Supporting Information for:

Atomistic Modelling of Spinel Oxide Particle Shapes and Reshaping under OER Conditions

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Table S1. Calculated lattice parameters (a,b) of investigated spinels in Angstrom (Å). c = 20 Å for all facets.

Calculated Lattice Parameters in Å				
Plane	$NiFe_2O_4$	$CoFe_2O_4$	$NiCo_2O_4$	$ZnCo_2O_4$
(001)	8.49 x 8.49	8.48 x 8.48	8.30 x 8.30	8.38 x 8.38
(110)	8.49 x 12.0	8.48 x 11.99	8.30 x 11.73	8.38 x 11.85
(111)	12.00 x 10.39	11.96 x 10.39	11.73 x 10.16	11.85 x 10.26

1. Slab Models for Surface Energy Calculations

The total number of atoms per unit cell for (001), (110), (111) slabs used in bare and adsorbed surface calculations are summarized in Table S2. Stoichiometric/symmetric slab were used for the bare surface calculations, while stoichiometric/non-symmetric inverse spinel slabs were used for the covered adsorbed surfaces, also those slabs comparatively shown in Figure S1.

Table S2. The number of atoms in the unit cell used in bare and adsorbed surface calculations of $CoFe_2O_4$.

Number of atoms/unit cell		
Slabs	For Bare Surface	for Adsorbed Surface
(001)	56 (8Co, 16Fe, 32O)	41 (6Co, 11Fe, 24O)
(110)	126 (18Co, 36Fe, 72O)	50 (7Co, 15Fe, 28O)
(111)	112 (16Co, 32Fe, 64O)	43 (7Co, 12Fe, 24O)

For (001), the slab involves a larger number of atoms (56 atom/unit cell) for the stoichiometric system shown in Figure S1a, whereas protruding Fe in tetrahedral position (B^T) on top surface was eliminated in the smaller (001) slab (41 atoms/unit cell) to keep approximate symmetry (Figure S1.b). For (110), in the bigger extended slab (126 atoms, Figure S1.c), which involve 2 Co^O, 2 Fe^O, 3 Fe^T and 8 surface oxygens on top and bottom surfaces, one tetrahedral Fe in top and one tetrahedral Fe on bottom surfaces were eliminated to keep approximate symmetry. As for smaller slab for (110), i.e., 50 atom/unit cell in Figure S1.d , presented surface cut, Co^O, Fe^O, 2 Fe^T and 4 surface oxygens on top and bottom surfaces, is already protected symmetry but not stoichiometry because symmetry and stoichiometry are not compatible at the same time for this small slab of (110) surface. As for (111), in bigger extended slab (112 atoms, Figure S1.e), 2 octahedral Co from top and 2 octahedral Co from bottom were eliminated to keep approximate symmetry. In smaller slab (43 atom/unit cell in Figure S1.f) for (111), one octahedral Co is added to keep approximate symmetry at the expense of stoichiometry. Again, symmetry and stoichiometry are not compatible at the same time in small unit cell for (111) as well.

