Supplemental info to “Theoretical evaluation of the surface electrochemistry of perovskites with promising photon absorption properties for solar water splitting”

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1 Heats of formation of perovskites

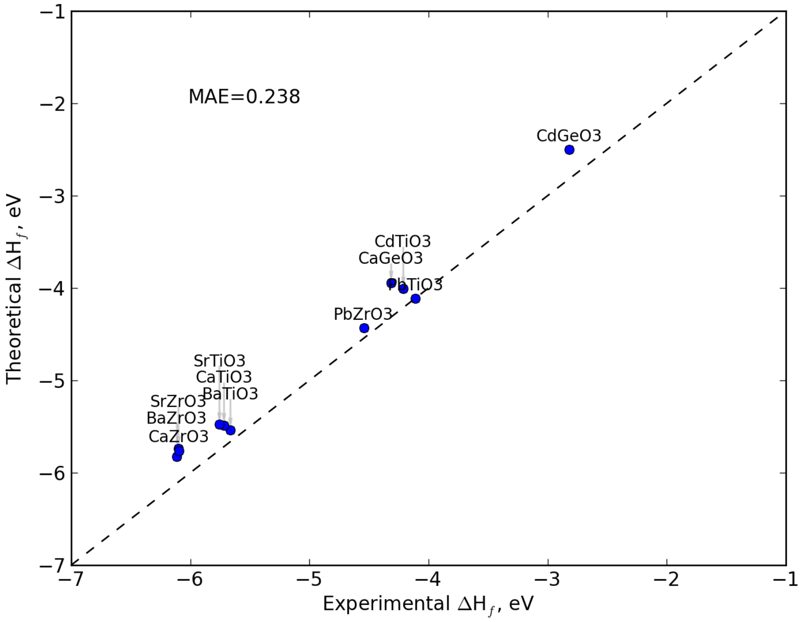

Figure 1: Comparison of heats of formation of perovskite oxides from DFT and experiment

Figure 1 displays the results of the analysis mentioned in the main text comparing theoretical heats of formation of ten common perovskite structures with those from experiment. Bulk structures are found by optimization of a 2x2 unit cell and subsequent lattice constant optimization. As shown, trends in heats of formation are well-described by theory with a mean absolute error (MAE) of around 0.24. ABO_3 experimental heats of formation are taken from ref. 1, which reports them relative to the precursor AO and BO_2 oxides. In order to avoid errors reported previously by Yan et al. [1] on group I and II oxides, we recalculate the data reported in [2] using the formula

$$\begin{aligned}\Delta H_{f,elemental}\left(ABO_3\right) &= H_f\left(ABO_3\right) - H_f\left(A\right) - H_f\left(B\right) - 3H_f\left(O\right)\\ &= \left[H_f\left(ABO_3\right) - H_f\left(AO\right) - H_f\left(BO_2\right)\right] + \left[H_f\left(AO\right) - H_f\left(A\right) - H_f\left(O\right)\right]\\ &\quad + \left[H_f\left(BO_2\right) - H_f\left(B\right) - 2H_f\left(O\right)\right]\\ &= \Delta H_{f,reported}\left(ABO_3\right) + \Delta H_f\left(AO\right) + \Delta H_f\left(BO_2\right)\end{aligned}$$

Theoretical heats of formation are calculated using references from structural optimization of each of the elemental component metals A and B. Oxygen reference energies are taken from the calculated enthalpy of water and hydrogen gas, using the experimental heat of formation of water, in order to avoid the well-known DFT error associated with oxygen gas, i. e.

$$H_f\left(O\right) = H_{f,theor}\left(H_2O\right) - H_{f,theor}\left(H_2\right) - \Delta H_{f,exp.}\left(H_2O\right)$$

According to Figure 1, theoretical ΔH_f agrees with experiment well, and provides some confidence that errors in DFT calculated binding energies for oxygenated adsorbates are on the order of 0.2-0.3 eV. Since the results reported are primarily overpotentials, there is also likely some form of error cancellation, since these overpotentials are calculated using differences between oxygenated adsorbate binding energies.

