Hydrogen Defects in Tetragonal ZrO_2 Studied Using Density Functional Theory

Electronic Supplementary Information

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1. The performance of the Makov-Payne (MP) correction.

We assessed the adequacy of the leading term of the MP correction by comparing its results with the results obtained by finite size scaling. This assessment was done on four selected defects which are $H_i^{\bullet}$, $H_i^{/}$, $H_O^{\bullet}$, and $(H_2)_{Zr}^{////}$. The first two are generally regarded very important defects in metal oxides, the third is the predominant in oxygen poor conditions in T-ZrO_2, and the last predominates in oxygen rich conditions in T-ZrO_2 and is representative for the highest possible charge state for a hydrogen defect in this work. The details of the simulation cells used to perform finite size scaling are summarized in Table SI.

Table SI. The details of the supercells used to perform the finite size scaling.

Number of T-ZrO_2 unit cells	1×1×1	2×2×2	3×3×3	4×4×4
Number of atoms	12	96	324	786
k-points	4×4×4	2×2×2	2×2×2	2×2×2
Kinetic energy cutoff	450 eV			

The formation energy of a defect after performing finite size scaling is denoted by E_{∞}^{f}. It is obtained by fitting the raw uncorrected results from four (or more) simulation cells of different sizes to the equation:

$$E^{f}(L) = E_{\infty}^{f} + \frac{a}{L} + \frac{b}{L^{3}},$$

where $E^{f}(L)$ is the uncorrected formation energy of the defect calculated from a supercell of length L which is defined as the cubic root of its volume. E_{∞}^{f}, a, and b are obtained from the

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fitting. We regard E_{∞}^{f} as the reference value for the formation energy of the defect and calculate the error in the results obtained from the $2\times2\times2$ supercell (with and without MP correction) with respect to this reference. Fig. S1 summarizes the results of this procedure for the four selected defects, $H_i^{\bullet}$, $H_i^{/}$, $H_O^{\bullet}$, and $(H_2)_{Zr}^{////}$.

