Supplementary Information

Investigating Surface Properties and Lithium Diffusion in Brookite-TiO_2

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Table S1. Surface energies of Brookite-TiO_2 using METADISE (interatomic potentials)[a]

(*hkl*) surface	Surface energy / (J m^{-2})
(210)	1.61
(110)	1.88
(101)	1.88
(001)	1.94
(212)	1.95
(211)	1.96
(201)	1.97
(010)	2.01
(111)	2.05
(012)	2.06
(221)	2.06
(021)	2.07
(100)	2.09
(112)	2.1
(120)	2.13
(011)	2.15
(121)	2.19
(102)	2.21
(122)	2.51
(301)	2.2
(140)	2.25

[a]Reference 1.

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Table S2. Surface energies of brookite-TiO_2 using DFT+U methods

(*hkl*) surface	(010)	(100)	(111)	(301)	(210)
PW91 U = 0 eV / (J m^{-2})	0.826	0.947	0.778	1.028	0.707
PW91 U = 7 eV / (J m^{-2})	1.165	0.995	1.017	1.318	0.865

For U = 7 eV, the cell parameters are from U = 0 eV, all ions are relaxed.

Table S3. Band gaps E_g and cell volumes V of rutile, anatase and brookite-TiO_2 using DFT+U methods

	Rutile	Anatase	Brookite
	E_g / eV | V / Å^3	E_g / eV | V / Å^3	E_g / eV | V / Å^3
PW91 U = 0 eV	1.91 | 63.86	2.22 | 140.10	2.32 | 263.13
PW91 U = 4 eV	2.25 | 65.52	2.51 | 144.43	2.52 | 270.82
PW91 U = 9 eV	2.78 | 67.92	3.20 | 150.84	3.21 | 283.10
PW91 U = 10 eV	2.95 | 68.41	3.52 | 152.07	3.39 | 285.32
LDA U = 0 eV	1.90 | 60.58	2.30 | 132.99	2.45 | 249.73
LDA U = 9 eV	2.91 | 64.85	3.32 | 143.61	3.34 | 269.49

Cell parameters and ionic positions are relaxed; J = 0.80 eV, U_{eff} = U – J; V experimental: rutile = 62.40 Å^3 (ref. 2), anatase = 137.35 Å^3 (ref. 3), brookite = 257.38 Å^3 (ref. 4).

The sensitivity of the band gaps to the value of U with this functional demonstrates that further verification is needed before using such empirically derived values of U to comparing bulk and surface band gaps. In Table 3, it can be observed that increasing the U value increases the overestimation of the cell/volumes parameters and increases the band gap. Without U, the error on the parameters of the three TiO_2 polymorphs with PW91 functional is 2%. From U = 4 eV (U_{eff} = 3.2 eV), the error is 5% and it is up to 11% for U = 10 eV. With LDA (CA), at U = 9 eV, the error on the volume cell is 3% for rutile and 5% for anatase and brookite.

References

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