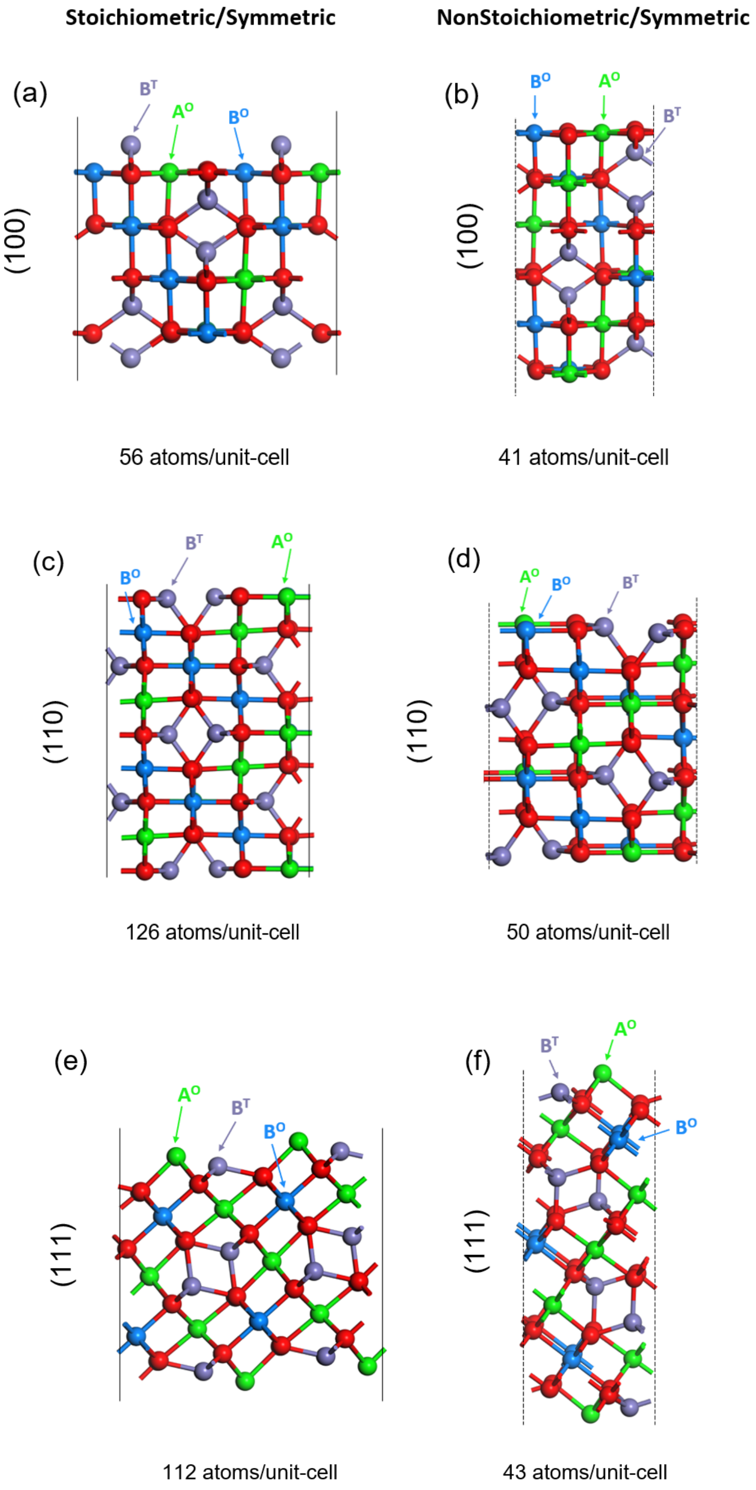


Figure S1. Stoichiometric (a, c, e) and Nonstoichiometric slabs (b, d, f) of inverse spinel (AB_2O_4) used for bare and covered surfaces of $CoFe_2O_4$, respectively. Symmetry was protected for all slab models.

2. Surface Coverage for [(001), (110), (111)] planes of $CoFe_2O_4$

2.1 Coverage on (001) surface

First, (001) facet of $CoFe_2O_4$ was subjected to adsorption. The nonstoci hiometric/symmetric (001) slab shown in Figure S1 with unit cell dimensions 5.99 Å X 5.99 Å X 25 Å, corresponding to 41 atoms per unit cell, was used for coverage.

To begin with, undissociated waters were included to cover and fill coordination of each metal site on the (001) surface. Then coverage by hydroxyls obtained via water dissociation (*OH + *H) was considered, and the relative affinity of *H2O and *OH on the metal sites were predicted by calculating the relative energy of the configurations associated with each coverage pattern. The sampling of several coverage patterns on the catalyst surface led us to determine the lowest energetic state (i.e.,resting state) on (001) plane of CoFe2O4.

In Figure S2, four different coverage options on the metal sites were reported together with relative energetics: (a) adsorbed undissociated waters on each metal sites, (b) adsorbed OH (*OH) on Fe sites, one pro- tonated lattice surface oxygen and adsorbed (*H2O) on Co sites; (c) adsorbed OH (*OH) on Co sites, one protonated lattice surface oxygen and adsorbed (*H2O) on Fe sites (d) adsorbed *OH on both Co and Fe metal sites and two protonated lattice surface oxygens. Note that the four configurations in Figure S2 have the same overall stoichiometry, thus the total electronic energies can be directly compared. The dissociated water coverage patterns on CoFe2O4 are the most favorable, however in this case both alternatives of one-degree dissociation of water (i.e.,*OH on M1 , *H2O on M2 and vice versa) resulted as lowest energy states (see Figure S2 (b),(c)). Another outcome is that the *OH coverage (Figure S2.(c)) is more stable (0.17 eV) than *H2O coverage in Figure S2.(a) (0.31 eV). Considering that for CoFe2O4 one-degree dissociation states (Figure S2.(b),(c)) are equally stable on the two metal sites, we can interpret two resting states on (001) of CoFe2O4.

