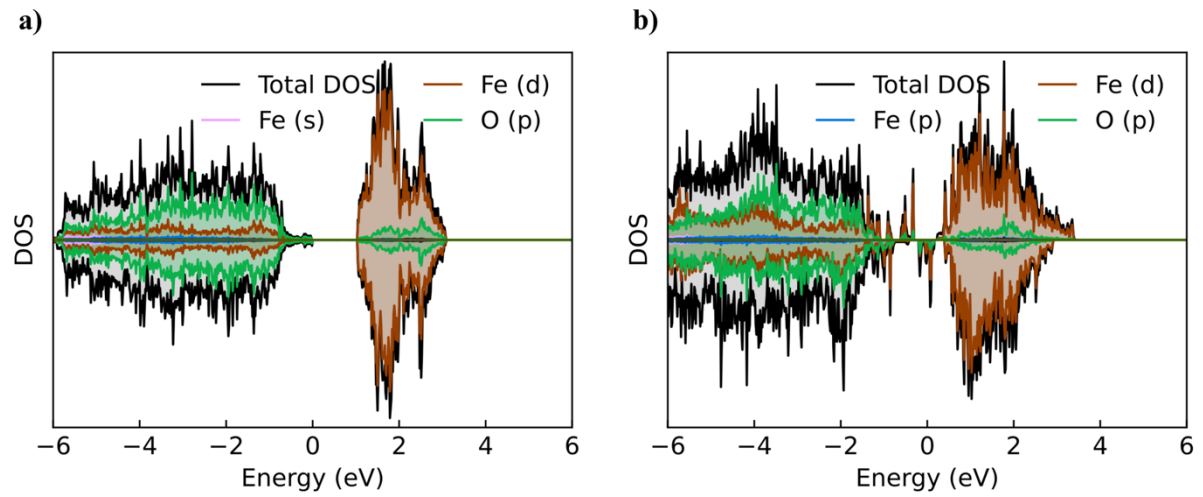


Figure S27. DOS of $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ -clean surface. **a)** Before electrochemical reduction, and **b)** after electrochemical reduction using VASPsol.

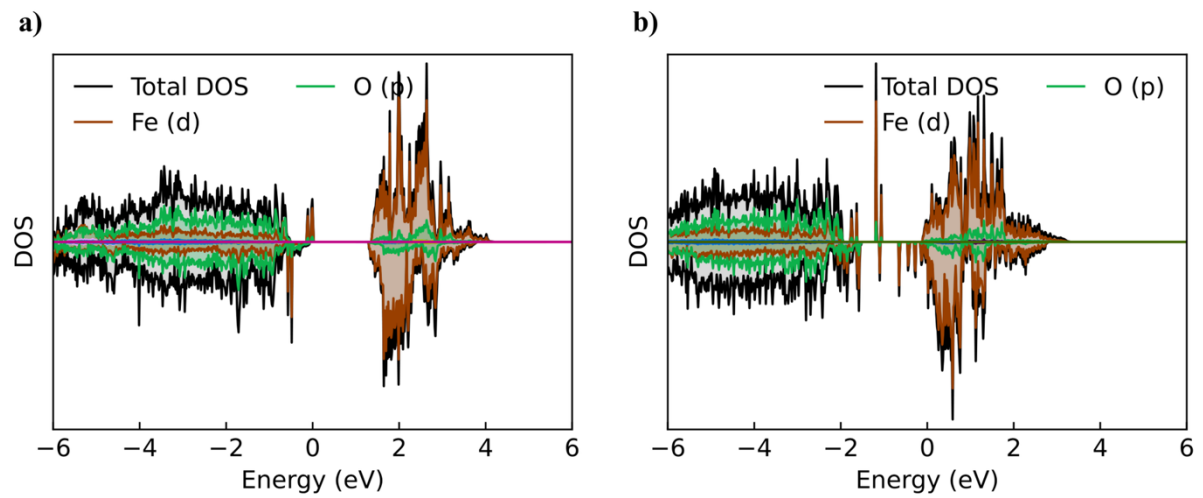


Figure S28. DOS of $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}8\text{*H}_{\text{sub}}$ surface. **a)** Before electrochemical reduction, and **b)** after electrochemical reduction using VASPsol.

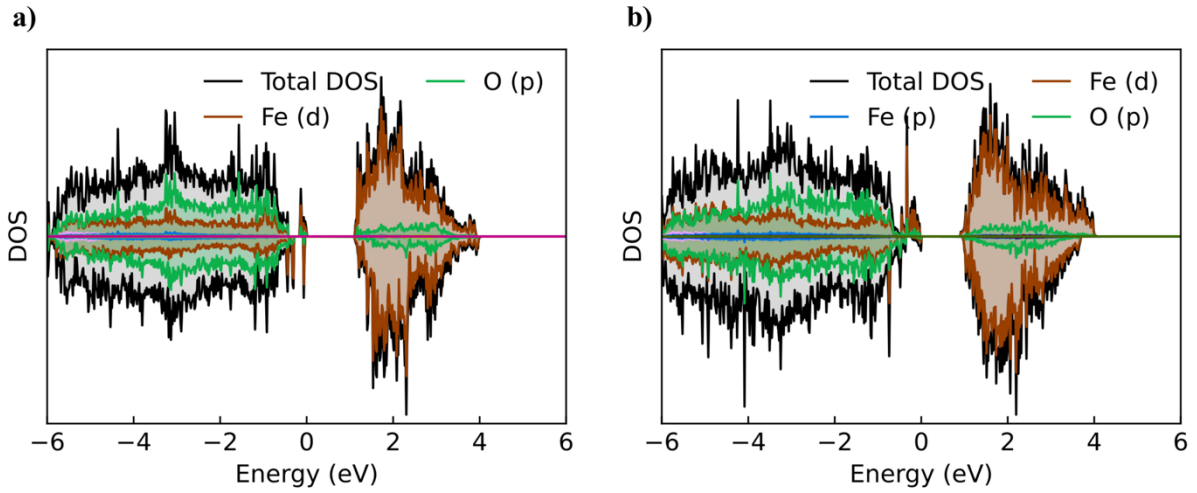


Figure S29. DOS of $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)\text{-}8\text{*H}_{\text{sub}}$ surface. **a)** Before electrochemical reduction, and **b)** after electrochemical reduction using VASPsol.

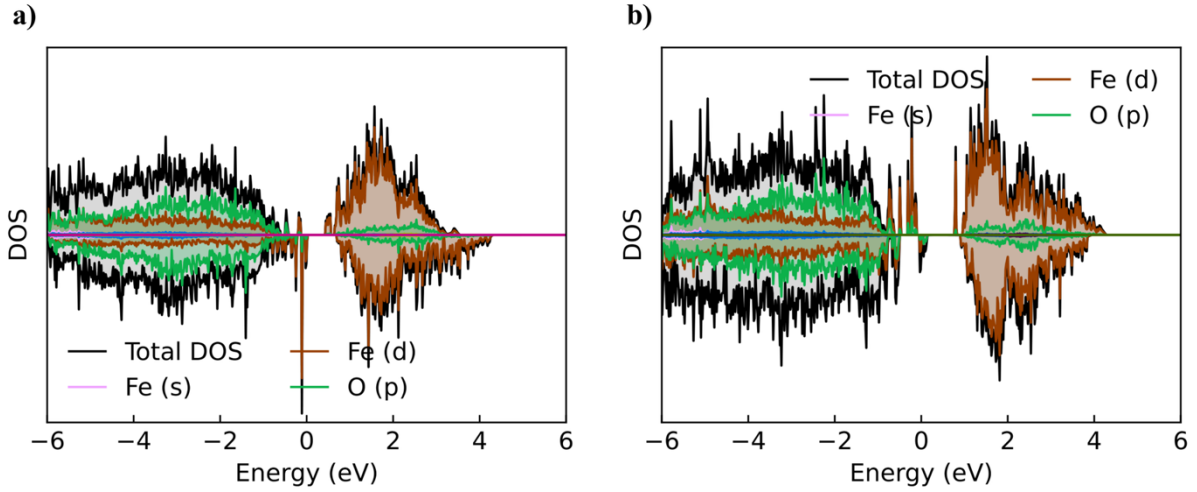


Figure S30. DOS of $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}\bar{1}0)\text{-}8\text{*H}_{\text{sub}}$ surface. **a)** Before electrochemical reduction, and **b)** after electrochemical reduction using VASPsol.

