Supporting information for:

**Ab Initio Thermodynamic Modeling of Electrified
Metal-Oxide Interfaces: Consistent Treatment of
Electronic and Ionic Chemical Potentials**

Zhenhua Zeng,^{†,‡} Martin Hangaard Hansen,[†] Jeffrey P. Greeley,[‡] Jan
Rossmeisl,[†] and Mårten E. Björketun^{*,†}

*Center for Atomic-scale Materials Design, Department of Physics, Technical University of
Denmark, DK-2800 Lyngby, Denmark, and School of Chemical Engineering, Purdue
University, West Lafayette, Indiana 47907, United States*

E-mail: martebo@fysik.dtu.dk

^{*}To whom correspondence should be addressed

[†]Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark,
DK-2800 Lyngby, Denmark

[‡]School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, United States

1 The anodic electrode potential and interface energies

At the SOFC anode (Ni-YSZ), the half reaction is given by

Under a given set of standard conditions ($T^0, p_{\text{H}_2\text{O}}^0, p_{\text{H}_2}^0$), the reaction will be in equilibrium at an absolute anodic potential U_{a}^0 ($\Phi_{\text{e}^-, \text{a}}^0$) and chemical potential $\mu_{\text{O}^{2-}}^0$. This means that $\mu_{\text{O}^{2-}}^0 - 2\mu_{\text{e}^-}^0 + \mu_{\text{H}_2}^0 = \mu_{\text{H}_2\text{O}}^0$ and $\Delta\mu_{\text{O}^{2-} - 2\text{e}^- + \text{H}_2|\text{H}_2\text{O}} = 0$. As $\mu_{\text{H}_2\text{O}}^0 - \mu_{\text{H}_2}^0 = \mu_{\text{O}_2}^0 + \Delta G_{\text{w}}^0$ (ΔG_{w}^0 is the H_2O standard free energy of formation), the equilibrium anodic potential U_{a}^0 can be expressed as,

$$U_{\text{a}}^0 = U^0 - \Delta U_{\text{w}}^0 \quad (\text{S2})$$

where U^0 is the equilibrium cathodic potential determined by Eq. 2 in the main text, and $\Delta U_{\text{w}}^0 = -\Delta G_{\text{w}}^0/e$ is the potential change associated with water formation. From Figs. 5,6 and Fig. S1, we see that the anodic potential (dash-dotted vertical lines) is always lower than the cathodic potential (dashed vertical lines). To distinguish it from the cathodic electrochemical potential, we have intentionally expressed the anodic electrochemical potential as $\Delta\mu_{\text{O}^{2-} - 2\text{e}^- + \text{H}_2|\text{H}_2\text{O}}$, which is 0 when Reaction S1 is in equilibrium. This occurs at an absolute anodic potential U_{a}^0 ($\Phi_{\text{e}^-, \text{a}}^0$) and chemical potential $\mu_{\text{O}^{2-}}^0$ under the above set of standard conditions.

At other electrode potentials U (Φ_{e^-}) and/or chemical potentials $\mu_{\text{O}^{2-}}$, similarly to the cathodic electrochemical potential, $\Delta\mu_{\text{O}^{2-} - 2\text{e}^- + \text{H}_2|\text{H}_2\text{O}}$ is given by

$$\begin{aligned} \Delta\mu_{\text{O}^{2-} - 2\text{e}^- + \text{H}_2|\text{H}_2\text{O}} &= \mu_{\text{O}^{2-}} - \mu_{\text{O}^{2-}}^0 + 2(\Phi_{\text{e}^-} - \Phi_{\text{e}^-, \text{a}}^0) \\ &= \Delta\mu_{\text{O}^{2-}} + 2\Delta\Phi_{\text{e}^-, \text{a}} = \Delta\mu_{\text{O}^{2-}} + 2e\Delta U_{\text{a}} \end{aligned} \quad (\text{S3})$$

For an interface with intrinsic potential U (Φ_{e^-}) and in equilibrium with H_2O and H_2

($\mu_{\text{O}^{2-}-2\text{e}^{-}+\text{H}_2|\text{H}_2\text{O}} = 0$), the free energy per interface metal atom is given by

$$G_{\text{int}}^{0,\Phi_{\text{e}^{-}}} = \frac{G_{N,n_{\text{O}}} - G_{N,0}}{N} - \frac{n_{\text{O}}}{N}(G_{\text{H}_2\text{O}} - G_{\text{H}_2}), \quad (\text{S4})$$

in analogy to Eq. 4 in the main text. For any $\Delta\mu_{\text{O}^{2-}-2\text{e}^{-}+\text{H}_2|\text{H}_2\text{O}} \neq 0$, the interface free energy is given by

$$G_{\text{int}}^{\Phi_{\text{e}^{-}}}(\Delta\mu_{\text{O}^{2-}-2\text{e}^{-}+\text{H}_2|\text{H}_2\text{O}}) = G_{\text{int}}^{0,\Phi_{\text{e}^{-}}} - \frac{n_{\text{O}}}{N}\Delta\mu_{\text{O}^{2-}-2\text{e}^{-}+\text{H}_2|\text{H}_2\text{O}}. \quad (\text{S5})$$