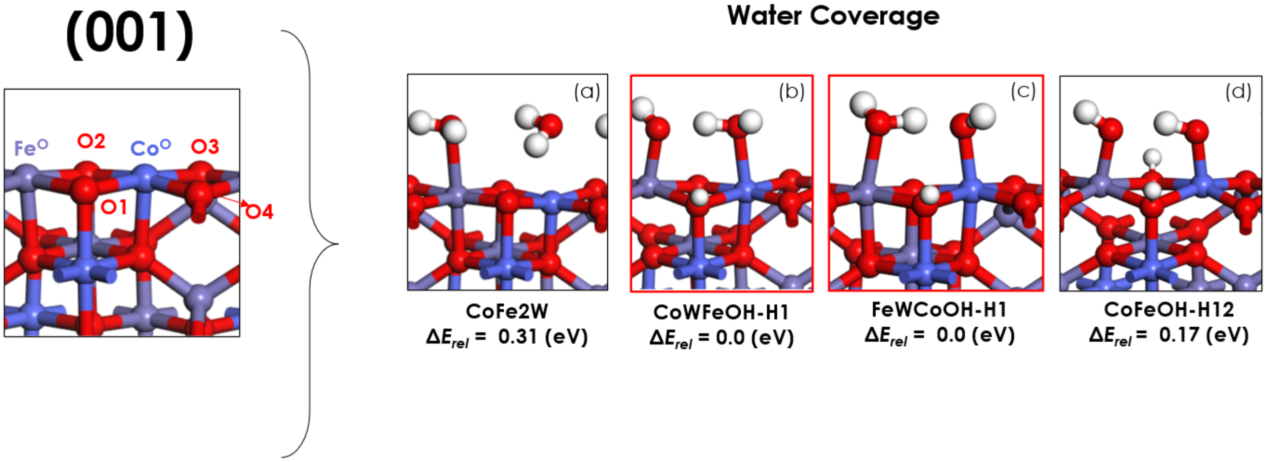


Figure S2. Water coverage patterns on $CoFe_2O_4$ (001). (a) Surface covered with adsorbed undissociated water molecules on each metal sites and nonprotonated lattice oxygens. (b) Adsorbed OH (*OH) on the Co site, while water is still adsorbed (*H2O) on the Fe site, and one lattice surface oxygen is protonated. (c) Adsorbed OH (*OH) on the Fe site, while water is still adsorbed (*H2O) on the Co site, and one lattice surface oxygen is protonated. (d) Adsorbed *OH on both Fe and Co metal sites, while two lattice surface oxygens are protonated. Oxygen, hydrogen, iron, and cobalt atoms are colored red, white, violet, and indigo blue, respectively.

Apart from stoichiometric coverage shown in Figure S2, off-stoichiometric patterns with excess H on surface oxygens were also tried and shown in configurations (a)-(c) in Figure S3 in the first row. In addition to the two water coverage that was considered in the Figure S2, additional configurations in which surface oxygens multiply protonated were also considered. As apparent from the energetics in Figure S3, these additional configurations do not correspond to the resting states of the CoFe2O4 system under realistic/reaction conditions (U=1.48-1.63V), while one configuration is marginally favored for the CoFe2O4 system only up to a bias of 1.31 V (state (a) in Figure S3). Note also that configurations alternative to that in Figure S3(c) have been also tried (i.e.,H_2O on Fe, OH on Co, and 2 surface proton) but eventually converged to the pattern of Figure S3(c).

In the second row in Figure S3, deprotonated configurations were shown in state (d): adsorbed OH (*OH) on the Co site, while water is still adsorbed (*H2O) on the Fe site but without any proton on surface oxy gens, and state (e): adsorbed OH (*OH) on the Fe site, while water is still adsorbed (*H2O) on the Co site and no proton on surface. Both configurations seems to be candidates for resting states at U = 1.63 (η=0.40 V) but state (e) will be used as resting state for further calculations when considered bias (U).