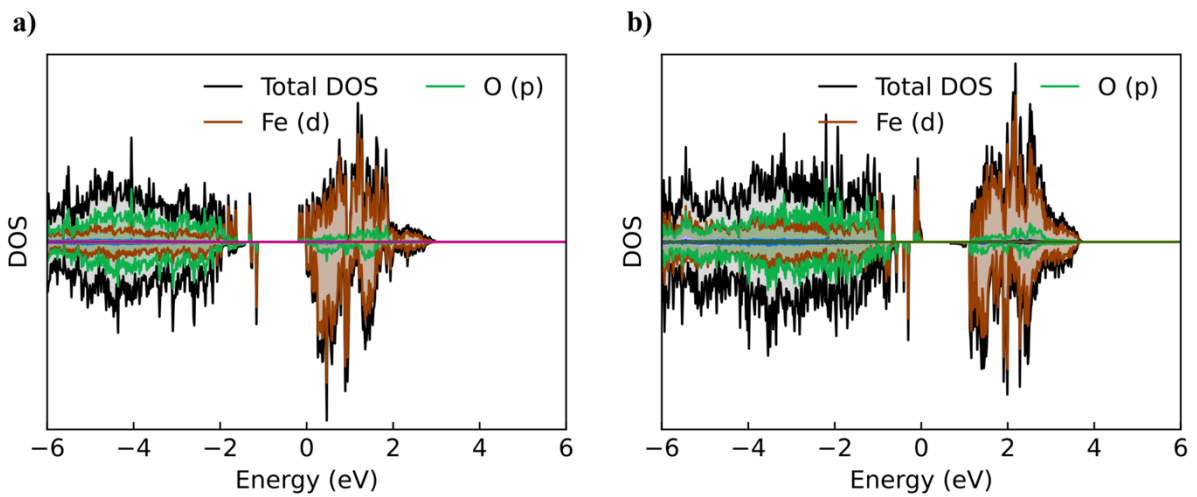


Figure S31. DOS of $\alpha\text{-Fe}_2\text{O}_3(0001)\text{-}12\text{*H}_{\text{sub}}$ surface. **a)** Before electrochemical reduction, and **b)** after electrochemical reduction using VASPsol.

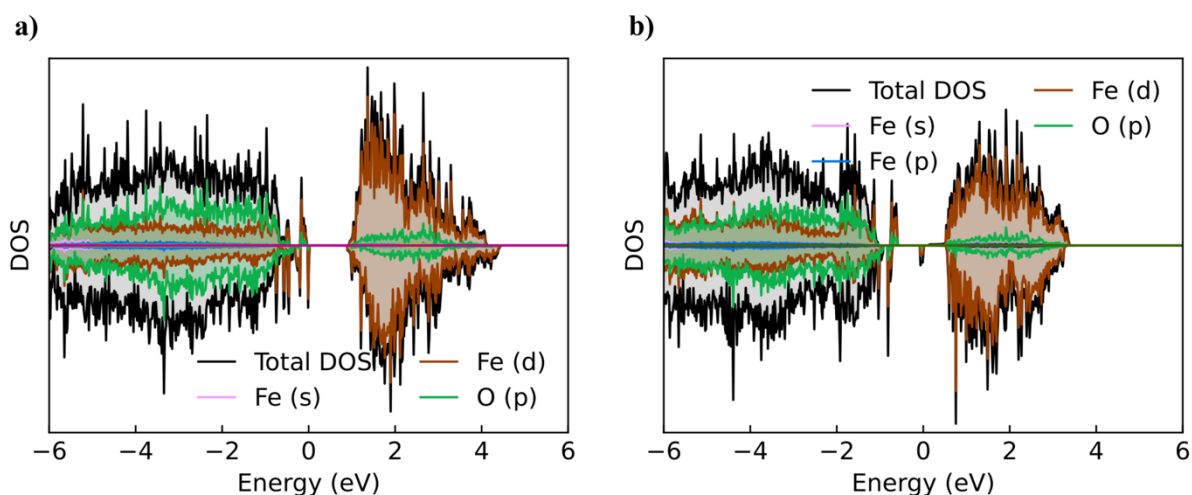


Figure S32. DOS of $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)\text{-}12\text{*H}_{\text{sub}}$ surface. **a)** Before electrochemical reduction, and **b)** after electrochemical reduction using VASPsol.

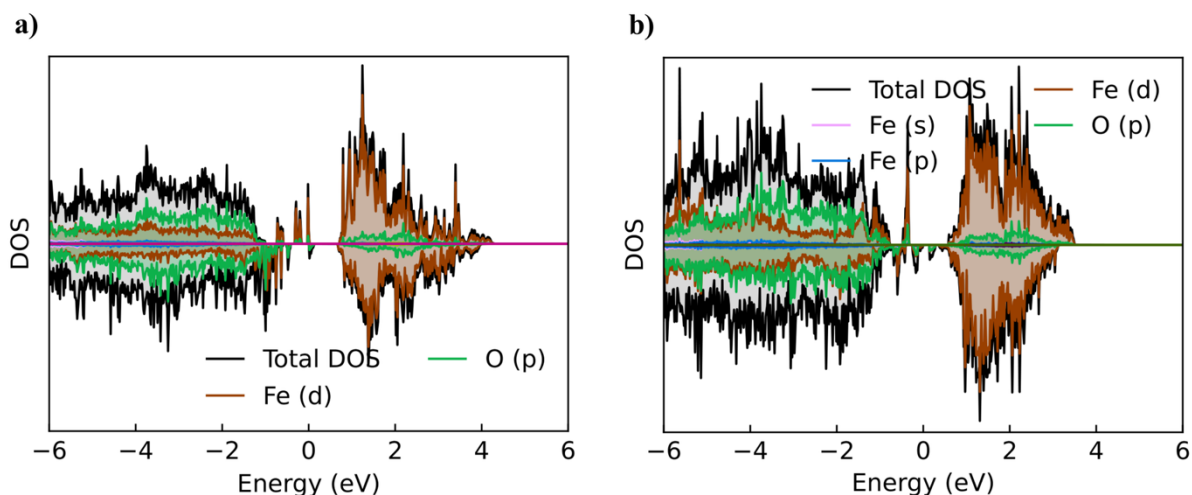


Figure S33. DOS of $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)\text{-}12\text{*H}_{\text{sub}}$ surface. **a)** Before electrochemical reduction, and **b)** after electrochemical reduction using VASPsol.

S9 The ZPE corrections, entropy contributions, and enthalpic contributions of the reference molecules

Table S13. The ZPE corrections, entropic contributions ($T = 298.15$ K), and enthalpic contributions of the reference molecules.

Reference molecule	ΔE_{ZPE} (eV)	$T\Delta S$ (eV)	$\int_0^{T=298.15} c_p dT$ (eV)
$\text{H}_{2(\text{g})}$	0.27	0.40	0.09
$\text{H}_2\text{O}_{(\text{g})}$	0.57	0.70	0.10

S10 Fe^{2+} and Fe^{3+} deposition analysis from the electrolyte

We examine Fe^{2+} and Fe^{3+} electrodeposition on the reduced surfaces of $\alpha\text{-Fe}_2\text{O}_3(0001)$, $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)$, and $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ facets from the electrolyte.

The reaction for the Fe^{2+} deposition is given as:



Here, R represents the reduced hematite surface, and Fe_{dep} is the deposited Fe atom.

The free-energy for the reaction is

$$\Delta G = G(\text{R-Fe}_{\text{dep}}) - G(\text{R}) - G(\text{Fe}^{2+} + 2\text{e}^-) \quad (47)$$

From the tables of standard potentials in aqueous solution:²⁸



U° denotes the equilibrium potential. The reaction free energy for Eq. (48) is $\Delta G = -2 \times e \times U^\circ = 0.90 \text{ eV}$.

From this, we can write:

$$0.90 \text{ eV} = \mu_{\text{Fe}} - \mu(\text{Fe}^{2+} + 2\text{e}^-) \quad (49)$$

Where μ_{Fe} is the chemical potential per bcc bulk iron atom. Finally, Eq. (49) becomes:

$$\mu(\text{Fe}^{2+} + 2\text{e}^-) = \mu_{\text{Fe}} - 0.90 \text{ eV} \quad (50)$$

Which is equivalent to:

$$G(\text{Fe}^{2+} + 2\text{e}^-) = \mu_{\text{Fe}} - 0.90 \text{ eV} \quad (51)$$

By substituting Eq. (51) into Eq. (47), we can calculate Gibbs free-energy at zero electrode potential ($U = 0$) and $\text{pH} = 0$ for Fe(II) deposition:

$$\Delta G(0,0) = G(\text{R-Fe}_{\text{dep}}) - G(\text{R}) - \mu_{\text{Fe}} + 0.90 \text{ eV} \quad (52)$$

In the same analysis, the Gibbs free-energy for the Fe^{3+} deposition on the reduced surface is derived. The equilibrium potential for $\text{Fe}^{3+} + 3\text{e}^- \rightleftharpoons \text{Fe}$; $U^\circ = -0.04 \text{ V}$ yields:

$$\Delta G(0,0) = G(\text{R-Fe}_{\text{dep}}) - G(\text{R}) - \mu_{\text{Fe}} + 0.12 \text{ eV} \quad (53)$$

At any applied electrode potential U and the $\text{pH} = 0$, the Gibbs free-energy is determined as:

$$\Delta G(U_{\text{RHE}}) = \Delta G(0,0) + \nu(\text{e}^-) \times U_{\text{RHE}} \quad (54)$$

Where $\nu(\text{e}^-)$ is the number of electrons transferred in the reaction.