2 Thermodynamic data

Corrections from pH to the equilibrium potentials of HER and OER are calculated via a Nernstian correction, i. e.

$$E_{eq,HER} = 0.00 \text{ V} - \frac{RT}{F}\ln\left([\mathrm{H}^+]\right) = -0.0592\mathrm{pH}$$
$$E_{eq,OER} = 1.23 \text{ V} - \frac{RT}{F}\ln\left([\mathrm{H}^+]\right) = 1.23 - 0.0592\mathrm{pH}$$

Table 1 shows data relevant to the calculation of overpotentials for each of the materials. Binding energies are reported using references of the gibbs free energy of liquid water and hydrogen.

Material	ΔE_{OH}	ΔE_O	ΔE_{OOH}	ΔE_{H-O}	ΔE_{H-B}
LiVO3	-1.628	-1.088	1.730	-1.576	0.510
SrSnO3	1.250	4.375	4.344	-1.257	1.350
BaSnO3	1.118	4.234	4.267	-1.451	1.235
MgTaO2N	-1.174	0.078	2.068	0.165	0.823
SrGeO3	0.501	2.747	3.422	-2.860	0.480
NaSbO3	0.092	2.683	3.487	-0.781	0.416
SrTaO2N	-0.974	-0.729	2.398	0.477	1.238
AgNbO3	-1.071	-1.156	2.365	0.460	0.130
CaGeO3	0.024	3.244	3.481	-1.032	1.068
CaSnO3	1.417	4.642	4.438	-0.917	1.644
SnTiO3	-1.440	-1.607	1.888	0.402	-0.136
LaTiO2N	-0.647	0.712	2.729	0.830	0.560
BaTaO2N	-0.725	0.260	2.697	0.679	0.864
CaTaO2N	-0.289	1.379	3.134	1.118	1.063

Table 1: Binding energies of adsorbates at $\theta = 0.25$

Table 2 displays data from the coverage conditions defined by the pourbaix diagram. For each of the OER intermediates (OH*, O*, and OOH*), the precursor state is a high coverage of O*, i. e. $\Theta_O = 0.75$. For the HER intermediates, the coverage is the most stable configuration at 0.0 V vs. RHE, which is shown in Figure 4 of the primary manuscript.

Material	ΔE_{OH}	ΔE_O	ΔE_{OOH}	ΔE_{H-O}	ΔE_{H-B}
BaTaO2N	0.596	2.732	3.841	0.679	0.864
SrTaO2N	-0.146	1.854	3.352	0.782	1.651
MgTaO2N	0.402	2.080	4.060	1.831	2.174
CaTaO2N	1.029	3.152	4.213	1.118	1.063
LaTiO2N	0.738	2.247	4.161	0.830	0.560
SnTiO3	0.481	1.822	3.709	0.889	1.471

Table 2: Binding energies of adsorbates at coverage from pourbaix diagram

Data corresponding to the free energy corrections to reference gas phase species and adsorbates, including vibrational corrections to the entropy and enthalpy is tabulated in Table 3.

Species	$T\Delta S$	ZPE	$\int_0^{300} C_v dT$	ΔG_{corr}
$H_2O(g)$	0.671	0.550	0.104	-0.017
$H_2(g)$	0.403	0.265	0.091	-0.047
OH*	0.082	0.342	0.050	0.311
O*	0.051	0.075	0.030	0.055
OOH*	0.138	0.461	0.080	0.404
H-O*	0.007	0.307	0.006	0.305
H-B*	0.032	0.118	0.021	0.107

Table 3: Free energy corrections for adsorbates and gas phase species

Gibbs free energies are calculated simply by adding the correction listed in the table above to the electronic energy listed in either table 2 or 3. Values in tables 2 and 3 include the free energy corrections to the gas phase references [3].