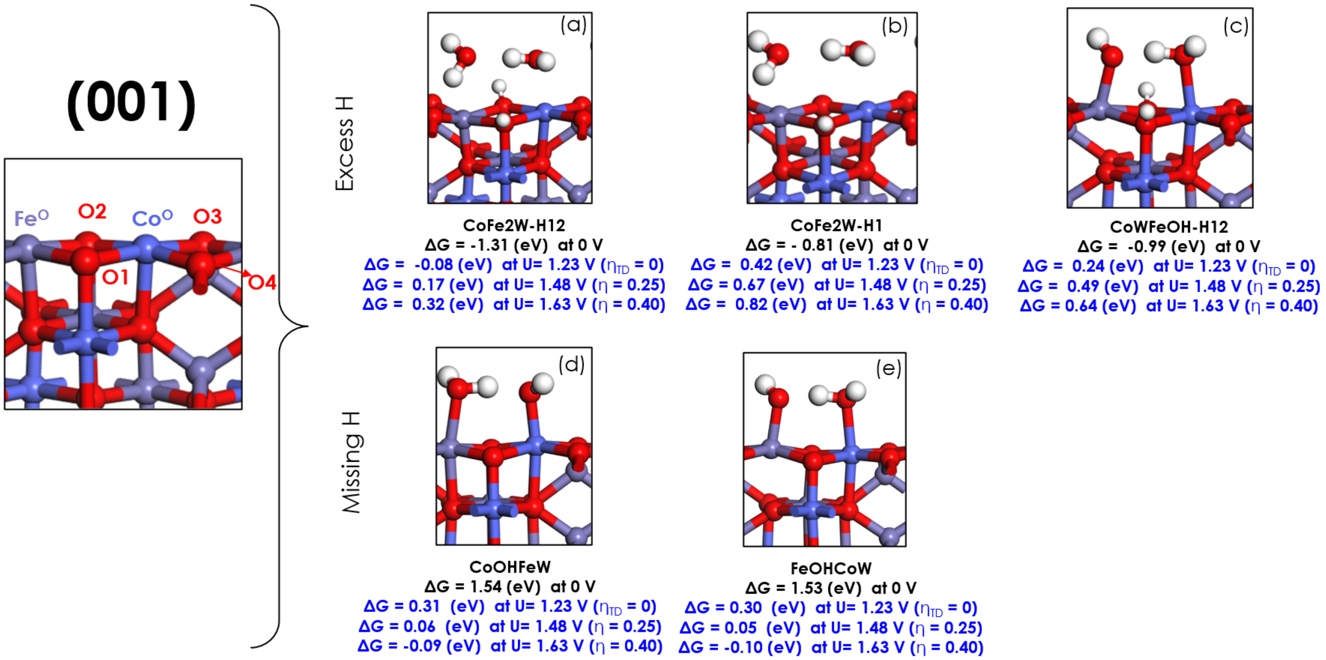


Figure S3. Off-stoichiometric coverage patterns on $CoFe_2O_4$ (001). (a-c) Surface covered with excess hydrogens on lattice oxygens. **(d-e)** Missing hydrogens with respect to two water coverage. Free energies referenced to the resting states in Figure S2. (b), (c). Energetics with respect to applied potentials (U = 1.23 V, 1.48 V and 1.63 V) has been reported each converged structure. The energetics are with respect to Figure S2 (b),(c) configurations. Oxygen, hydrogen, iron, and cobalt atoms are colored red, white, violet, and indigo blue, respectively.

2.2 Coverage on (110) surface

A similar coverage pattern on the (110) facet of $CoFe_2O_4$ inverse spinel was conducted using nonstoichiometric/symmetric slab, with unit cell dimensions 5.99 Å × 8.48 Å x 25 Å , corresponding to 50 atoms per unit cell.

The bare surface termination ended up with a significant distortion of the tetrahedral (under-coordinated) surface Fe atoms. As a first step of coverage on (110), O2 bridge was put as a chelate ligand on tetrahedral Fe-Fe atoms as stabilize the surface which explained in main text (see Figure 6) and The 4 surface lattice oxygens are labeled as O1, O2, O3, O4 along with octahedrally coordinated Co and Fe in surface.