Eq. (54) applies to $\text{pH} = 0$ and unit activity of the dissolved Fe species. Since the deposition reaction involves no protons, its driving force depends on the electrode potential on the SHE scale and, unlike the PCET steps, is not pH-independent on the RHE scale. The values for Fe^{3+}

differ from those for Fe^{2+} by the free energy of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in solution (1.48 eV per Fe atom at $U = -0.7$ V) and therefore contain no additional information on the surface.

The results of Gibbs free-energy changes for $\text{Fe}^{2+}/\text{Fe}^{3+}$ deposition on the reduced surfaces of $\alpha\text{-Fe}_2\text{O}_3(0001)$, $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)$, and $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ facets are provided in **Table S14**. At lower Fe^{2+} activity (a), the driving force for bulk Fe deposition decreases by $k_B T \ln(1/a)$ —0.059 eV per decade at 298 K—so that bulk deposition at $U = -0.7$ V remains exergonic down to $a \approx 10^{-8}$.

Table S14. Gibbs free-energy changes of $\text{Fe}^{2+}/\text{Fe}^{3+}$ deposition on the reduced surfaces of $\alpha\text{-Fe}_2\text{O}_3(0001)$, $\alpha\text{-Fe}_2\text{O}_3(10\bar{1}0)$, and $\alpha\text{-Fe}_2\text{O}_3(1\bar{2}10)$ facets from the electrolyte at an applied electrode potential of $U = -0.7$ V vs. RHE.

Facet	Reduced surface	No. of deposited $\text{Fe}^{2+}/\text{Fe}^{3+}$ atom(s)	$\Delta G/\text{eV}$ @ $U = -0.7$ V vs. RHE ($\text{Fe}^{2+}/\text{Fe}^{3+}$)
(0001)	$\alpha\text{-Fe}_2\text{O}_3\text{-clean}$	1	2.59/1.11
		2	4.90/1.94
	$\alpha\text{-Fe}_2\text{O}_3\text{-}8*\text{H}_{\text{sub}}(\text{partial})$	1	2.08/0.60
		2	5.08/2.12
	$\alpha\text{-Fe}_2\text{O}_3\text{-}12*\text{H}_{\text{sub}}$	1	2.64/1.16
		2	6.04/3.08
(10 $\bar{1}0$)	$\alpha\text{-Fe}_2\text{O}_3\text{-clean}$	1	2.32/0.84
		2	4.58/1.62
	$\alpha\text{-Fe}_2\text{O}_3\text{-}8*\text{H}_{\text{sub}}(\text{partial})$	1	4.14/2.66
		2	7.39/4.43
	$\alpha\text{-Fe}_2\text{O}_3\text{-}12*\text{H}_{\text{sub}}$	1	4.25/2.77
		2	7.51/4.55
(1 $\bar{2}10$)	$\alpha\text{-Fe}_2\text{O}_3\text{-clean}$	1	3.16/1.68
		2	5.75/2.79
	$\alpha\text{-Fe}_2\text{O}_3\text{-}8*\text{H}_{\text{sub}}(\text{partial})$	1	3.21/1.73
		2	6.88/3.92
	$\alpha\text{-Fe}_2\text{O}_3\text{-}12*\text{H}_{\text{sub}}$	1	4.53/3.05
		2	6.62/3.66

S11 AIMD simulations analysis

To assess the structural stability of the most favorable (0001) facet of hematite for electrochemical reduction, AIMD simulations were performed under NVT conditions for both the clean and $12*\text{H}_{\text{sub}}$ -hydrogenated surfaces was simulated for 20 ps. A comprehensive set of stability metrics was monitored throughout the trajectory: temperature evolution to evaluate thermal equilibration and energy conservation; root-mean-square deviation (RMSD) of surface Fe and O atoms to quantify structural drift and assess surface stability; Fe–O coordination numbers to monitor the integrity of the surface lattice and detect bond breaking or reconstruction; O–H bond distances and H–H bond distances for the hydrogenated surface to track the stability of surface hydroxyl groups and identify proton transfer or H_2 formation;

layer-resolved z-position evolution to examine vertical atomic displacements and surface rumpling; and slab thickness, defined as the difference between the maximum and minimum z-coordinates of surface Fe atoms, to evaluate overall vertical stability. The results show that both the clean and 12*H_{sub} surfaces remain structurally stable for the 20 ps simulation time, with no irreversible bond breaking, significant surface reconstruction, or unphysical atomic migration. For the clean surface, dissociation of water molecules was observed, resulting in the formation *OH intermediates on Fe sites and *H intermediates on hematite surface O sites. For 12*H_{sub} surface, the maximum H–H bond distance criterion for H₂ formation was defined as 0.90 Å. Nevertheless, no H₂ molecules were observed during the simulation. After 7.5 ps, the average O–H bond distance increases slightly, suggesting a gradual elongation of the O–H bonds. The hematite slab thickness increased during the first ~2–3 ps, indicating initial relaxation of the hydrated surface. After this equilibration period, the thickness fluctuates around ~12.3 Å without continuous drift, suggesting that the hematite slab remains structurally stable on the simulated timescale (cf. **Figure S48**). The observed fluctuations are consistent with thermal motion at the target temperature (300 K), confirming the reliability of the AIMD trajectories for subsequent analysis. The RMSD analysis of the surface Fe–O atoms clearly demonstrates the structural stability of both clean and 12*H_{sub} surfaces. The average surface Fe–O coordination number is about 5. The corresponding plots are provided in **Figures S34–S48**.

S11.1 AIMD structural stability analysis of the clean hematite (0001) surface

Temperature vs. time

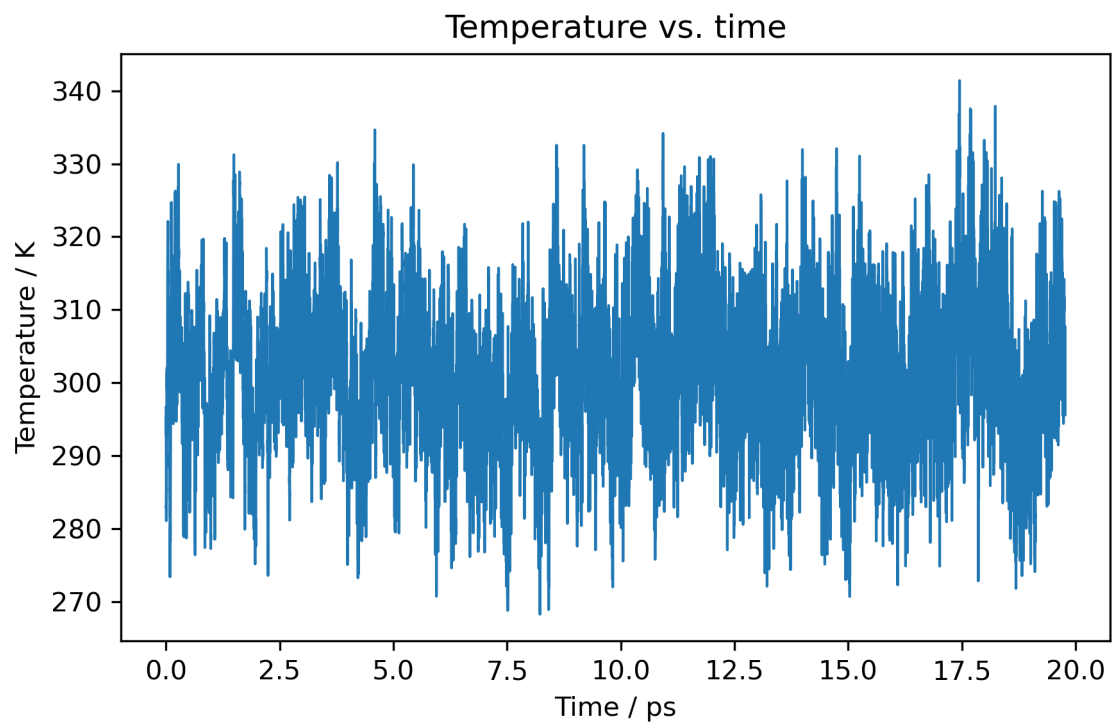


Figure S34. Temperature vs. time for clean surface.

