Hybrid Functional Study Of The Electro-oxidation Of Water On Pristine And Defective Hematite (0001)

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Supporting Information Available

OER reaction energy landscape calculated using PBE + U

Table S1: The calculated free energy difference of different reaction steps and the overpotential with PBE + U.

Surface terminations	ΔG_1 (eV)	ΔG_2 (eV)	ΔG_3 (eV)	ΔG_4 (eV)	ΔG_5 (eV)	Overpotential (V)
R-Fe-Fe-$(OH)_3$	0.05	-0.03	1.89	1.67	1.34	0.66
R-Fe-Fe-$(OH)_3$ (O vacancy)	1.42	-0.85	0.53	2.99	0.83	1.76
R-Fe-Fe-O_3	-0.19	1.36	2.14	1.54	0.08	0.91
R-Fe-Fe-O_3 (O vacancy)	-1.36	1.89	1.75	1.82	0.48	0.66

Table S2: The calculated potential limiting step and onset potential with HSE and PBE + U (in eV).

Termination	Potential limiting step	Onset potential (Ref.[1])
R-Fe-Fe-$(OH)_3$ (HSE)	4	0.99
R-Fe-Fe-$(OH)_3$ (PBE + U)	3	0.66 (0.56)
defective R-Fe-Fe-$(OH)_3$ (HSE)	4	1.29
defective R-Fe-Fe-$(OH)_3$ (PBE + U)	4	1.76 (1.86)
R-Fe-Fe-O_3 (HSE)	4	0.45
R-Fe-Fe-O_3 (PBE + U)	3	0.91 (0.86)
defective R-Fe-Fe-O_3 (HSE)	4	1.10
defective R-Fe-Fe-O_3 (PBE + U)	2	0.66 (0.60)

Stoichiometric and asymmetric slab

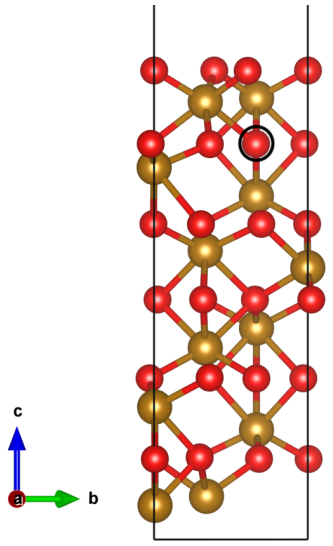

Figure S1: The stoichiometric and asymmetric slab of R-Fe-Fe-O_3 termination. The red color ball indicates oxygen atom, white color ball is hydrogen atom, and brown ball is Fe atom. The black circle indicates the subsurface O atom removed to create defective surface structure.

Relaxed structure information

Surface electronic structure information

Table S3: The calculated subsurface O vacancy formation energy and O adsorption energy (referenced to O_2 gas molecule.) on the stoichiometric and asymmetric slab of R-Fe-Fe-O_3 termination (in eV).

Symmetric slab	
subsurface O vacancy	1.69
O adsorption energy	0.087
Asymmetric slab	
subsurface O vacancy	-0.13
O adsorption energy	-1.00

Table S4: The optimised atomic structure of top layer O and Fe atoms of O terminated surface (HSE results) with surface lattice constants a = 5.032Åand c = 33.852 Å.

Termination	Atomic coordinates (inner)			Bond length (Å)	
R-Fe-Fe-O_2	x	y	z	d(O-Fe1)	d(O-Fe2)
O1	0.1267	0.4271	0.4056	1.75	1.83
O2	0.3036	0.0209	0.4027	1.77	1.80
Fe1	0.0525	0.6754	0.3776		
Fe2	0.3233	0.3107	0.3700		
R-Fe-Fe-O_3	x	y	z	d(O-Fe1)	d(O-Fe2)
O1	0.6787	0.5895	0.4094	1.6797	1.8947
O2	0.3037	0.9140	0.4061	1.6940	2.0924
O3	0.0503	0.3398	0.3956	1.7139	1.8172
Fe1	0.9844	0.6333	0.3839		
Fe2	0.3547	0.2657	0.3809		
R-Fe-Fe-O_3 (with O_v)	x	y	z	d(O-Fe1)	d(O-Fe2)
O1	0.6670	0.5883	0.4098	1.88	1.93
O2	0.2956	-0.0837	0.4074	1.73	1.86
O3	0.0577	0.3448	0.3946	1.71	1.82
Fe1	-0.0244	0.6288	0.3841		
Fe2	0.3535	0.2573	0.3791		
R-Fe-Fe-O_2-OH	x	y	z	d(O-Fe1)	d(O-Fe2)
O1	0.2872	0.00337	0.40501	1.91	1.935
O2	0.3037	0.9140	0.4061	2.00	1.761
O3	0.0623	0.3785	0.4011	1.755	1.81
Fe1	0.9844	0.6333	0.3839		
Fe2	0.3547	0.2657	0.3809		
R-Fe-Fe-O_2-OOH	x	y	z	d(O-Fe1)	d(O-Fe2)
O1	0.2988	0.0101	0.4016	1.916	1.933
O2	0.6494	0.6141	0.4007	1.807	1.764
O3	0.0443	0.3839	0.4004	1.750	1.817
Fe1	0.9844	0.6333	0.3839		
Fe2	0.3547	0.2657	0.3809		

Table S5: The optimised atomic structure of top layer O and Fe atoms of OH terminated surface (HSE results).