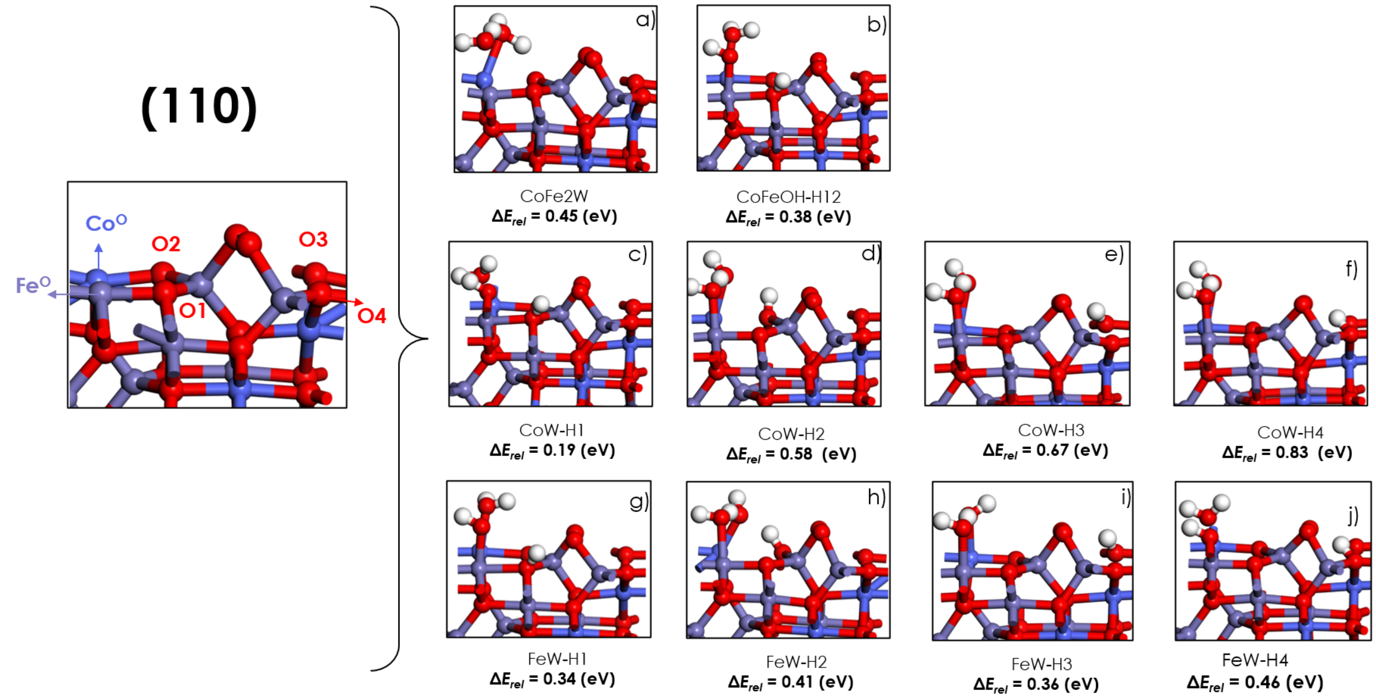
In Figure S4 and Figure S5, four different water coverage options were tried to adsorbed on the metal sites, together with their relative energetics: (i) adsorbed undissociated waters on each metal sites, (ii) adsorbed OH (*OH) on Fe sites, one protonated lattice surface oxygen and adsorbed (*H2O) on Co sites; (iii)adsorbed OH (*OH) on Co sites, one protonated lattice surface oxygen and adsorbed (*H2O) on Fe sites, (iv) adsorbed *OH on both Co and Fe metal sites and two protonated lattice surface oxygens. Note that the all optimized configurations in Figure S4 and Figure S5 (a-p) have the same overall stoichiometry, thus the total electronic energies can be directly compared.

The nomenclature of intended initial geometry was written under each Figure from (a) to (p) in Figure S4. For example, **CoFe2W** denotes two waters on Co and Fe sites in Figure S4.(a), or **FeW-H1** denotes water on Fe and O1 oxygen was protonated in Figure S4.(g) or **CoFeOH-2H12** denotes OH adsorption on both Co and Fe site along with two protonation on surface oxygens (O1 and O2) in Figure S5.(k**).** However, it was seen that some initial geometries optimized differently than intended initial geometries. The energetics of shown figures belong to optimized configurations.

As it seen from the configurations in first row (b) and third row [(g)-(j)] n Figure 4.9, when adsorbed OH (*OH) is placed on the Co site, it eventu ally converged to have *H2O adsorption on this site. OH (*OH) adsorption on Co sites were not preferred on the (110) surface. On the other side in the second row in [(c)-(f)] in Figure S4, the configurations with Co sites adsorbed with water and Fe sites adsorbed with (*OH) were converged as intended.

In Figure S5, Co and Fe sites were adsorbed OH (*OH) and two pro- tons on surface oxygens were tried. However, with an exception in the case of state (k) and (n), hydrogens from lattice oxygen numbered as O2 were captured by the Co sites, converged as water on the Co site. The resting state was found to be state (m) converging as OH on bridge region between the octahedrally coordinated Co and Fe metals and two protons on O1 and O4 surface lattice oxygens. The energetics of the rest of the configurations ranged from 0.2 eV to 1 eV with respect to the resting state (m) in Figure S5.

In Figure S6, off-stoichiometric coverage patterns with excess hydrogens on lattice oxygens on $CoFe_2O_4$ (110) were shown in state (a-e), and in state (f) with a missing hydrogen compared to two water coverage on octahedral Co-Fe sites. The state (f) was converged to have *OH adsorption on Fe and *H_2O on Co site, although the reverse pattern was tried (i.e.,*OH on Co and *H_2O on Fe) initially. Applied potentials (U) of 1.23 V, 1.48 V and 1.63 V was considered to find resting state in different reaction conditions. According to energetics, state (f) in Figure S6 is the resting state under $U > 1.24$ V.