RMSD of surface Fe and O atoms vs. time

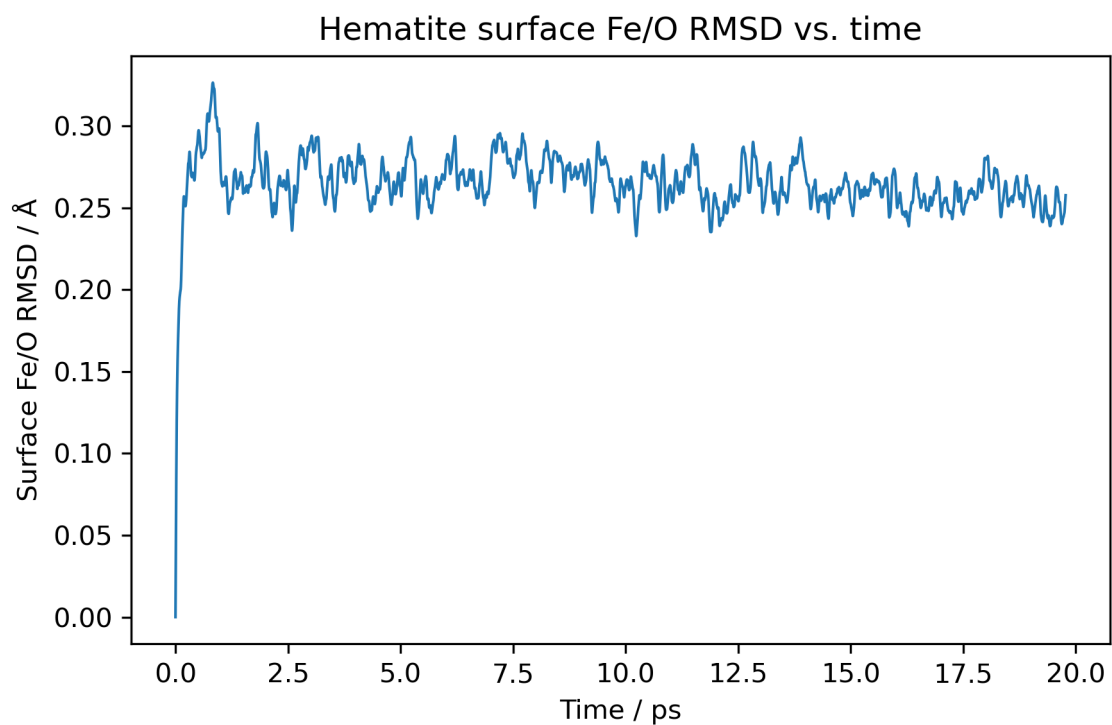


Figure S35. RMSD of surface Fe and O atoms vs. time for clean surface.

Fe-O coordination numbers vs. time

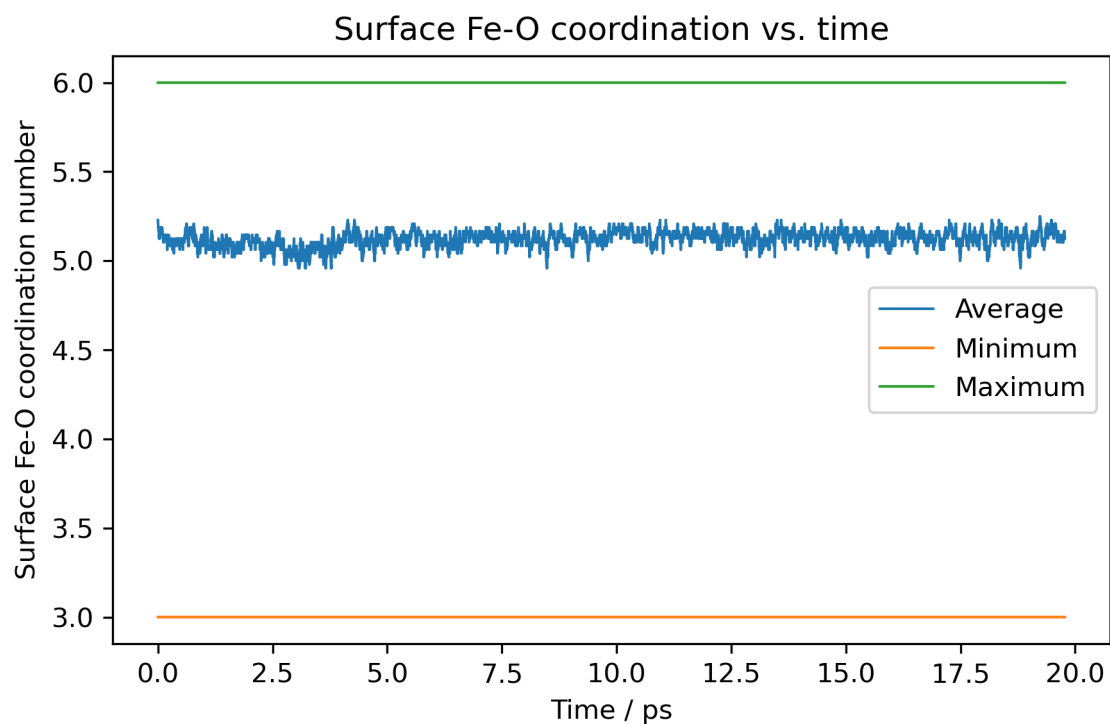


Figure S36. Surface Fe-O coordination numbers vs. time for clean surface.

H-H bond distances vs. time

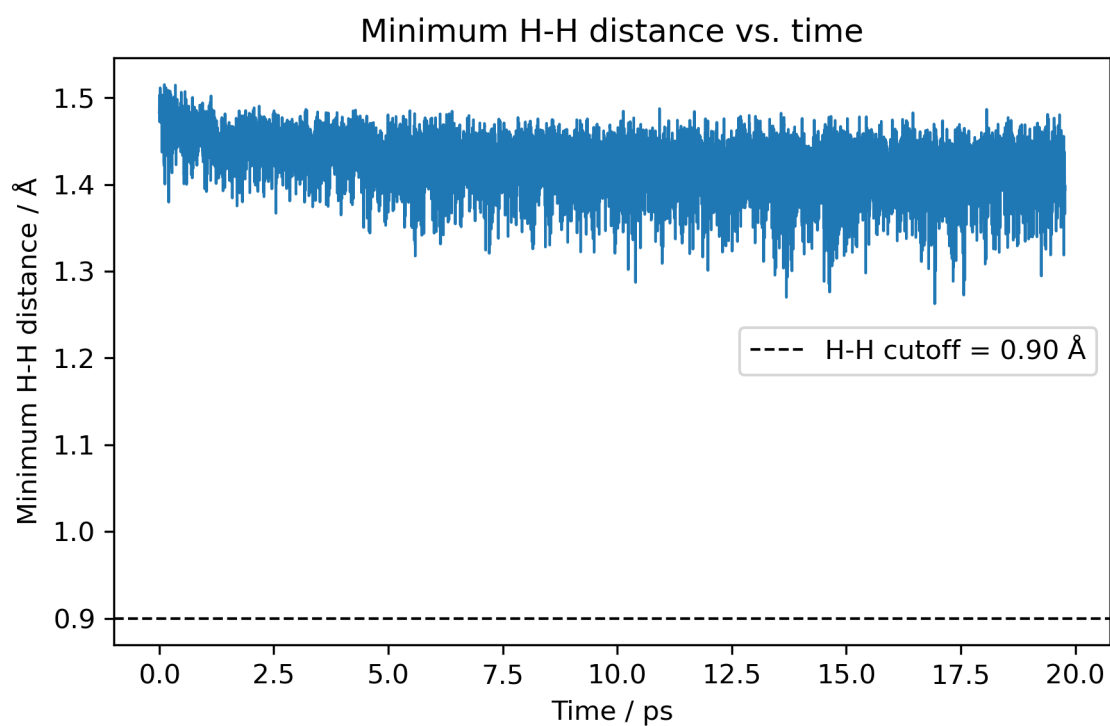


Figure S37. Minimum H-H distance vs. time for clean surface.