$$\Delta G_{ads} = \Delta E_{ads} + \Delta G_{corr}$$

Overpotential is calculated by taking the maximum free energy difference for the reaction steps in the mechanism below:

$$* + H_2O \rightarrow OH* + H^+ + e^- \tag{1}$$

$$OH* \rightarrow O* + H^+ + e^- \tag{2}$$

$$O* + H_2O + \rightarrow OOH* + H^+ + e^- \tag{3}$$

$$OOH* \rightarrow O_2 + H^+ + e^- \tag{4}$$

These differences are calculated as

$$\begin{aligned} &\Delta G_1 = \Delta G_{OH} \\ &\Delta G_2 = \Delta G_O - \Delta G_{OH} \\ &\Delta G_3 = \Delta G_{OOH} - \Delta G_O \\ &\Delta G_4 = 4.92 - \Delta G_{OOH} \\ &\eta_{OER} = \min\left(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\right) \end{aligned}$$

The overpotentials for hydrogen evolution are calculated by taking minimum absolute value of each binding energy.

$$\eta_{HER} = \min\left(\left|\Delta G_{H-O}\right|, \left|\Delta G_{H-B}\right|\right)$$

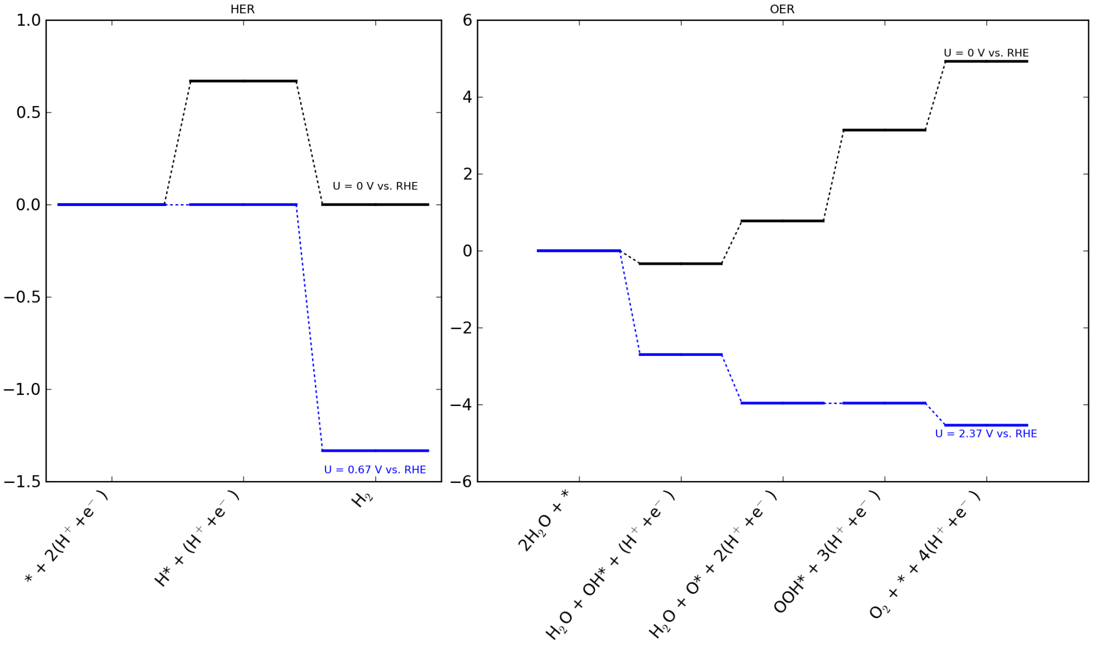

Figure 2: Free energy diagram of HER and OER on $LaTiO_2N$ at 0 V vs. RHE and the limiting potential for each reaction