CoFe2W ΔE_{rel} = 0.45 (eV)

CoFeOH-H12 ΔE_{rel} = 0.38 (eV)

CoW-H1 ΔE_{rel} = 0.19 (eV)

CoW-H2 ΔE_{rel} = 0.58 (eV)

CoW-H3 ΔE_{rel} = 0.67 (eV)

CoW-H4 ΔE_{rel} = 0.83 (eV)

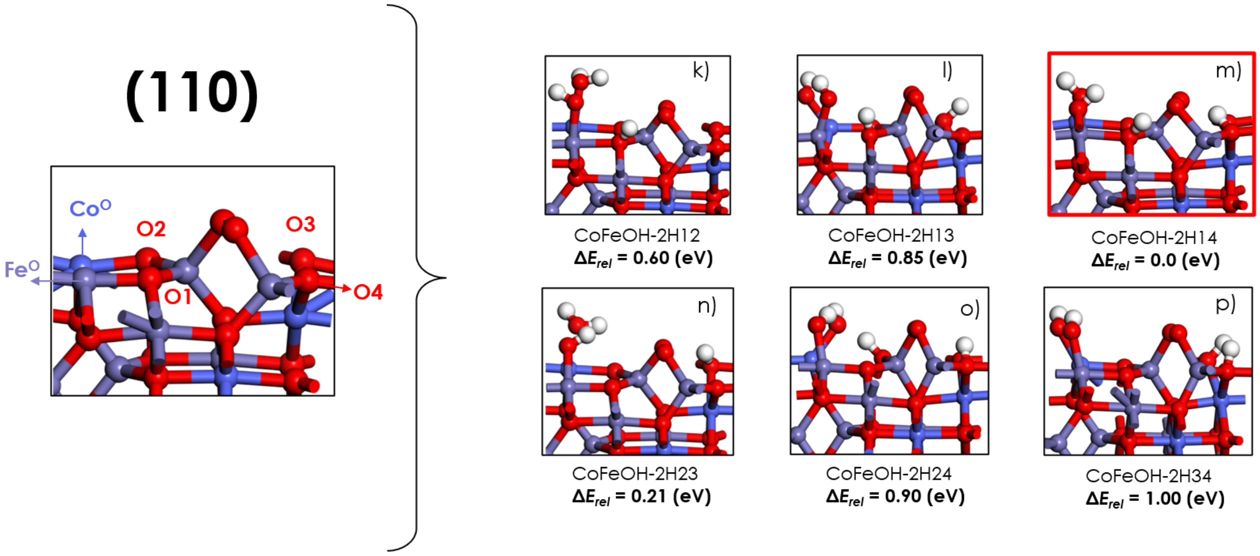
FeW-H1 ΔE_{rel} = 0.34 (eV)

FeW-H2 ΔE_{rel} = 0.41 (eV)

FeW-H3 ΔE_{rel} = 0.36 (eV)

FeW-H4 ΔE_{rel} = 0.46 (eV)

Figure S4. Dissociated water Coverage patterns on $CoFe_2O_4$ (110). Oxygen, hydrogen, iron, and cobalt atoms are colored red, white, violet, and indigo blue, respectively.



CoFeOH-2H12 ΔE_{rel} = 0.60 (eV)

CoFeOH-2H13 ΔE_{rel} = 0.85 (eV)

CoFeOH-2H14 ΔE_{rel} = 0.0 (eV)

CoFeOH-2H23 ΔE_{rel} = 0.21 (eV)

CoFeOH-2H24 ΔE_{rel} = 0.90 (eV)

CoFeOH-2H34 ΔE_{rel} = 1.00 (eV)

Figure S5. Dissociated water Coverage patterns on $CoFe_2O_4$ (110). Oxygen, hydrogen, iron, and cobalt atoms are colored red, white, violet, and indigo blue, respectively.