Layer-resolved z-position vs. time

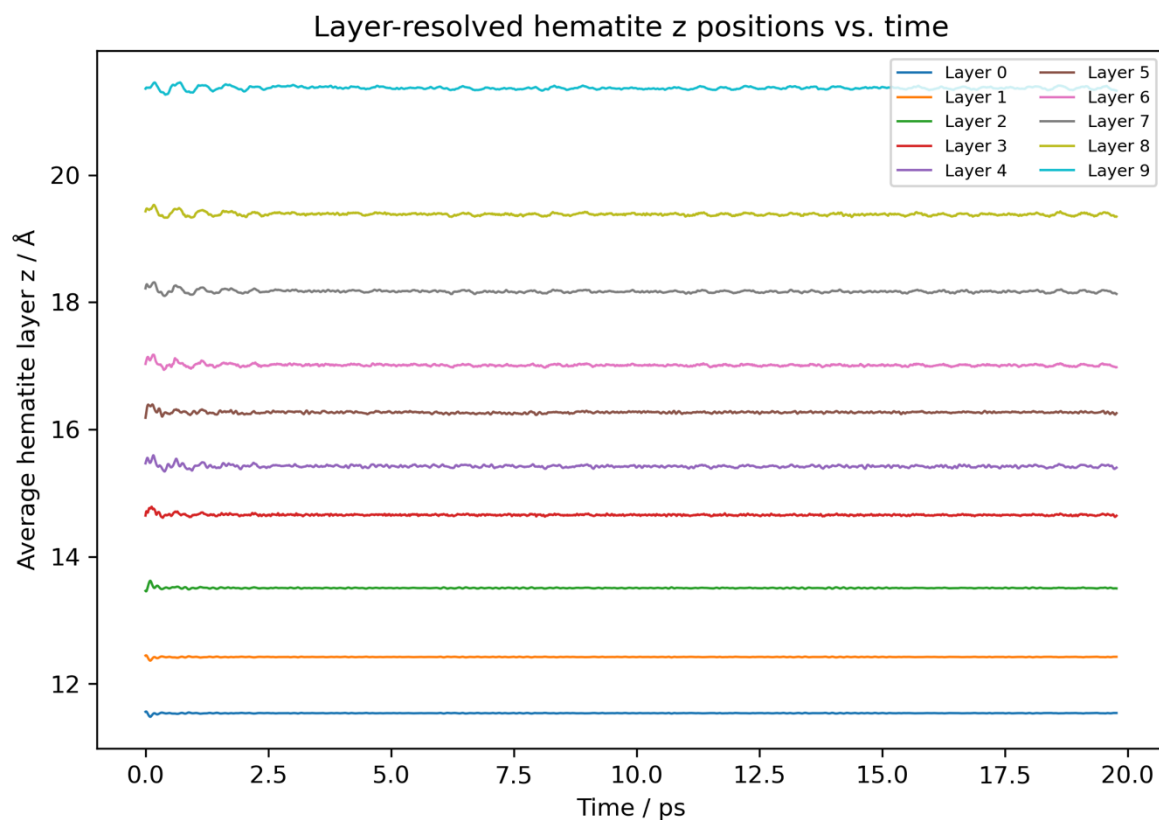


Figure S38. Layer-resolved hematite z positions vs. time for clean surface.

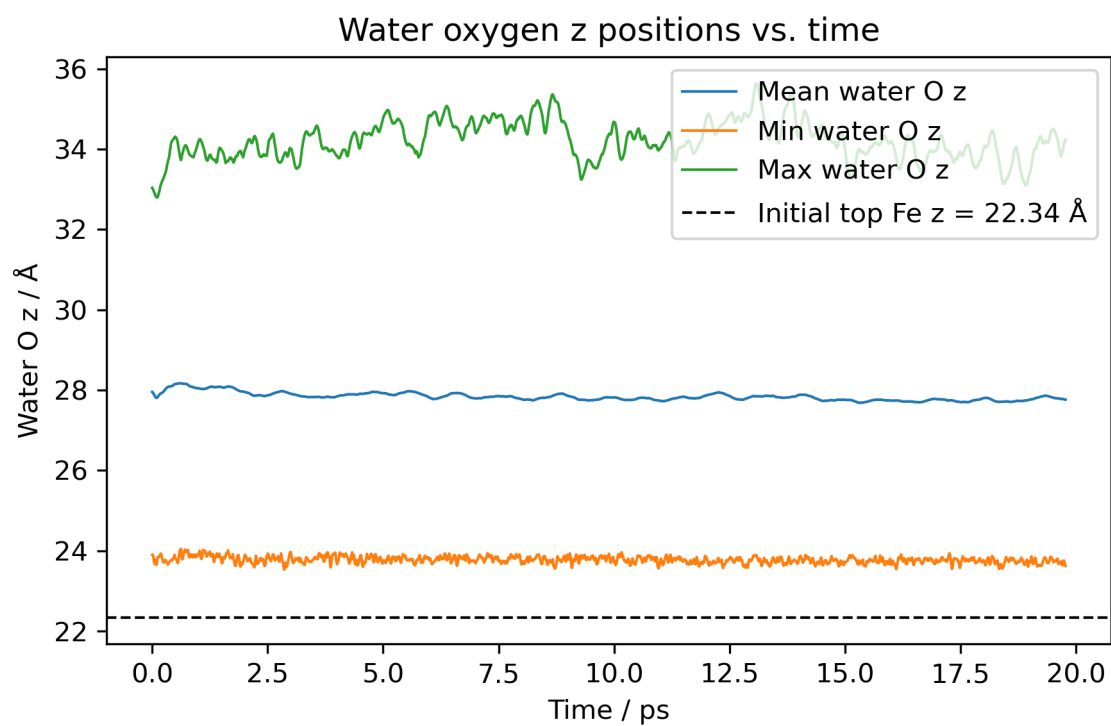


Figure S39. Water oxygen z positions vs. time for clean surface.

Slab thickness vs. time

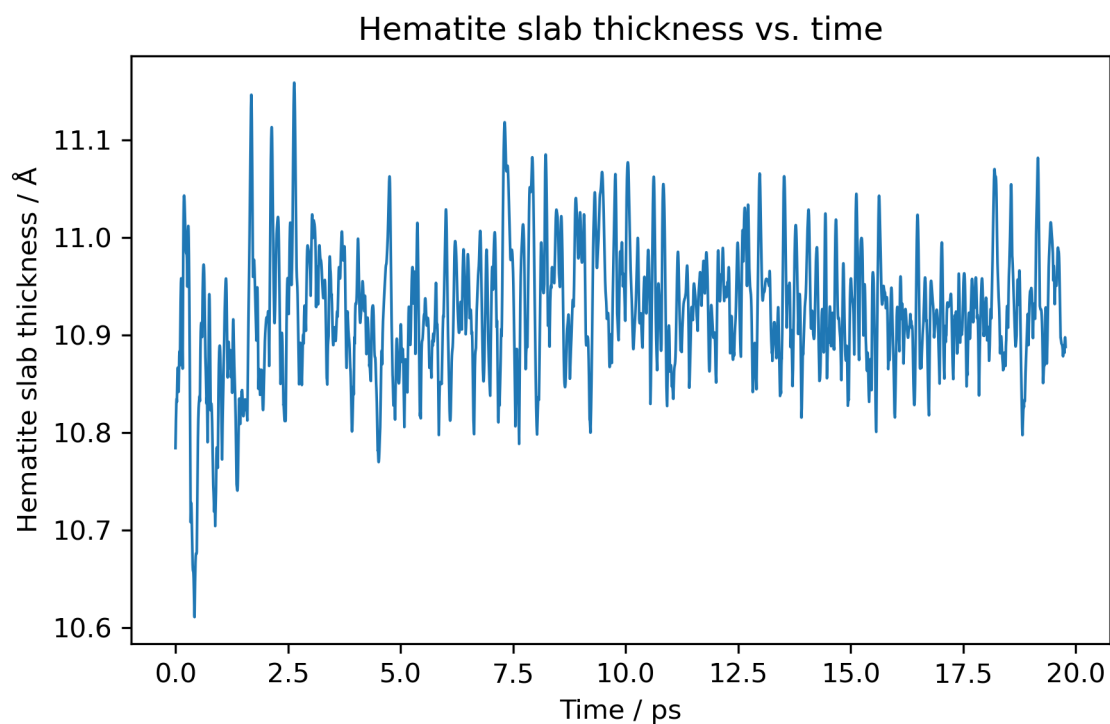


Figure S40. Hematite slab thickness vs. time for clean surface.

S11.2 AIMD structural stability analysis of the $12 \times H_{\text{sub}}$ hematite (0001) surface

Temperature vs. time

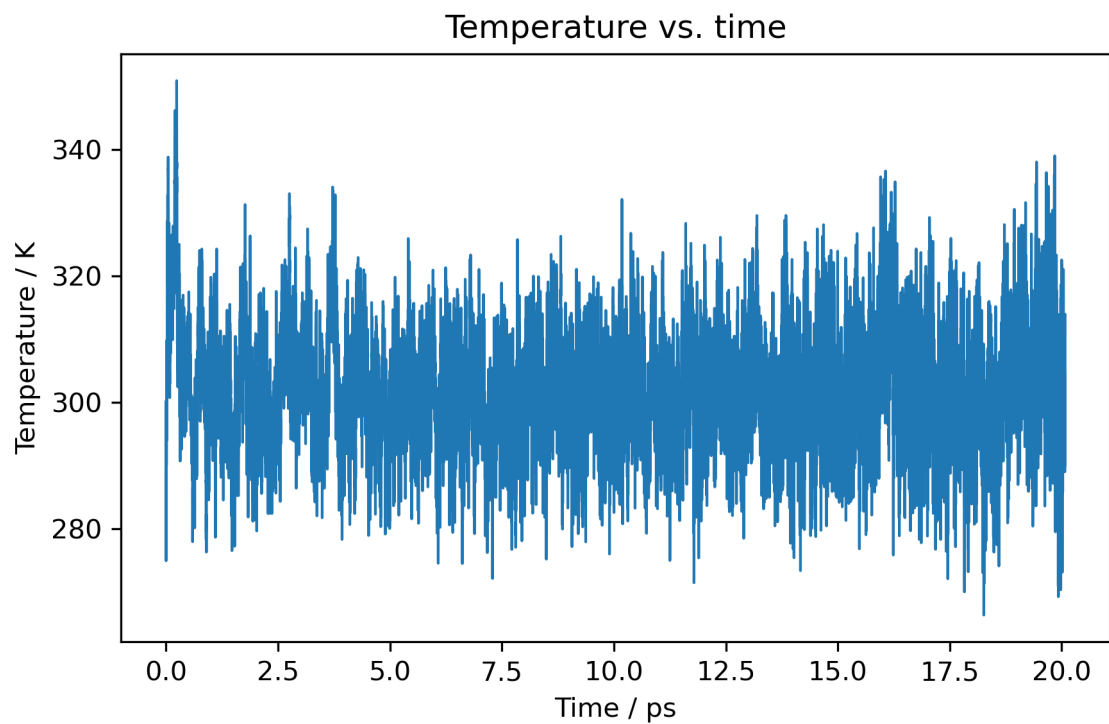


Figure S41. Temperature vs. time for $12 \times H_{\text{sub}}$ surface.