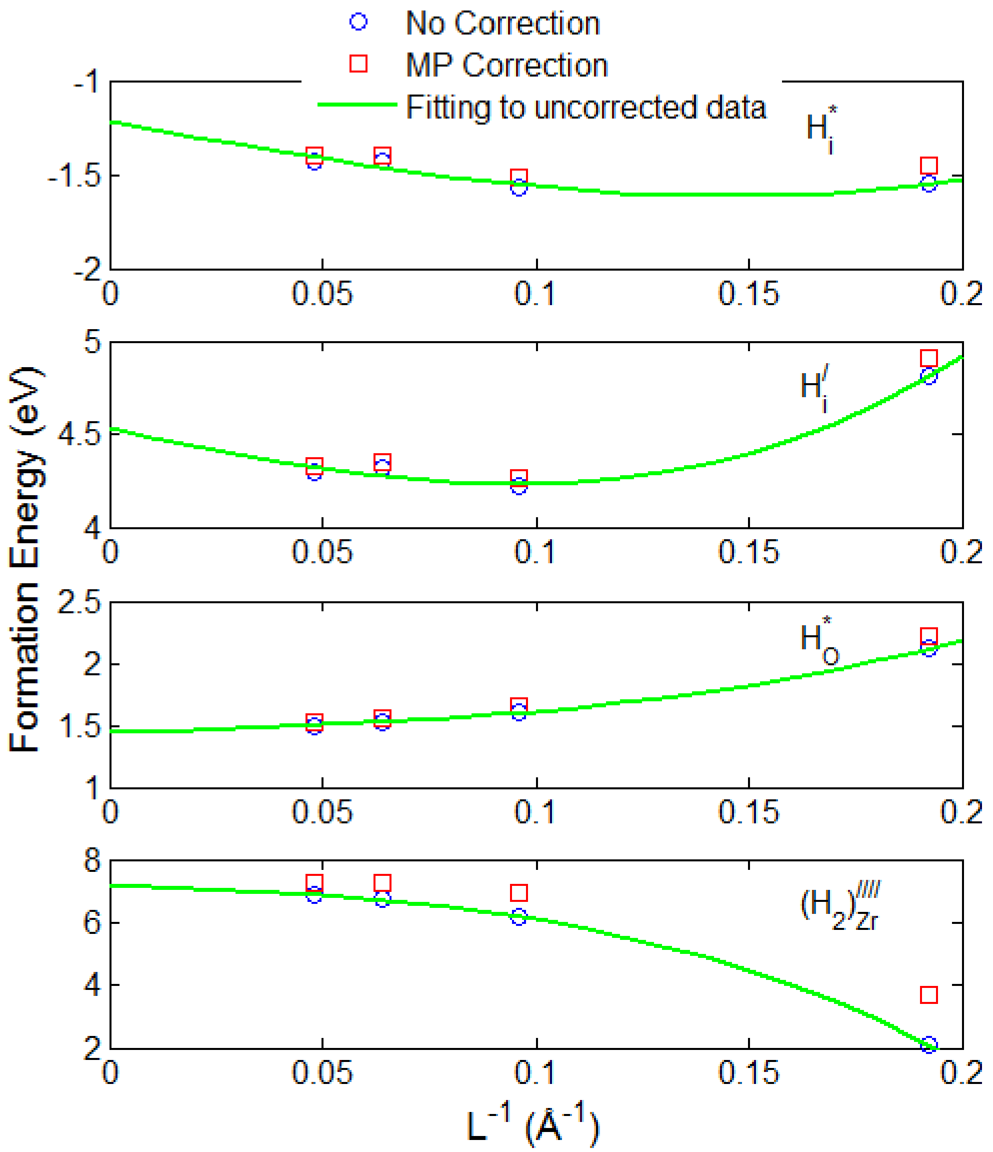

FIG. S1. The formation energy of $H_i^{\bullet}$, $H_i^{/}$, $H_O^{\bullet}$, and $(H_2)_{Zr}^{////}$ obtained without correction and with the MP correction. The fitting was performed on the uncorrected results to obtain reference values.

In Table SII we provide a summary for the formation energies (at zero chemical potential of electrons and in oxygen rich conditions) for the selected defects using the three schemes: finite size scaling, raw uncorrected results, and MP corrected results. We also show in the table the value of the thermodynamic transition level (+/-) for the interstitial hydrogen. In general MP correction performs reasonably well (maximum error in the formation energy is 0.3 eV) and including it is better than leaving the formation energies without any corrections at all. Finite size scaling is of course more robust, however it is computationally very expensive and indeed impractical when it comes to study 30 charged defect as in this work and for each one of the 30 we need to consider several crystallographic structures (for example 12 structures for $H_i^\bullet$ only**)**.

Table SII. Summary of the values of the formation energies of the defects on which the finite size scaling was performed. These values are at zero chemical potential of electrons and in oxygen rich conditions. Also shown the (+/-) thermodynamic transition level for the interstitial hydrogen. All energies are in eV.

	Reference value obtained by finite size scaling, E_∞^f	Raw results without correction (error) $2\times2\times2$ unit cells	Makov-Payne corrected results (error) $2\times2\times2$ unit cells
$H_i^\bullet$	-1.22	-1.57 (-0.35)	-1.52 (-0.30)
$H_i^/$	4.53	4.22 (-0.31)	4.27 (-0.26)
$H_O^\bullet$	1.44	1.60 (0.16)	1.65 (0.21)
$(H_2)_{Zr}^{////}$	7.17	6.17 (-1.00)	6.96 (-0.21)
(+/-) for H_i	2.87	2.91 (0.04)	2.91 (0.04)

2. The values of the chemical potentials and reference energies.

Table SIII. The chemical potential of all the species in the two limiting extremes considered in this work. Also shown the DFT energies of the reference states that sets the bounds on the chemical potentials as discussed in the paper. All energies are in eV.