Termination	Atomic coordinates (inner)			Bond length (Å)	
R-Fe-Fe-$(OH)_2$	x	y	z	d(O-Fe1)	d(O-Fe2)
O1	0.3688	0.0519	0.4136	1.99	2.03
O2	0.0414	0.3454	0.4092	1.98	2.14
Fe1	0.0838	0.7035	0.3794		
Fe2	0.3319	0.2911	0.3675		
R-Fe-Fe-$(OH)_3$	x	y	z	d(O-Fe1)	d(O-Fe2)
O1	0.3093	0.9924	0.4077	1.90	2.21
O2	0.6811	0.6468	0.4075	1.97	2.06
O3	0.0339	0.3649	0.4074	1.89	2.075
Fe1	0.0052	0.6664	0.3770		
Fe2	0.3455	0.3335	0.3703		
R-Fe-Fe-$(OH)_3$ (with O_v)	x	y	z	d(O-Fe1)	d(O-Fe2)
O1	0.3723	0.0542	0.4028	2.00	1.99
O2	0.6227	0.6581	0.4142	1.91	2.12
O3	0.0036	0.3714	0.4168	1.98	2.08
Fe1	0.9713	0.6923	0.3868		
Fe2	0.2867	0.3472	0.3738		
R-Fe-Fe-$(OH)_2$-O	x	y	z	d(O-Fe1)	d(O-Fe2)
O1	0.3396	0.0155	0.4087	1.94	2.03
O2	0.0431	0.3450	0.4069	1.94	2.04
O3	0.7107	0.6435	0.4051	1.81	2.06
Fe1	0.0135	0.6712	0.3802		
Fe2	0.35689	0.3326	0.3700		
R-Fe-Fe-$(OH)_2$-OOH	x	y	z	d(O-Fe1)	d(O-Fe2)
O1	0.0572	0.3684	0.4068	1.89	2.04
O2	0.3206	-0.0092	0.4052	1.87	2.04
O3	0.6978	0.6543	0.4036	1.88	2.13
Fe1	0.9844	0.6333	0.3839		
Fe2	0.3547	0.2657	0.3809		

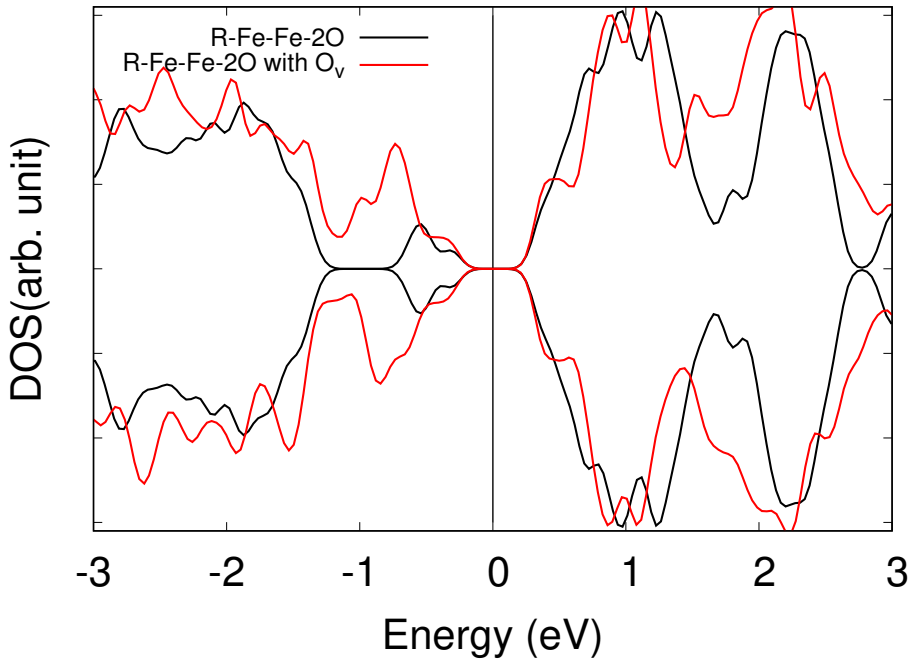

Figure S2: The total DOS of pristine and defective R-Fe-Fe-O_2. The Fermi energy level is set to 0 eV for both surfaces.