RMSD of surface Fe and O atoms vs. time

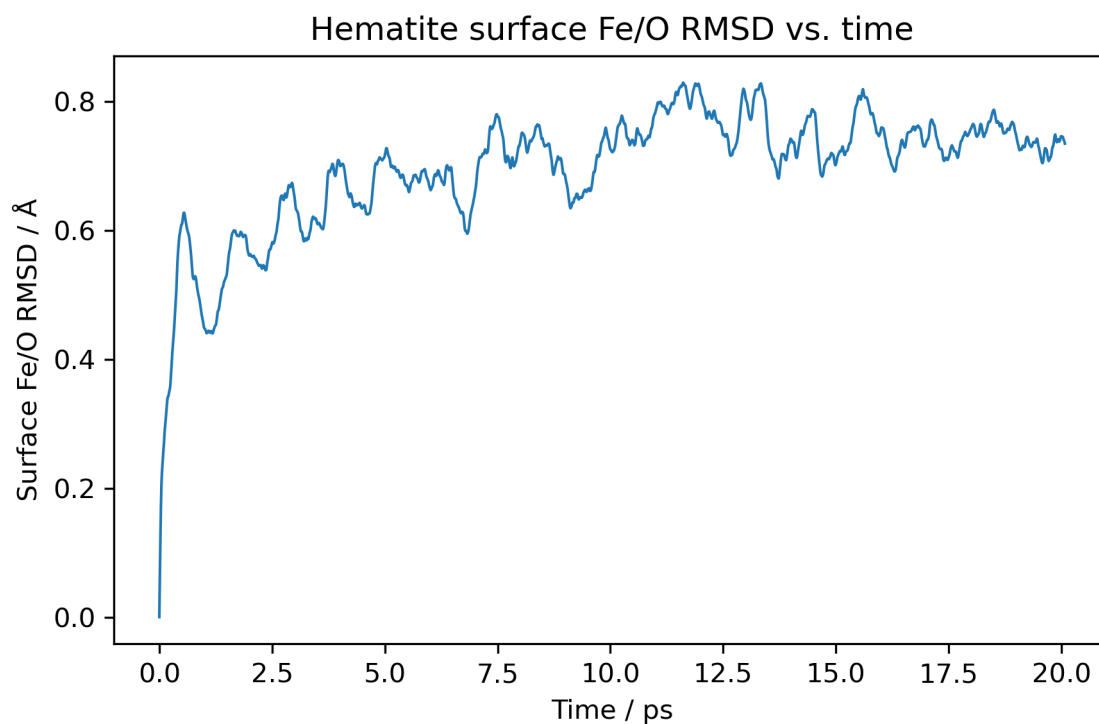


Figure S42. RMSD of surface Fe and O atoms vs. time for 12*H_{sub} surface.

Fe-O coordination numbers vs. time

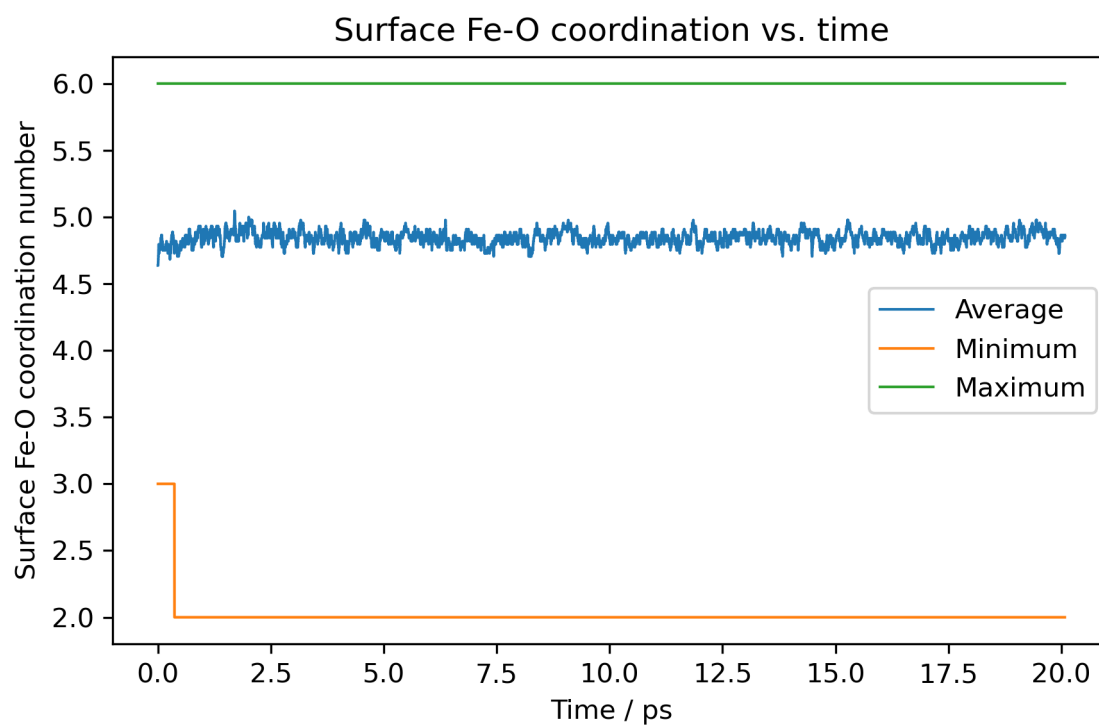


Figure S43. Surface Fe-O coordination numbers vs. time for 12*H_{sub} surface

Average O-H bond distances vs. time

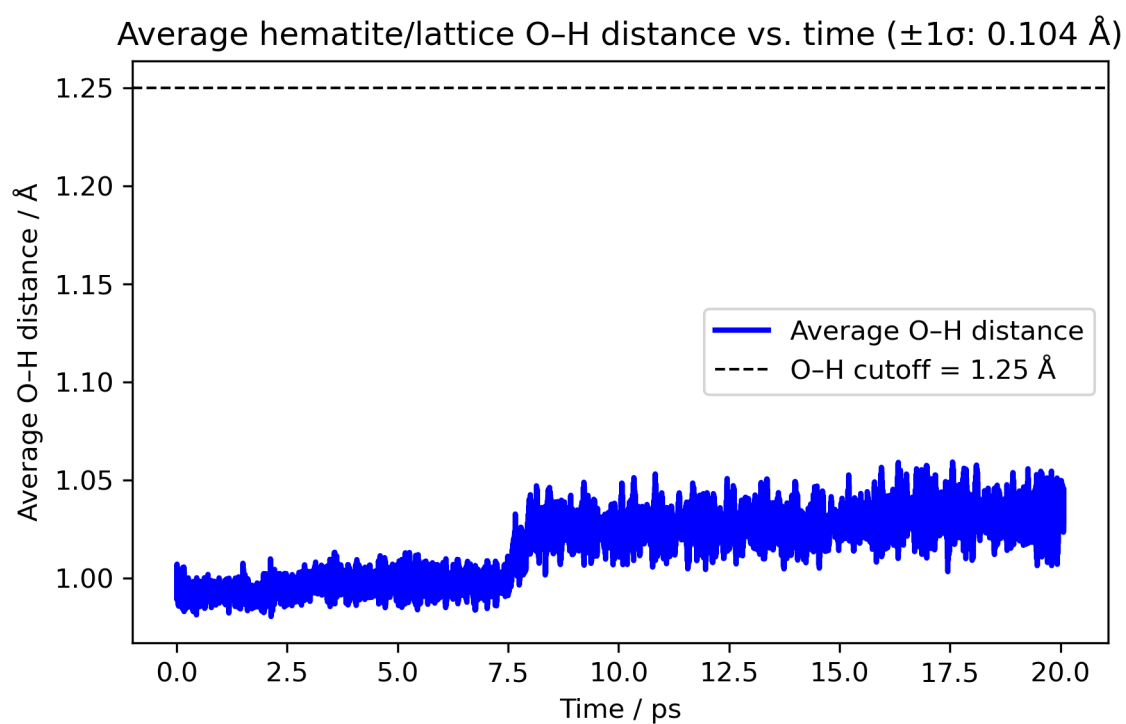


Figure S44. Average hematite/lattice O-H distances vs. time for 12*H_{sub} surface.