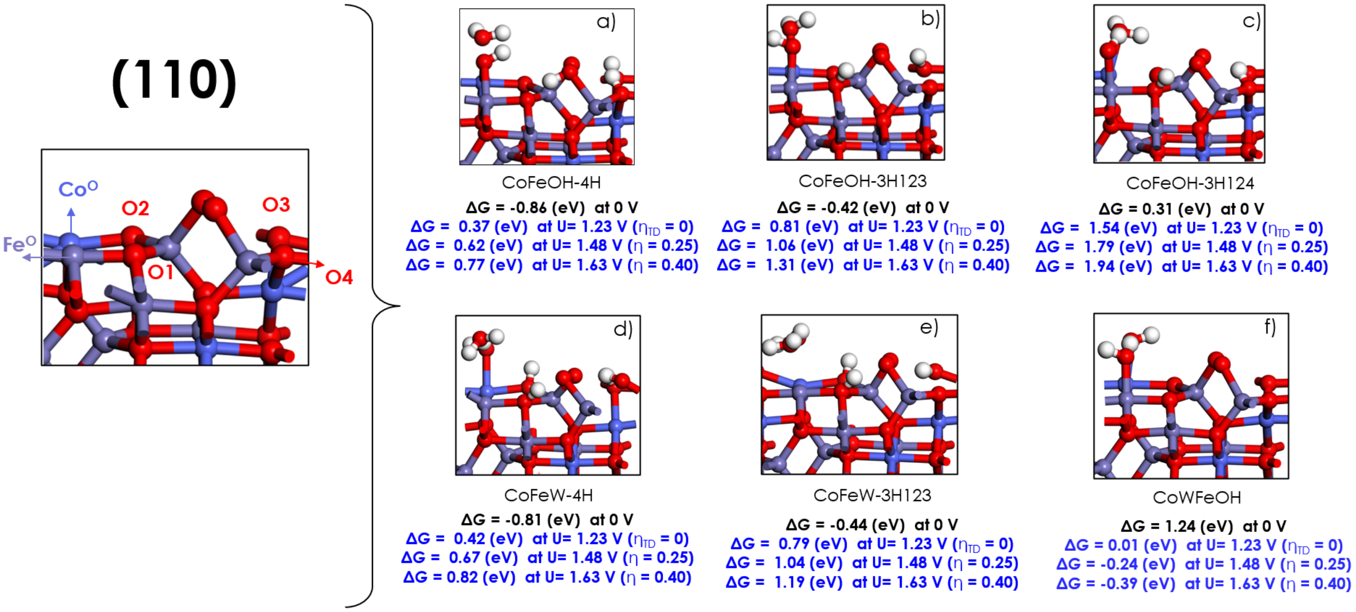


Figure S6. Off-stoichiometric coverage patterns on $CoFe_2O_4$ (110) with **(a-e)** excess hydrogens on lattice oxygens, and **(f)** with missing hydrogen. Free energies referenced to the resting states in Figure S5 (m). Energetics with respect to applied potentials (*U* = 1.23 V , 1.48 V and 1.63 V) has been reported each converged structure. Oxygen, hydrogen, iron, and cobalt atoms are colored red, white, violet, and indigo blue, respectively.

2.3 Coverage on (111) surface

A similar coverage pattern on the (111) facet of CoFe2O4 inverse spinel was carried out using nonstoichiometric/symmetric slab as shown in Figure S1, with unit cell dimensions 5.99 Å × 5.19 Å x 25 Å, corresponding to 43 atoms per unit cell.

As first step of the coverage, O_2 bridge was put on tetrahedral Fe and octahedral Co site. Because of the surface cut, one Fe valence coordination and three Co valence coordination are missing. The addition of O2 bridge has the effect of partially completing the coordination of the upper layer and thus lowering the energy. As a result, the O_2 bridge stabilizes the surface by 0.72 eV, similarly to what occurs on the (110) facet. However, while tetrahedral Fe completes its four coordination, two coordination are still missing for octahedral Co (see Figure S7 (left)).

As a next step of coverage, two water molecules were put near the Co surface atom in order to complete its two missing octahedral coordination in Figure S7(a). The surface was stabilized by 3.22 eV with respect to bare plane. Then, dissociated water coverage pattern (OH* + *H) was followed by protonating surface lattice oxygens in state (b) and (c) in Figure S7. It was observed that undissociated water adsorption in state (a) will be the resting state on (111) facet of CoFe2O4 up to U = 1.50 V. In the excess hydrogen scheme in state (d) in Figure 4.12 instead, one of the water coordinated to Co dissociates on the surface oxygen during the convergence, and in terms of energetics this configuration will not be considered as resting state under bias (U=1.23 V, 1.48 V and 1.63 V). However, in the state (e) in Figure S7, which is a coverage pattern that has one missing hydrogen with respect to state (a), water and *OH complete the missing coordination of Co and this state will be resting state $U > 1.50$.

