Supporting Information:

Structural and electronic features of β-$Ni(OH)_2$ and β-NiOOH from first principles

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S1. Qualitative effect of $U-J$ parameter

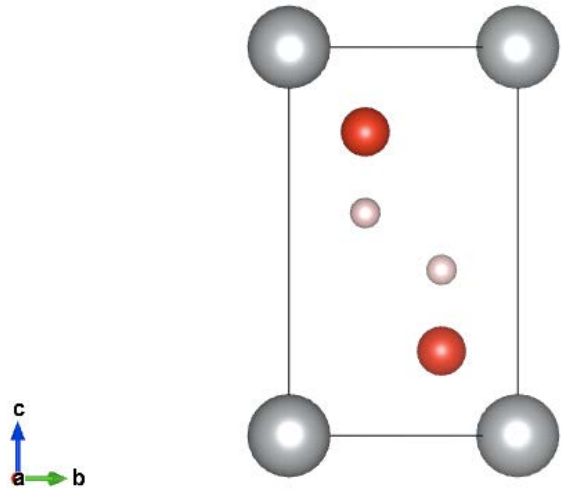
To justify our use of Li and Selloni's $U-J$ parameter,[1] we conducted a brief study of the effect of this parameter on the qualitative results for the staggered β-NiOOH structure. We found that it had only a limited impact on the lattice parameters.

Table 1: Effect of $U-J$ parameter on results

***U−J* parameter**	**Normalized Energy** (eV)	Lattice Parameters		
		a (Å)	*b* (Å)	*c* (Å)
2.5	-20.625	2.91	2.96	4.80
3.0	-20.374	2.91	2.95	4.81
3.8	-19.983	2.91	2.95	4.83
4.5	-19.654	2.92	2.96	4.82
5.5	-19.206	2.93	2.96	4.84
6.0	-18.994	2.94	2.96	4.82
6.5	-18.793	2.95	2.97	4.82
7.0	-18.602	2.96	2.98	4.80
Experiment	—	2.82	2.82	4.84

[1] Li, Y.; Selloni, A. *ACS Catal.* **2014**, *4*, 1148.

S1. Optimized coordinates for β-$Ni(OH)_2$



Ni = grey

O = red

H = off-white

Unit cell parameters: $a = b = 3.172$ Å, $c = 4.659$ Å; $\alpha = \beta = 90.0°$, $\gamma = 120.0°$

Atomic coordinates:

Ni -0.0000000000000000 0.0000000000000000 -0.0000000000000000

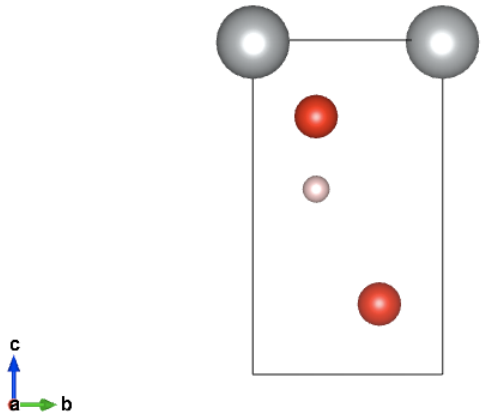
O 0.3333333429999996 0.6666666870000029 0.2180267046808849

O 0.6666666269999979 0.3333333129999971 0.7819733253191107

H 0.3333333429999996 0.6666666870000029 0.4269616305827629

H 0.6666666269999979 0.3333333129999971 0.5730383694172372

S2. Optimized coordinates for unstaggered β-NiOOH



Ni = grey

O = red

H = off-white

Unit cell parameters: $a = b = 2.974$ Å, $c = 4.544$ Å; $\alpha = \beta = 90.0°$, $\gamma = 120.0°$

Atomic coordinates:

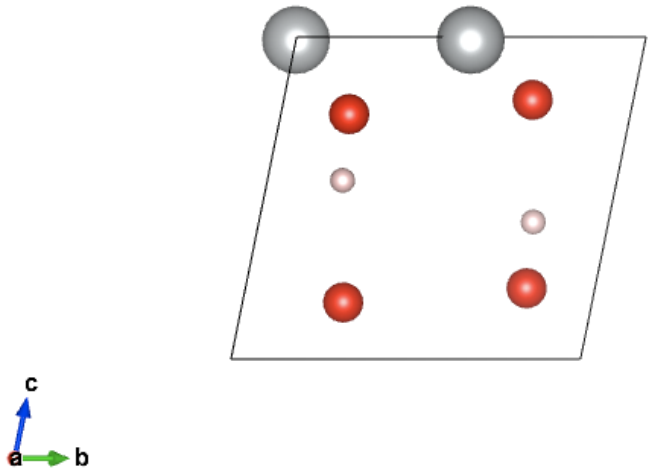
Ni -0.0000000000000000 -0.0000000000000000 0.9935935892891448