H-H bond distances vs. time

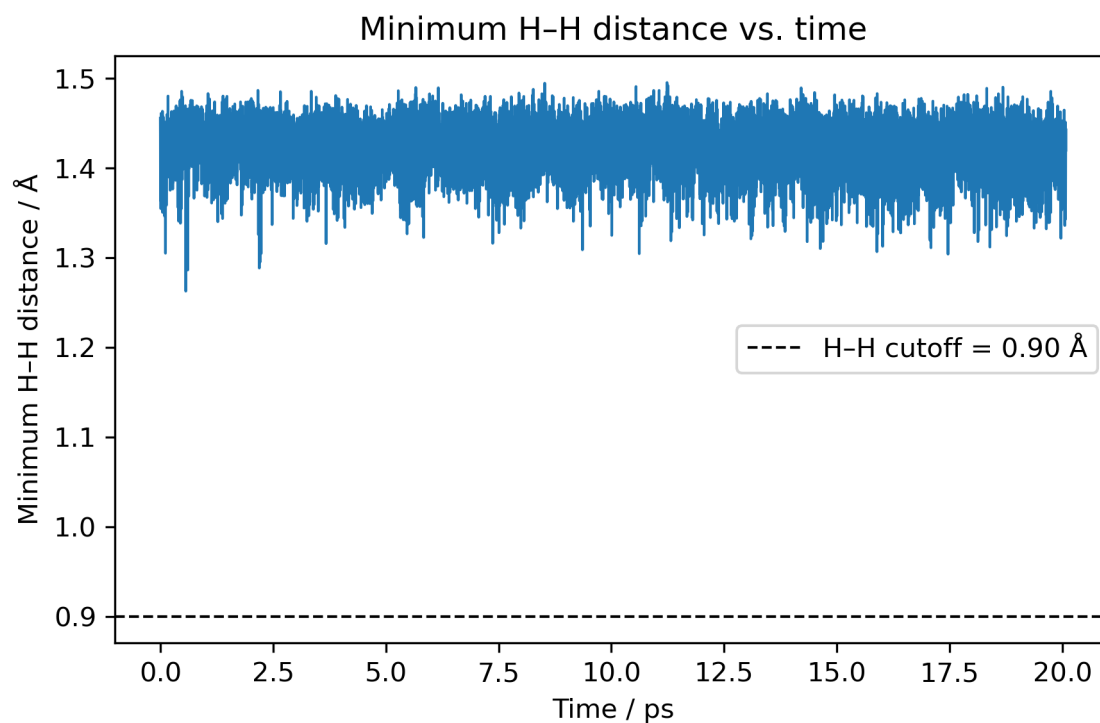


Figure S45. Minimum H-H distance vs. time for 12*H_{sub} surface.

Layer-resolved z-position vs. time

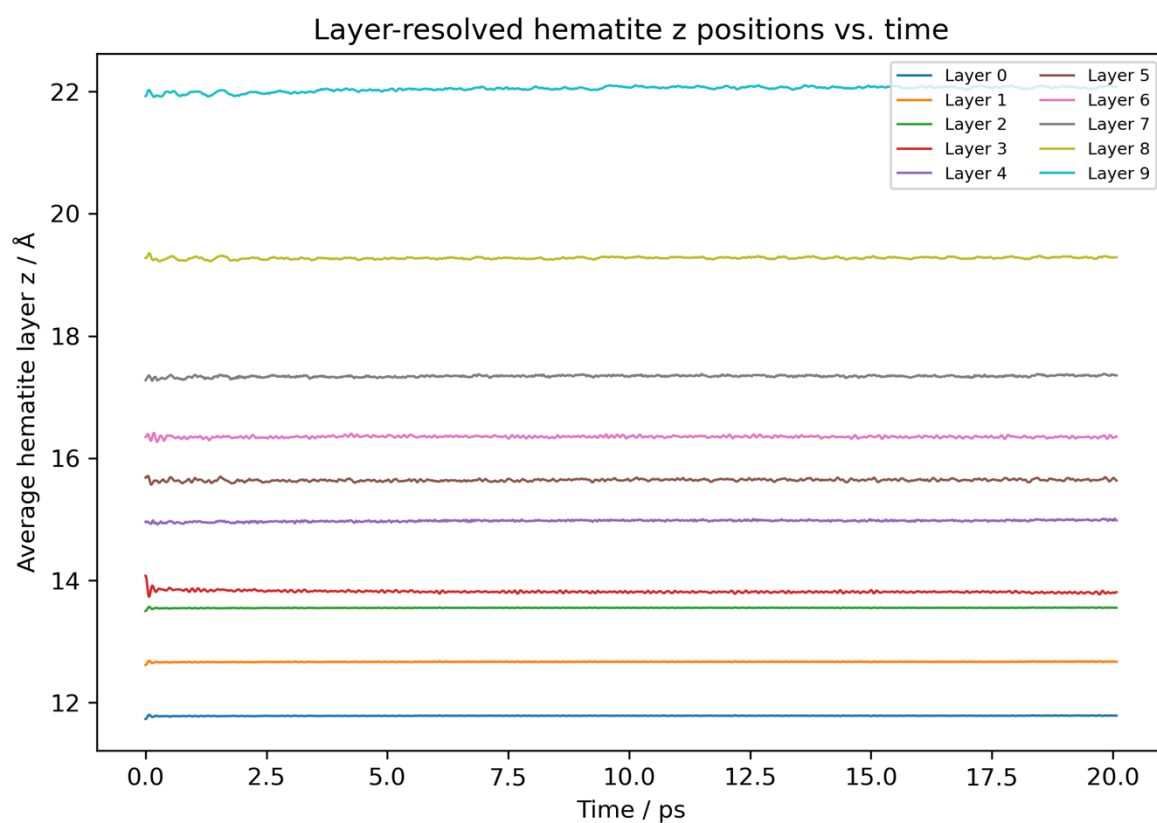


Figure S46. Layer-resolved hematite z positions vs. time for 12*H_{sub} surface.

Water oxygen z-position vs. time

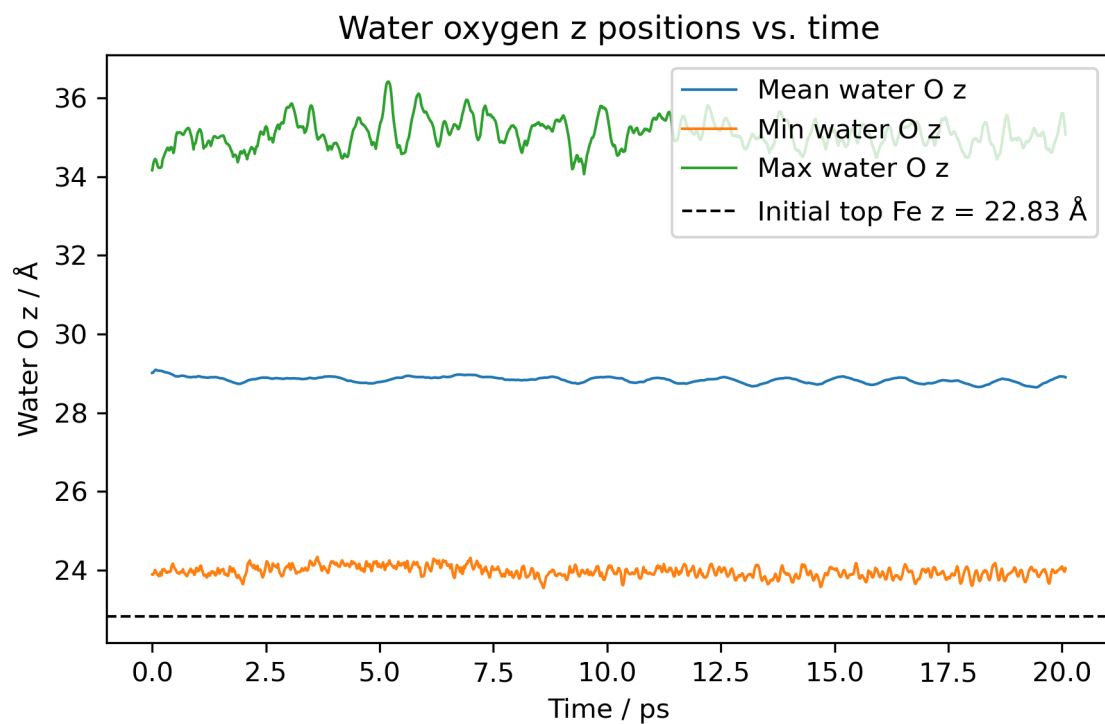


Figure S47. Water oxygen z positions vs. time for 12*H_{sub} surface.