Chemical potential	oxygen rich	oxygen poor
μ_O	-4.93	-9.93
μ_H	-4.65	-3.38
μ_{Zr}	-18.56	-8.55
$E_{Zr-metal}^{DFT}, E_{O_2}^{DFT}, E_{H_2}^{DFT}, E_{H_2O}^{DFT}, E_{ZrO_2}^{DFT}$	-8.55, -9.85, -6.77, -14.23, -28.41	

3. Example of applying the binding energy definition given in equation (2) in the paper.

Suppose we want to calculate the binding energy, E_b, of the complex $H_{Zr}^{''''}$ according to the definition, $E_b = \max(E_{C,q}^f - \sum_k^{///} E_{D_k,q_k}^f)$. One needs to apply the three constraints indicated by primes on the summation sign. The first constraint is the conservation of species which dictates that this complex is formed by association of a zirconium vacancy and interstitial hydrogen. Next, to apply charge conservation, it is convenient to look at all the possible charge states that one of the constituents of the complex can take and then deduce the corresponding charge state of the other constituent(s) that would lead to charge conservation. In this particular example, interstitial hydrogen can take a charge of -, 0, or +, which implies that the corresponding zirconium vacancy has to have a charge of 3-, 4-, or 5-, respectively. However, it is not possible for a zirconium vacancy to take a charge state of 5-. Thus, we are left with only two possibilities $(H_i^{'}, V_{Zr}^{'''})$ and $(H_i^x, V_{Zr}^{''''})$. Finally, when applying the last constraint related to eliminating the possibility of a negative-U defect as a constituent of the complex, we exclude the neutral interstitial hydrogen and thus we are left only with the following possibility:

$$H_{Zr}^{''''} \Leftrightarrow H_i^{'} + V_{Zr}^{'''}$$

The binding energy of $H_{Zr}^{////}$ according to this reaction is -1.28 eV. In this example, after applying all the constraints we ended up with only one possible reaction. If one ends up with multiple reactions then the binding energy of the complex would be the maximum over all reactions energies.

4. Summary of the defects that were excluded from the discussion in the paper and the reason of the exclusion.

In the paper we presented a systematic way to investigate all the charge states of hydrogen defects. However, some of these charge states (including neutral) may not be realizable because of electron or hole delocalization. This is the first reason to exclude some of the charge states from further study. Second, if the defect under consideration is a complex whose binding energy is positive, we exclude this defect from further analysis since it is not stable thermodynamically and is expected to dissociate even if it was driven to form under non-equilibrium conditions. In the following table we summarize all the excluded defects and the underlying reason.

Table SIV. Summary of the defects excluded from the discussion in the paper and the reason.

Defect	**Reason of exclusion**
	Interstitial hydrogen
H_i^x	Charge does not localize on the defect. However, we discussed it in the paper because of the wide interest in studying interstitial hydrogen in oxides.
$(H_2)_i^{\bullet}$	Charge does not localize on the defect.

Hydrogen-oxygen vacancy complexes	
$H_O^{\bullet\bullet}$	Positive binding energy, +0.59 eV. See also the footnote of Table I in the paper.
$H_O^{\bullet\bullet\bullet}$	Positive binding energy, +0.61 eV.
$(2H)_O^{\bullet\bullet}$	Positive binding energy, +0.38 eV.
$(2H)_O^{\bullet\bullet\bullet}$	Charge does not localize on the defect and positive binding energy, +0.67 eV.
Hydrogen-zirconium vacancy complexes	
$H_{Zr}^{/////}$	Charge does not localize on the defect and positive binding energy, +2.74 eV.
$H_{Zr}^{///}$	Positive binding energy, +1.45 eV.
$H_{Zr}^{//}$	Positive binding energy, +1.50 eV.
$H_{Zr}^{/}$	Positive binding energy, +1.53 eV.
H_{Zr}^{x}	Positive binding energy, +1.41 eV.
$H_{Zr}^{\bullet}$	Positive binding energy, +1.21 eV.
$(H_2)_{Zr}^{/////}$	Charge does not localize on the defect.
$(H_2)_{Zr}^{///}$	Charge does not localize on the defect.
$(H_2)_{Zr}^{\bullet}$	Charge does not localize on the defect.