O 0.3333333429999996 0.6666666870000029 0.2108796127005685

O 0.6666666870000029 0.3333333429999996 0.7712512015821987

H 0.6666666870000029 0.3333333429999996 0.5542456314280861

S3. Optimized coordinates for staggered β-NiOOH



Ni = grey

O = red

H = off-white

Unit cell parameters: *a* = 2.926 Å, *b* = 5.913 Å, *c* = 4.839 Å; α = 80.0°, β = 90.0°, γ = 119.7°

Atomic coordinates:

Ni 0.0001414474793099 0.0001414474793099 0.9904182668421649

Ni -0.0000255241004750 0.4999744758995250 0.9903781100555626

O 0.2879690960235300 0.2879690960235300 0.1762871815705414

O 0.3045330563958609 0.8045330863958630 0.2203675447047104

O 0.6953717989863464 0.1953717839863414 0.7604442575574865

O 0.7120555358575940 0.7120555358575940 0.8045027009700531

H 0.7152769792463785 0.2152769642463737 0.5549835470050328

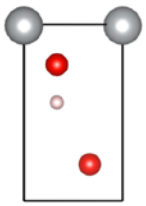
H 0.2846777001114631 0.7846777301114652 0.4258631832944474

S4. Supercells used to test effect of staggering proton positions

Ni = grey

O = red

H = off-white



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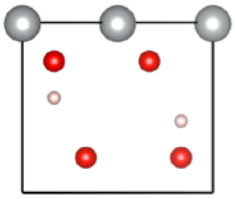

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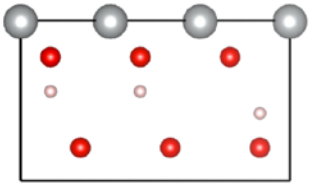

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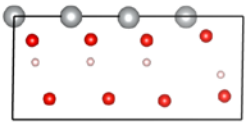

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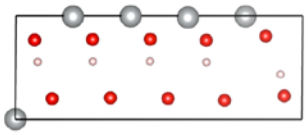

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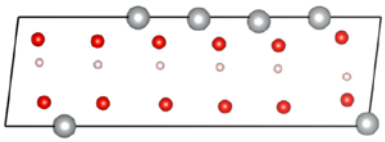


1 × 6 × 1

S5: Further spin configuration calculations

Another set of calculations was performed to test the preference of the staggered β-NiOOH structure for a low-spin, d^7 configuration. Eight different initial configurations were generated for the ferromagnetic case (see Table 2). Although each nickel ion was spin up, there were varying numbers of high-spin nickel ions. These were relaxed to determine if a mixed-spin, ferromagnetic case is lowest in energy.

Upon optimization of the staggered structure, each of the structures relaxed to a low-spin system. The lattice parameters and final spin moments of the optimized structures varied and therefore had different energies. The arrows and circles in the final spin state describe the spin directions on each nickel ion. 'FM' denotes that the structure relaxed to a ferromagnetic configuration. The up arrows correspond to positive magnetic moments on the nickel atoms, while the down arrows correspond to negative magnetic moments on the nickel atoms. The circles denote magnetizations on nickel atoms that are close to 0.

Initial spin configuration	**Initial number of low spin**	**Final spin state**	**Final number of low spin**	**Energy** (eV)
FM	0	FM	8	**-19.01**
FM	1	○↑↑↑ ○↓↓↓	8	**-19.03**
FM	2	FM	8	**-19.01**
FM	3	↑↑○○ ○↑↑↑	8	**-19.31**
FM	4	FM	8	**-19.01**
FM	5	FM	8	**-19.01**
FM	6	FM	8	**-19.01**
FM	7	○↑↑○ ↑↑↑↑	8	**-19.25**
FM	8	FM	8	**-19.01**

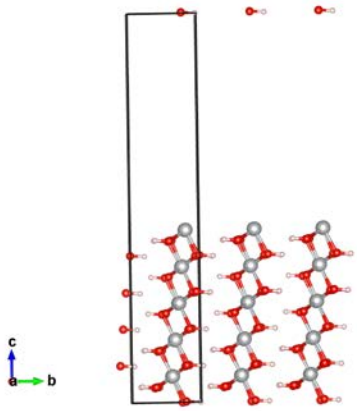
Table 2: Initial and final spin configurations for mixed-spin, ferromagnetic configurations