Slab thickness vs. time

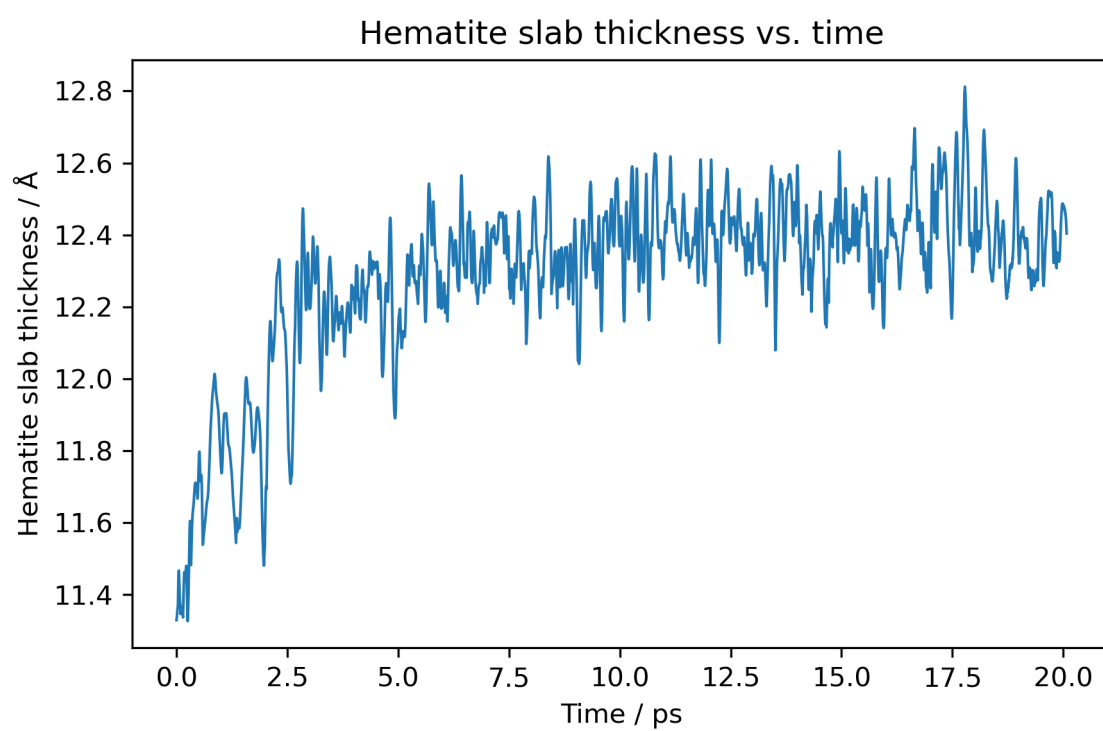


Figure S48. Hematite slab thickness vs. time for 12*H_{sub} surface.

S12 Appendix

Snapshot of the dynamics: clean surface

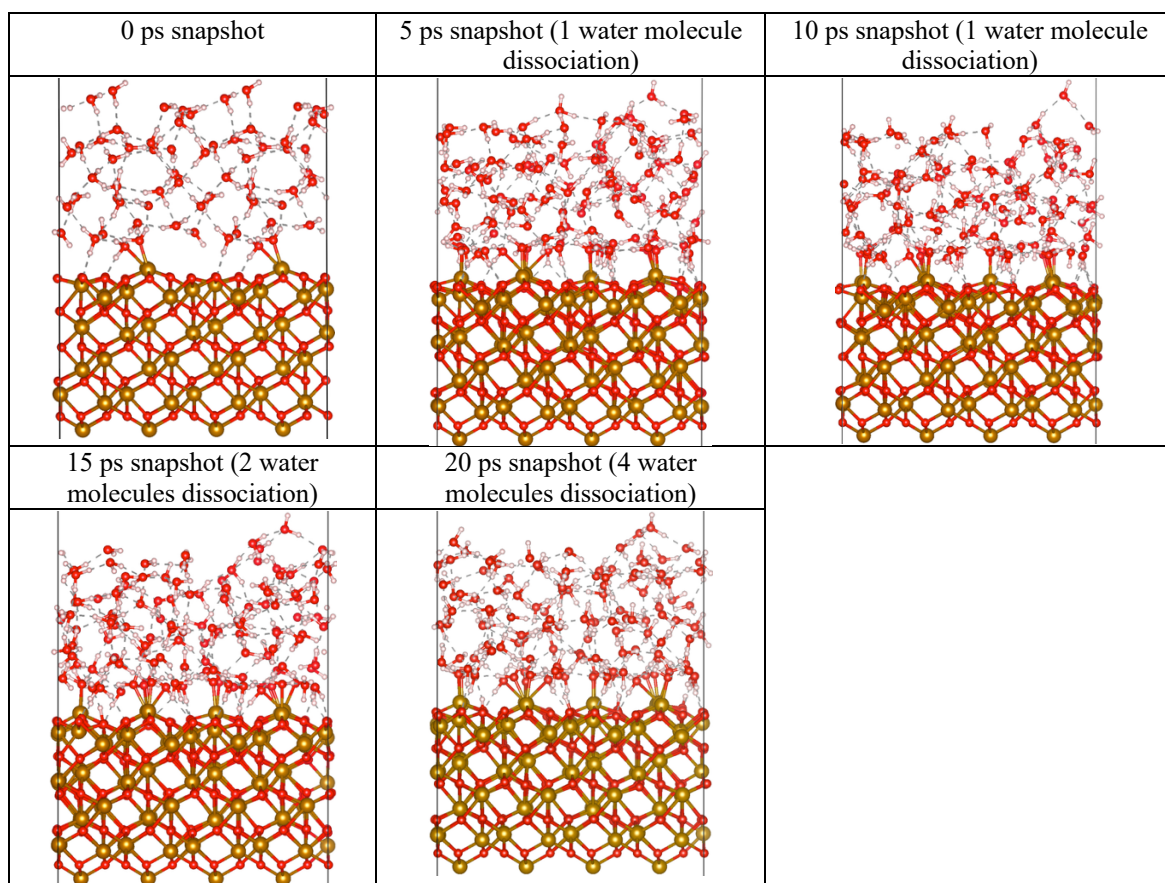


Figure S49. Snapshot of AIMD simulation in 5 ps steps for clean surface.

Snapshot of the dynamics: 12*H_{sub} surface

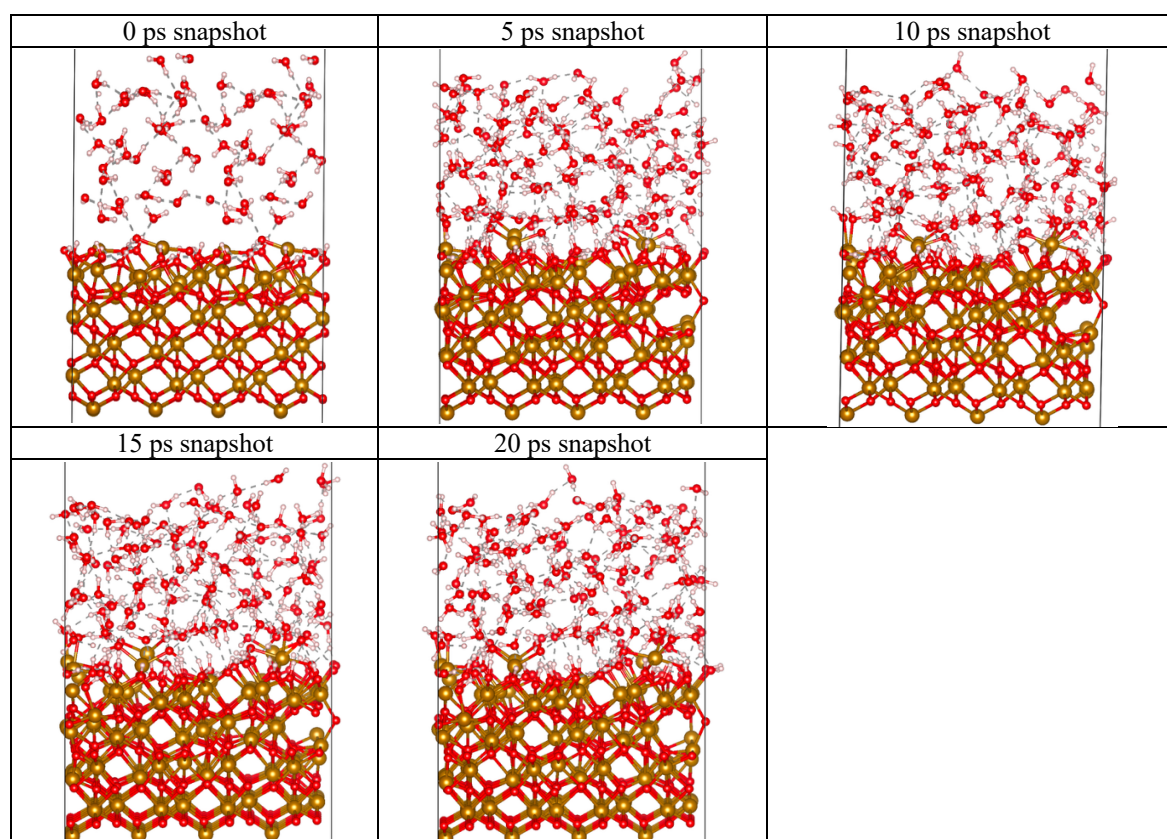


Figure S50. Snapshot of AIMD simulation in 5 ps steps for 12*H_{sub} surface.

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