Impact of nitrogen and carbon on defect equilibrium in ZrO_2

H. D. Taylor, J. L. Lyons¹, C.E. Dreyer², A. Janotti³, C.G. Van de Walle*

Materials Department, University of California, Santa Barbara, CA 93106-5050

Abstract

We investigate the electronic properties of nitrogen and carbon impurities in ZrO_2 using density functional theory with a hybrid functional. It is commonly accepted that N substitutes on the O site and is stable in the -1 charge state (N_{O}^-). The N_{O}^- acceptors are then compensated by donor defects such as O vacancies in the $+2$ charge state. We test the validity of this assumption by determining the formation energies of all relevant charge states of nitrogen and oxygen vacancies as a function of Fermi level. We also examine the effects of carbon, a common unintentional impurity in ZrO_2 . We find that carbon impurities have relatively low formation energies and would indeed incorporate easily during growth of ZrO_2 , but they do not affect the equilibrium between nitrogen and oxygen vacancies. Our results show that the Kröger-Vink picture is valid for common growth conditions and the dominant defects are N_{O}^- and V_{O}^{+2} .

Keywords: Fuel cell materials, First-principles calculations, Yttria-stabilized zirconia polycrystal, Solid Oxide Fuel Cell (SOFC)

*Corresponding author

¹Present address: Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973

²Present address: Department of Physics and Astronomy, Rutgers, The State University of New Jersey, Piscataway, NJ 08854

³Present address: Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716

1. Introduction

Zirconia (ZrO_2) is of great interest for an array of technological applications, including solid oxide fuel cells (SOFCs) [1], thermal barrier coatings in gas turbines [2], and high- κ dielectrics in metal-oxide semiconductor field-effect transistors (MOSFETs) [3]. In SOFCs, the addition of impurities may be used for functionalization of the material and improving performance. Yttria-stabilized zirconia (YSZ) is employed in SOFCs because doping with yttrium produces oxygen vacancies to enable mobile oxygen ion conduction. Yttrium incorporates on the Zr site, acting as an acceptor (Y_{Zr}^-). To satisfy charge neutrality, one oxygen vacancy in the +2 charge state is created for every 2 Y ions substituted on Zr sites.

Oxygen vacancies are also invoked as compensation centers for impurities such as nitrogen, based on the assumption that these impurities incorporate on the oxygen site and are stable in acceptor charge states. The intentional doping of N in ZrO_2 films has been shown to lead to increased ionic conductivity in SOFCs at high temperatures[4]. Nitrogen incorporation in ZrO_2 is often described using the following mechanism,

Here we use the notation in which the superscripts indicate the charge state of the defect or impurity [5]; in Kröger-Vink notation[6], a negative charge state would be indicated by a $'$ (N_{O}'), and a positive charge state by a $\bullet$ ($\text{V}_{\text{O}}^{\bullet\bullet}$).

5 Several experimental and computational studies base their conclusions on Eq. (1) [7, 8, 9, 10], assuming that N is only stable in the N_{O}^- acceptor charge state. In the present work, we perform a comprehensive first-principles study of the nitrogen impurity in all possible configurations and all relevant charge states of N in ZrO_2 . Combining these results with results for V_{O} allows us to assess
10 whether the mechanism embodied in Eq. (1) is sufficient, or whether any other charge states or configurations of nitrogen need to be considered. We also study carbon impurities as they are commonly found unintentionally incorporated in

ZrO₂ thin films[11].

Previous first-principles calculations on N and C in ZrO₂ were limited to
15 neutral charge states[12, 13, 14]. In wide-band gap materials, impurities often
occur in many different charge states depending on the Fermi-level position.
Therefore, studying only a single charge state provides incomplete information
on the behavior of the impurity. We determine the stability of the impurities
by calculating their formation energies as a function of Fermi-level position
20 in the band gap and the chemical potentials of the atomic reservoirs[5]. The
previous first-principles studies on nitrogen and carbon in ZrO₂ used the local
density approximation (LDA) or generalized gradient approximation (GGA)
within density functional theory (DFT)[12, 13, 14]. LDA and GGA severely
underestimate the band gap, leading to large errors in the position of the charge-
25 state transition levels within the band gap[5]. In the present study we use a
hybrid functional, which has been proven much more accurate than traditional
functionals in describing the defect formation energies and defect levels in wide-
band-gap materials[15].

The details of the calculation are outlined in Sec. II. Results for the configu-
30 rations and the behavior of the impurities under different experimental growth
conditions are discussed in Sec. III.

2. Computational Methods

Our calculations are based on the generalized Kohn-Sham theory with the
screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE)[16, 17] as
35 implemented in the Vienna Ab-initio Simulation Package (VASP) [18]. The HSE
mixing parameter was set to include 32% of Hartree-Fock exchange such that
the calculated band gaps for tetragonal and monoclinic ZrO₂ (5.82 eV and 5.29
eV, respectively) fall within the range of reported experimental values (from 5.0
to 5.8 eV [19]). We have found that this mixing parameter well describes the
40 band gaps and lattice parameters of ZrO₂ as well as similar oxide materials such
as Al₂O₃ and HfO₂ [20, 21]. The calculated lattice parameters for tetragonal

ZrO₂ are $a = 3.61$ Å, $c = 5.18$ Å, and for monoclinic ZrO₂ $a = 5.16$ Å, $b = 5.21$ Å, and $c = 5.31$ Å. These lattice parameters are in close agreement with the experimental values for tetragonal ZrO₂ ($a = 3.61$ Å, $c = 5.18$ Å) [22] and for
45 monoclinic ZrO₂ ($a = 5.15$ Å, $b = 5.21$ Å, $c = 5.32$ Å) [23].