2 Free energy calculations

As indicated in the main text, the free energies of the interface models and the gas phase species are obtained from DFT calculations and standard tables. For the gas phase species, the free energy is calculated with the formula:

$$G = E^{\text{DFT}} + ZPE - TS \quad (\text{S6})$$

where E^{DFT} is the total energy from DFT calculations, ZPE is the zero-point energy obtained from experimental vibrational frequencies, TS is the product of the temperature (T) and the entropy (S), which can be expressed further by $TS = TS^{\circ} + k_{\text{B}}T \ln(p/p^{\circ})$. S° is tabulated standard entropy, k_{B} is the Boltzmann constant, and p is the partial pressure. For solid species, the ZPE and TS terms are rarely influenced in the interface formation processes. Besides, the phonon calculation is very time consuming for the systems considered in the present work. Thus, we have neglected these two terms in the interface free energy calculations. We note that for the solid-liquid interface, treated in a previous paper,^{S1} the solvation entropy of protons at the interface (or more correctly in the double layer) may be somewhat different than in the bulk electrolyte, which would slightly shift the potential where a certain coverage transitions into another. However, the scheme and the trends

presented in the present paper and in Ref. S1 are still valid.

3 Most stable Ni-YSZ models at each vacancy concentration

The cartesian coordinates of the most stable Ni-YSZ triple phase boundary (TPB) models at each vacancy concentration are given in Table S1.

Table S1: Cartesian coordinates of the Ni-YSZ TPB model with 0 oxygen vacancies. The supercell is a (7.307241 Å, 12.656514 Å, 23.483351 Å) orthorhombic box. The most stable TPB models with 1 to 6 oxygen vacancies are obtained by consecutively removing oxygen No.34, No.67, No.47, No.46, No.41 and No.42.

No.	element	x(Å)	y(Å)	z(Å)
1	Zr	1.826810	1.054709	5.745792
2	Zr	5.480431	1.054709	5.745792
3	Zr	0.000000	4.218838	5.745792
4	Zr	3.653621	4.218838	5.745792
5	Zr	1.826810	7.382966	5.745792
6	Zr	5.480431	7.382966	5.745792
7	Zr	0.000000	10.547095	5.745792
8	Zr	3.653621	10.547095	5.745792
9	Zr	0.007973	2.075688	8.622697
10	Zr	3.648911	2.072791	8.625543
11	Zr	5.482687	5.278778	8.616024
12	Zr	0.016120	8.464757	8.712133
13	Zr	3.639404	8.464091	8.712289
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Table S1 – continued

No.	element	x(Å)	y(Å)	z(Å)
14	Zr	1.830665	11.570876	8.698908
15	Zr	0.053021	-0.179826	11.785031
16	Zr	3.629485	-0.177029	11.796177
17	Zr	5.484255	3.238608	11.728451
18	Zr	-0.089961	6.337551	11.605059
19	Zr	3.750858	6.334572	11.605329
20	Zr	1.832089	9.573929	11.851840
21	Y	1.828812	5.258603	8.767129
22	Y	5.482522	11.602442	8.774664
23	Y	1.832101	3.012176	11.909465
24	Y	5.485006	9.522700	11.884233
25	O	1.826810	5.273547	6.491584
26	O	5.480431	5.273547	6.491584
27	O	0.000000	8.437676	6.491584
28	O	3.653621	8.437676	6.491584
29	O	1.826810	11.601804	6.491584
30	O	5.480431	11.601804	6.491584
31	O	0.000000	2.109419	6.491584
32	O	3.653621	2.109419	6.491584
33	O	-0.110565	6.335300	9.477746
34	O	3.768445	6.335445	9.478296
35	O	1.829011	9.530272	9.547727
36	O	5.480492	9.349412	9.577614
37	O	0.116989	12.772225	9.574783

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Table S1 – continued

No.	element	x(Å)	y(Å)	z(Å)
38	O	3.546129	12.770782	9.574958
39	O	1.825329	2.989465	9.657403
40	O	5.488831	3.089784	9.604673
41	O	-0.066163	4.344530	12.621566
42	O	3.728545	4.342401	12.615561
43	O	1.818425	8.051599	13.470392
44	O	5.483399	7.322342	12.650827
45	O	0.109360	10.557931	12.674766
46	O	3.553930	10.551975	12.673705
47	O	1.834052	0.676497	12.828747
48	O	5.449372	0.139026	13.506802
49	O	1.826810	3.164128	5.000000
50	O	5.480431	3.164128	5.000000
51	O	0.000000	6.328257	5.000000
52	O	3.653621	6.328257	5.000000
53	O	1.826810	9.492385	5.000000
54	O	5.480431	9.492385	5.000000
55	O	0.000000	0.000000	5.000000
56	O	3.653621	0.000000	5.000000
57	O	-0.057537	4.146171	7.945446
58	O	3.715633	4.144480	7.949535
59	O	1.827566	7.451650	7.966333
60	O	5.481630	7.374306	7.886961
61	O	0.057427	10.520752	7.960245
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Table S1 – continued