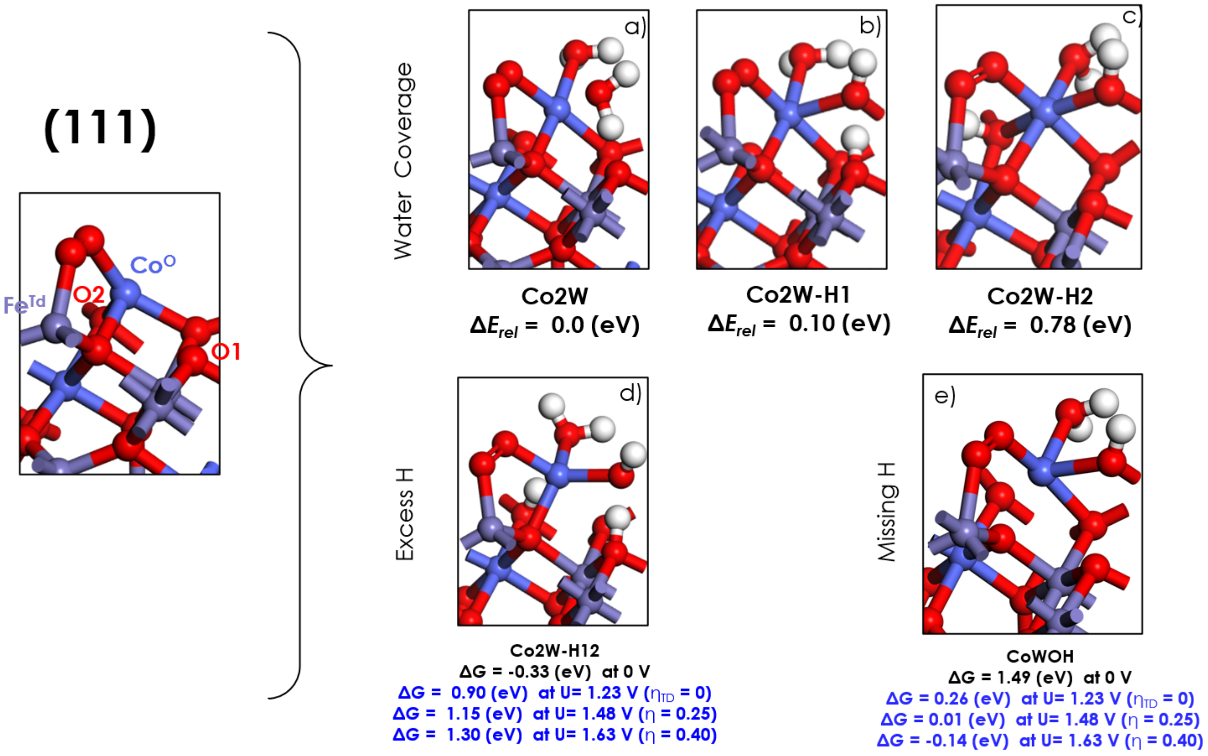


Figure S7. Water coverage (a-c), and off-stoichiometric coverage patterns on $CoFe_2O_4$ (111) with (d) excess hydrogens on lattice oxygens and (e) missing hydrogen. Free energies referenced to the resting states in (a). Energetics with respect to applied potentials (U = 1.23 V , 1.48 V and 1.63 V) has been reported under converged structure (d and e). Oxygen, hydrogen, iron, and cobalt atoms are colored red, white, violet, and indigo blue, respectively.

DFT Surface Energies in J/m^2 under oxygen pressure							
$CoFe_2O_4$	***U* =1.63 V**						
Facets	**10^{-4} atm**	**0.1 atm**	**0.5 atm**	**1atm**	**5 atm**	**15atm**	**30 atm**
(001)	0.71	0.71	0.71	0.71	0.71	0.71	0.71
(110)	1.34	0.96	0.88	0.84	0.75	0.69	0.65
(111)	1.30	0.68	0.53	0.47	0.32	0.23	0.16

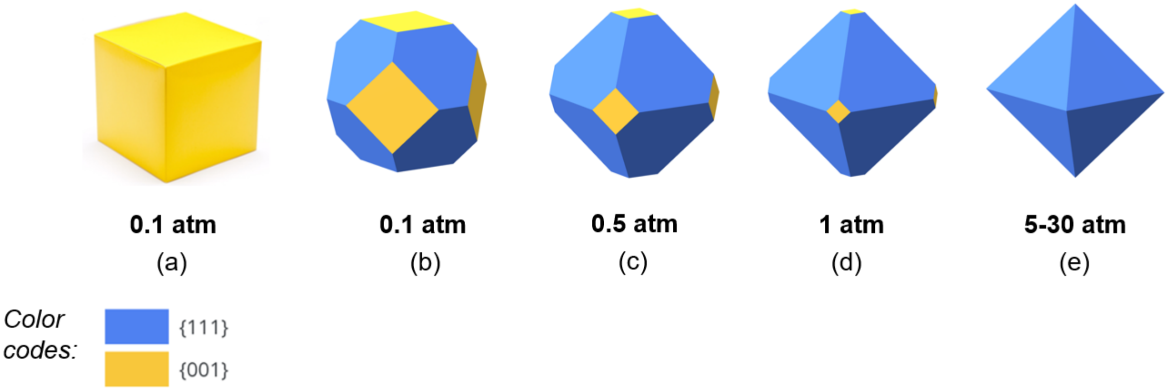


Figure S8. Calculated DFT Surface Energies with oxygen pressure (10^{-4} to 30 atm) on (001), (110) and (111) surfaces of $CoFe_2O_4$ under applied potential U = 1.63 V vs SHE (above). Wullf NP shapes of $CoFe_2O_4$ under U= 1.63 V, ranged from 10^{-4} atm (a) to 30 atm (e). Color codes: blue for (111), yellow for (001) facets.