S6. Surfaces of staggered β-NiOOH tested

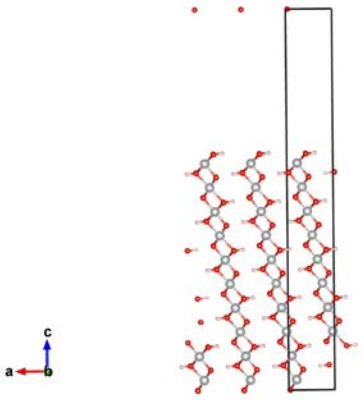
Ni = grey

O = red

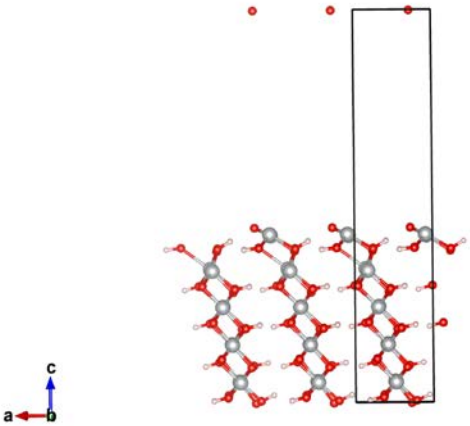
H = off-white



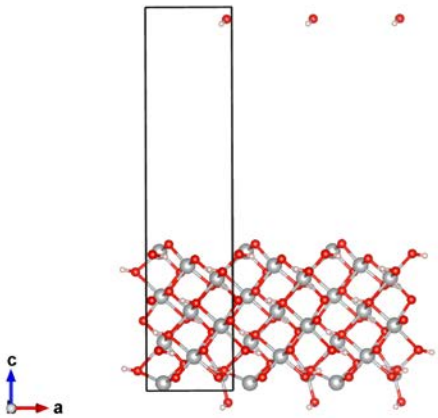
(1 0 0)



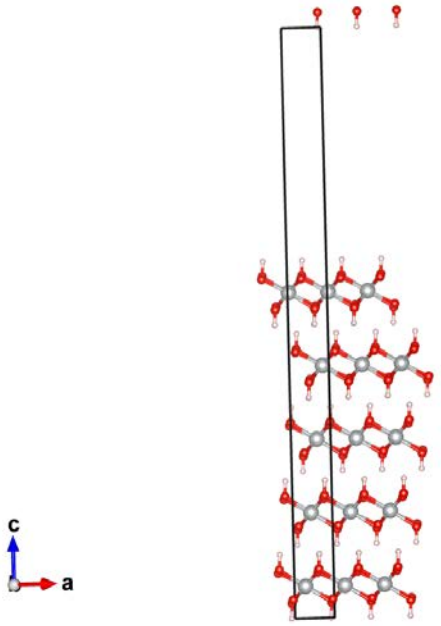
(0 1 0)



(1 0 1)



(1 1 1)



(0 0 1)

S7. Lattice parameters and *k*-point meshes of β-$Ni(OH)_2$ and β-NiOOH surfaces

Table 3: Lattice parameters and *k*-point meshes for β-$Ni(OH)_2$ surfaces

Surface	Number of atoms in slab cell	Lattice parameters			*k*-point mesh
		a (Å)	*b* (Å)	*c* (Å)	
(1 0 0)	20	3.172	4.659	27.819	3 x 2 x 1
(0 1 0)	20	4.659	3.172	27.819	2 x 3 x 1
(1 0 1)	20	6.636	3.172	26.588	2 x 3 x 1
(1 1 1)	20	5.494	5.636	22.287	2 x 2 x 1
(0 0 1)	20	3.172	3.172	37.614	3 x 3 x 1

Table 4: Lattice parameters and *k*-point meshes for staggered β-NiOOH surfaces

Surface	Number of atoms in slab cell	Lattice parameters			*k*-point mesh
		a (Å)	*b* (Å)	*c* (Å)	
(1 0 0)	30	5.913	4.839	26.929	3 x 3 x 1
(0 1 0)	30	4.839	5.852	39.811	3 x 3 x 1
(1 0 1)	30	5.654	5.913	26.004	3 x 3 x 1
(1 1 1)	30	5.654	6.961	24.167	3 x 2 x 1
(0 0 1)	30	5.852	5.913	38.093	3 x 3 x 1