No.	element	x(Å)	y(Å)	z(Å)
62	O	3.599828	10.520703	7.958842
63	O	1.829717	1.071262	7.870366
64	O	5.481611	1.125050	7.921624
65	O	-0.227784	1.928664	11.572080
66	O	3.887101	1.933836	11.555214
67	O	1.829345	5.576111	11.234324
68	O	5.484354	5.262541	10.964772
69	O	0.183435	8.322895	11.110637
70	O	3.472690	8.319925	11.114140
71	O	1.834978	11.571935	10.985561
72	O	5.488476	11.713141	11.089767
73	Ni	1.809529	0.893677	14.724079
74	Ni	4.246859	0.851611	14.780301
75	Ni	6.677588	0.849823	14.762831
76	Ni	0.569496	2.916558	14.592290
77	Ni	3.049716	2.917302	14.601641
78	Ni	5.463521	2.919433	14.644322
79	Ni	1.811657	5.022107	14.430760
80	Ni	4.213874	5.000691	14.379270
81	Ni	6.717122	5.002502	14.377573
82	Ni	0.589946	7.135916	14.594301
83	Ni	3.042208	7.133172	14.591860
84	Ni	5.468816	7.034998	14.548627
85	Ni	0.600889	1.680032	16.693806
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Table S1 – continued

No.	element	x(Å)	y(Å)	z(Å)
86	Ni	3.015942	1.677305	16.703503
87	Ni	5.466505	1.683117	16.768053
88	Ni	1.807234	3.788462	16.462528
89	Ni	4.243275	3.810285	16.482075
90	Ni	6.680159	3.814230	16.480416
91	Ni	1.816013	6.179776	16.517061
92	Ni	4.261998	6.180141	16.463871
93	Ni	6.674563	6.184390	16.465028
94	Ni	1.814274	2.810142	18.550591
95	Ni	4.243950	2.789596	18.554250
96	Ni	6.694257	2.791097	18.550930
97	Ni	0.592851	4.924213	18.189433
98	Ni	3.030360	4.921818	18.190520
99	Ni	5.466812	4.903492	18.211542

4 The dependence of the interfaces on the Hubbard U

Due to the self-interaction problem in conventional DFT, the band gap is usually underestimated. As the band gap is important for the position of electronic energy levels at electrode-electrolyte interfaces, and for the description and manipulation of electrode potentials,^{S2} we have decided to introduce a 5 eV Hubbard U on oxygen-2p, zirconium-4d and yttrium-4d orbitals. The effect of Hubbard U can be seen in Fig S1. Basically, the Hubbard U does not influence the trends, i.e. the oxygen vacancy concentration increases when the

Figure S1: Free energies of Ni-YSZ triple phase boundaries at reference pressure $p_{\text{O}_2} = 1$ bar and $T = 1000$ K without (a) and with (b) Hubbard U correction, as a function of electrode potential relative to the hydrogen equilibrium potential ($\text{H}_2\text{O}(\text{g}) \leftrightarrow \text{H}_2(\text{g}) + \text{O}^{2-} - 2e^-$). The color bar indicates the θ_O (negative values of θ_V), normalized by the number of Ni atoms in contact with the electrolyte. The solid lines are linear fits to the data points, emphasizing the trends. The dashed and dash-dotted vertical lines mark, respectively, the oxygen and hydrogen equilibrium potentials at the current temperature and the dotted vertical line marks the oxygen equilibrium potential at the reference $T = 673$ K.

potential is lowered. However, it widens the range of the electrode potential from around 2 V to more than 3 V, shifts individual systems along the potential axis, alters the potential region where a particular vacancy concentration dominates, and, consequently, predicts different and clearer transitions from one vacancy concentration to another. For example, at the equilibrium anodic potential at 1000 K, Ni-YSZ with 3 oxygen vacancies at the interface is predicted to be the most stable interface without Hubbard U correction, while the stoichiometric Ni-YSZ phase with 2 oxygen vacancies is most stable when the Hubbard U correction is applied. This demonstrates the important role played by the Hubbard U correction in getting accurate quantitative predictions of potential dependent interfaces. As stated in the main text, since the present paper is of conceptual nature, the U value was chosen based on previous DFT+U investigations of oxide band structures and band-gap energies,^{S3,S4} and we have not attempted to derive it from first-principles. But we emphasize that, to identify the true atomic-scale structure at a specific potential, it is crucial to carefully tune the Hubbard U and other computational parameters.

References

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