

Supplementary Material

OER trends on TiO₂ anatase hydroxylated surfaces: A DFT study

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Table S1 Calculated DFT adsorption energies of OER HO*/HO*/HOO* intermediates on Ti_c, O_{3c}, O_b sites using BEEF-vdW functional.

Surface	Hydroxylated surfaces	$\Delta E_{\text{HO}^*}(\text{eV})$ on Ti _c	$\Delta E_{\text{O}^*}(\text{eV})$ on Ti _c	$\Delta E_{\text{HOO}^*}(\text{eV})$ On Ti _c
(100)	4OH _b 3OH _c 1*c	-0.64	2.12	2.45
	4OH _b 2OH _c 1Oc1*c	1.86	4.77	4.62
	4OH _b 1OH _c 2Oc1*c	2.14	5.01	4.28
	4OH _b 3Oc1*c	2.05	5.06	4.28
	3OH _b 1Ob3Oc1*c	2.04	5.12	
	2OH _b 2Ob3Oc1*c	2.03	5.12	
	4Ob4*c	1.86	4.87	4.83
	4Ob1OH _c 3*c	1.99	5.04	4.84
	1OH _b 3Ob 4*c	-0.56	2.09	2.77
	1OH _b 3O _b 1OH _c 3*c	1.78	4.79	4.75
	2OH _b 2O _b 4*c	-0.78	-0.51	2.52
	(101)	4OH _b 3OH _c 1*c	-0.81	1.82
4OH _b 2OH _c 1Oc1*c		1.48	4.25	4.38
4OH _b 1OH _c 2Oc1*c		1.75	4.55	4.34
4OH _b 3Oc1*c		1.76	4.55	4.29
3OH _b 1O _b 3Oc1*c		1.97	4.85	
2OH _b 2O _b 3Oc1*c		2.06	4.92	
4O _b 4*c		2.06	5.12	4.5
4Ob1OH _c 3*c		2.16	5.32	4.57
4O _b 2OH _c 2*c		2.17	5.21	4.45
1OH _b 3O _b 4*c		-0.65	2.14	2.41
2OH _b 2O _b 4*c		-0.94	-0.66	2.32
4OH _b 1O _c		-1.01	-0.85	2.20
4OH _b 1O _c 1OH _c 2*c		-0.81	1.84	2.18

	4OH _b 2O _c 2* _c	1.64	4.51	4.30
		$\Delta E_{HO^*}(eV)$ on O _{3c}	$\Delta E_{O^*}(eV)$ on O _{3c}	$\Delta E_{HOO^*}(eV)$ on O _{3c}
(100)	4OH _b 1OH _c 2O _c 1* _c	1.17	3.04	3.85
	4OH _b 3O _c 1* _c	0.81	2.88	3.6
(101)	4OH _b 1OH _c 2O _c 1* _c	1.07	2.80	4.17
	4OH _b 3O _c 1* _c	0.97	2.73	3.97
		$\Delta E_{HO^*}(eV)$ on O _b	$\Delta E_{O^*}(eV)$ on O _b	
(100)	3OH _b 1O _b 3O _c 1* _c	0.83	1.86	-
	2OH _b 2O _b 3O _c 1* _c	0.54	1.74	-
(101)	3OH _b 1O _b 3O _c 1* _c	0.14	1.71	-
	2OH _b 2O _b 3O _c 1* _c	0.08	0.77	-
		$\Delta E_{HO^*}(eV)$ on 2Ti _b	$\Delta E_{O^*}(eV)$ on 2TiO _b	
(100)	3OH _b 1* _b 3O _c 1* _c	0.81	3.27	4.1
	2OH _b 1O _b 1* _b 3O _c 1* _c	0.88	3.38	3.91
(101)	3OH _b 1* _b 3O _c 1* _c	0.59	3.2	3.35
	2OH _b 1O _b 1* _b 3O _c 1* _c	0.76	3.4	3.72

Table S2 DFT Zero point energy corrections (ZPE) and entropy corrections at room temperatures (TS)

	ZPE	TS
H ₂ (g)	0.28	0.41
H ₂ O (g)	0.58	0.67
O* (on Ti _c)	0.085	
O* (on O _{3c})	0.076	
O* (on O _b)	0.076	
HO* (on Ti _c)	0.36	
HO* (on O _{3c})	0.36	
HO* (on O _b)	0.36	
HOO* (on Ti _c)	0.47	

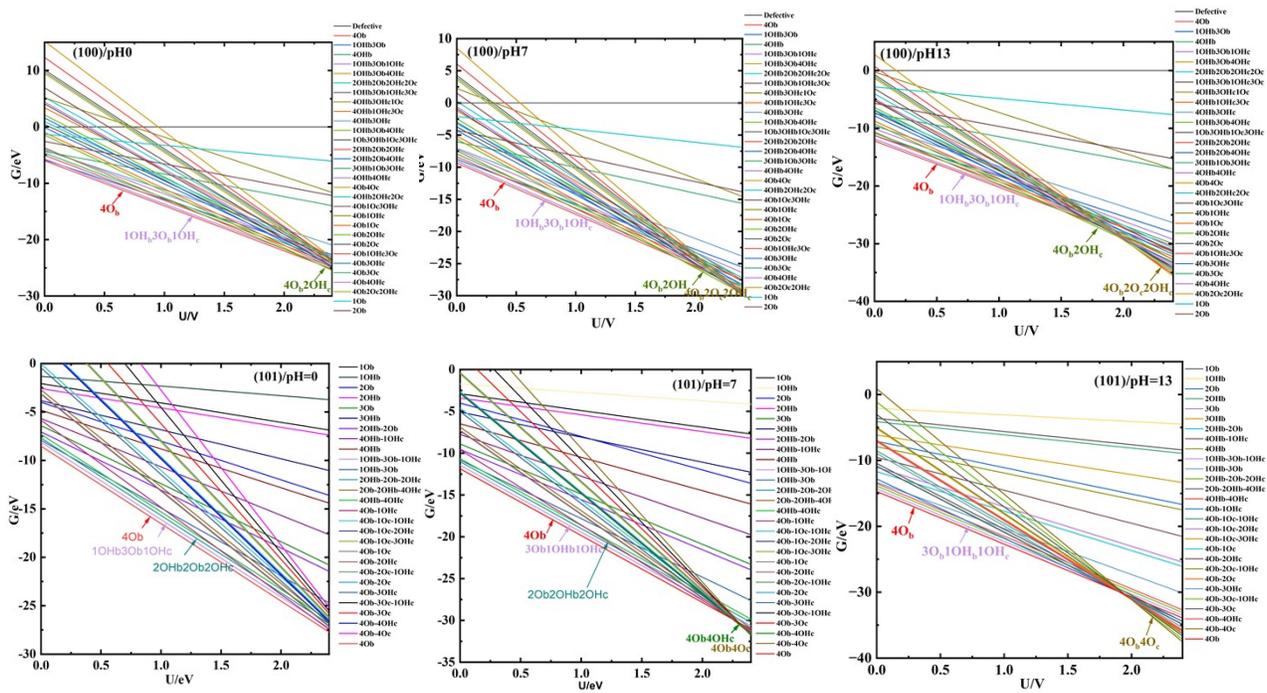


Figure 1 DFT based surface Pourbaix diagrams of (100) and (101) surfaces at pH=0, 7 and 13