3 Convergence of adsorption energies

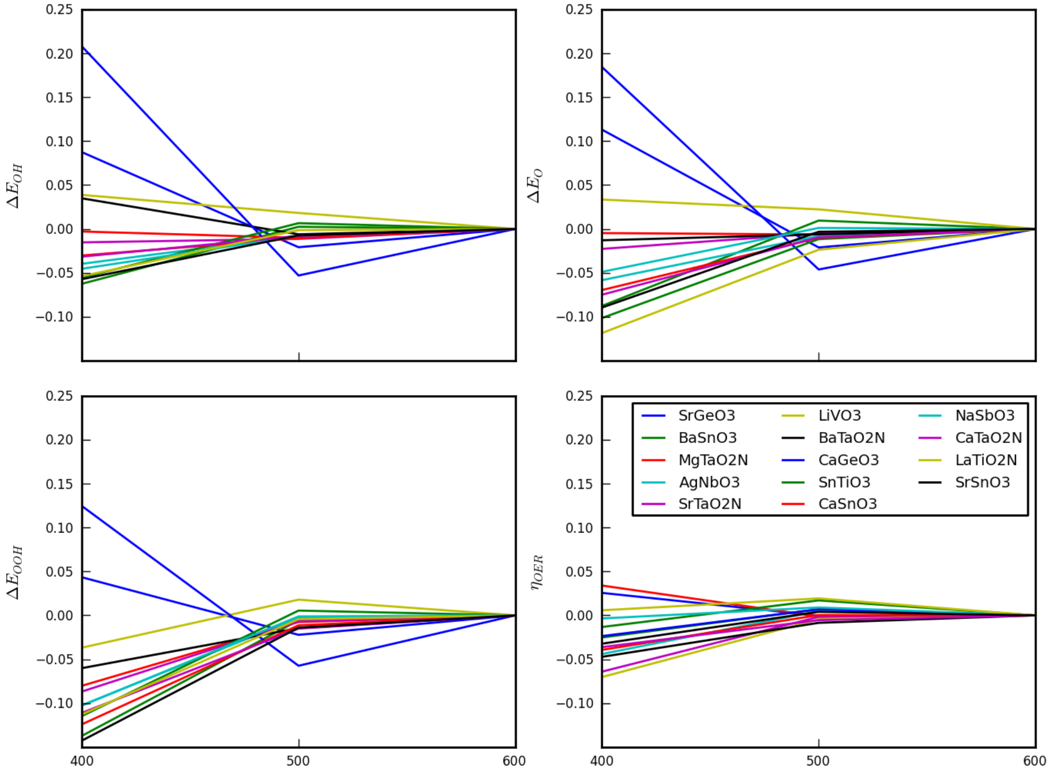

Figure 3: Adsorption energies as a function of cutoff

400 eV was chosen as a cutoff energy for the adsorbate calculations. In Figure 3, we show electronic energies from geometries optimized using 400 eV cutoff using 500 and 600 eV. Adsorption energies may be perturbed by up to 0.2 eV when using higher cutoff energies, but the overpotentials are well-described by the lower cutoff calculations, having differences of only 0.05 eV or less when compared to the 600 eV calculations.

4 Symbol glossary

η_{HER}	Theoretical HER overpotential, potential over the HER equilibrium potential (0 V vs. RHE) at which all steps of Volmer-Heyrovsky mechanism are downhill in free energy
η_{OER}	Theoretical OER overpotential, potential over the oxygen evolution equilibrium potential (1.23 V vs. RHE) at which all of the steps in the oxygen evolution mechanism proceeding through OH*, O*, and OOH* are downhill in free energy
ΔG_{OH}	free energy energy of adsorption of OH*
ΔG_{O}	free energy of adsorption of O*
ΔG_{OOH}	free energy of adsorption of OOH*
ΔG_{H-O}	free energy of adsorption of H* to the O-site on the perovskite surface
ΔG_{H-B}	free energy of adsorption of H* to the B-site of the ABO_3 perovskite surface
ΔH_f	bulk enthalpy or heat of formation
$E_{eq,X}$	equilibrium potential for half-reaction X
H_2O/O_2	equilibrium potential for oxygen evolution half-reaction
H^+/H_2	equilibrium potential for hydrogen evolution half-reaction
E_{vac}	Surface O vacancy formation
U_{SHE}	potential vs. the standard hydrogen electrode
U_{RHE}	potential vs. the reversible hydrogen electrode
θ_X	monolayers of adsorbate X, number of adsorbed species/number of free surface B-sites

References

[1] Jun Yan, Jens S. Hummelshøj, and Jens K. Nørskov. Formation energies of group i and ii metal oxides using random phase approximation. *Phys. Rev. B*, 87:075207, Feb 2013.

[2] Alexandra Navrotsky. Thermochemistry of perovskites. *Perovskite: A structure of great interest to geophysics and materials science*, pages 67–80, 1989.

[3] Christopher J Cramer. *Essentials of computational chemistry: theories and models.* John Wiley & Sons, 2013.