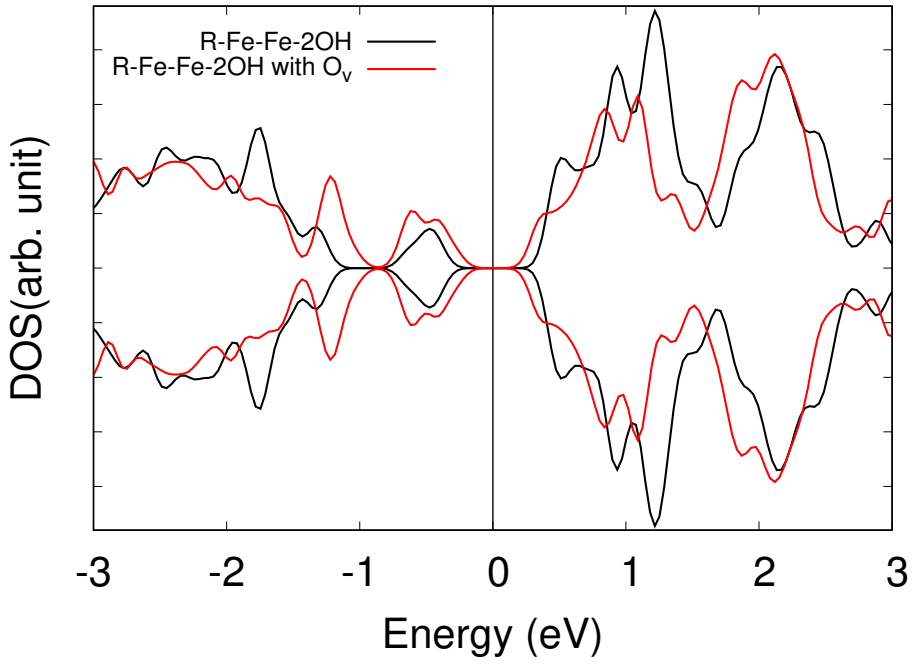

Figure S3: The total DOS of pristine and defective R-Fe-Fe-$(OH)_2$. The Fermi energy level is set to 0 eV for both surfaces.

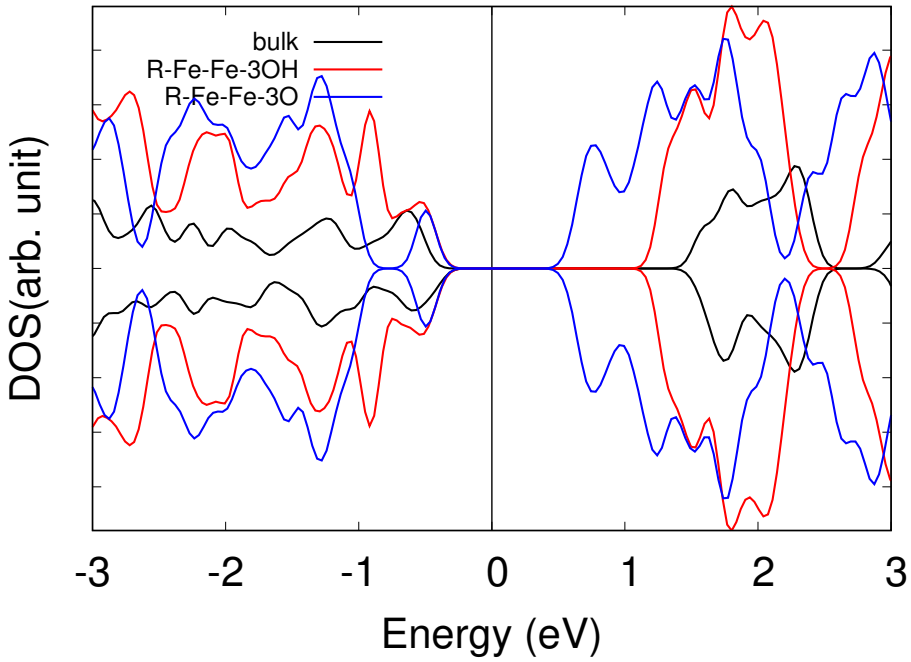

Figure S4: The total DOS of bulk, R-Fe-Fe-$(OH)_3$ and R-Fe-Fe-O_3. The Fermi energy level is set to 0 eV for all structures.

References

(1) Hellman, A.; Iandolo, B.; Wickman, B.; Grönbeck, H.; Baltrusaitis, J. Electro-oxidation of water on hematite: Effects of surface termination and oxygen vacancies investigated by first-principles. *Surface Science* **2015**, *640*, 45 – 49, Reactivity Concepts at Surfaces: Coupling Theory with Experiment.