The impurities are studied using the supercell approach with periodic boundary conditions [5]. We use a 108-atom supercell for tetragonal ZrO₂ and a 96-atom supercell for monoclinic ZrO₂. The electron-ion interactions are treated using projector augmented wave potentials [24], with a cutoff of 400 eV for
50 the plane-wave basis set. Lattice relaxations and symmetry-broken configurations were taken into account. Spin polarization was considered for supercells containing an odd number of electrons.

Taking the nitrogen impurity on an oxygen site (N_O) as an example, the formation energy in charge state q is calculated as [5]:

$$E^f(\text{N}_\text{O}^q) = E_\text{tot}(\text{N}_\text{O}^q) - E_\text{tot}(\text{ZrO}_2) - \mu_\text{N} + \mu_\text{O} + q\epsilon_\text{F} + \Delta^q, \quad (2)$$

where $E_\text{tot}(\text{N}_\text{O}^q)$ is the total energy of the supercell containing N_O in charge state q and $E_\text{tot}(\text{ZrO}_2)$ is the total energy of the bulk oxide in the same supercell. The
55 Fermi level ϵ_F is referenced to the valence-band maximum (VBM). Δ^q is the charge-state dependent correction due to the finite size of the supercell [25, 26].

The chemical potentials μ_N and μ_O are referenced to the energy per atom of isolated N₂ and O₂ molecules, and μ_Zr is referenced to the energy per atom of Zr bulk. μ_O and μ_Zr are treated as variables but must satisfy the stability condition of ZrO₂:

$$\mu_\text{Zr} + 2\mu_\text{O} = \Delta H_f(\text{ZrO}_2), \quad (3)$$

where $\Delta H_f(\text{ZrO}_2)$ is the formation enthalpy of ZrO₂. The chemical potential μ_N is bounded by the formation of secondary phases, in this case Zr₃N₄:

$$3\mu_\text{Zr} + 4\mu_\text{N} \leq \Delta H_f(\text{Zr}_3\text{N}_4) \quad (4)$$

Similarly, the upper limit of μ_C is bounded by the formation enthalpy of CO₂. The calculated formation enthalpies $\Delta H_f(\text{ZrO}_2) = -10.89$ eV, $\Delta H_f(\text{Zr}_3\text{N}_4) = -7.74$

eV, and $\Delta H_f(\text{CO}_2) = -4.08$ eV are in good agreement with the experimental values[27].

The chemical potentials can be chosen to describe specific growth or processing conditions. Here we use μ_{O} of an O_2 gas at a given temperature and pressure to relate the results to the growth conditions of ZrO_2 . In the following we will present results using chemical potentials for the oxygen-rich limit ($\mu_{\text{O}} = 0$) and two methods typical for the large-scale synthesis of ZrO_2 for SOFC application, the co-precipitation method ($\mu_{\text{O}} = -1.40$ eV) and the skull melting method ($\mu_{\text{O}} = -2.63$ eV)[7]. These chemical potential values were derived using the temperature and pressure conditions reported in the literature[28, 7].

In tetragonal ZrO_2 , Zr is eightfold coordinated by O atoms and O is fourfold coordinated by Zr atoms. The lengths of the Zr-O bonds range from 2.07 Å to 2.36 Å. In monoclinic ZrO_2 , Zr is sevenfold coordinated with O atoms. Three of the O atoms are coordinated by three Zr atoms and four of the O atoms are fourfold coordinated to Zr atoms. The Zr-O bonds for threefold coordinated O atoms (referred to as O3 from here on) are 2.07 to 2.15 Å in length, and for fourfold coordinated O atoms (O4) 2.15 to 2.24 Å.

3. Results and Discussion

3.1. Nitrogen on a substitutional oxygen site

We first discuss the results for the tetragonal phase. In Fig. 1 we show the formation energy as a function of Fermi level for the stable charge states of N_{O} in tetragonal ZrO_2 , at $\mu_{\text{O}} = -2.63$ eV (corresponding to the skull melting method). The slope of each line corresponds to the charge state of the impurity. The Fermi-level positions where the slope changes correspond to the charge-state transition levels (q/q'). For Fermi-level positions below the transition level (q/q') the defect is stable in the charge state q , and for Fermi levels above (q/q') the defect is stable in the charge state q' . The charge states determine the electrical activity of the impurity.

Figure 1: Formation energy as a function of Fermi level for N_O in tetragonal ZrO_2 in various charge states for $\mu_O = -2.63$ eV. Each line corresponds to a formation energy for a specific charge state as defined by Eq (2). The thick blue lines indicate the energetically most favorable charge state for each Fermi level in the band gap. The Fermi level is referenced to the VBM of ZrO_2 .

Nitrogen substituting on an O site is commonly assumed to be present in the neutral or -1 charge states. We indeed find that N_O is stable in the -1 charge state for Fermi levels above 2.28 eV. However, for Fermi levels lower in the band gap, N_O can also occur in the $+3$, $+4$, and $+5$ charge states; i.e., acting as a donor rather than an acceptor. Note that the neutral charge state is never thermodynamically stable. The presence of these positive charge states implies that the negative charge state of nitrogen might not be the only one playing a role in the reaction expressed by Eq. (1). Nitrogen could thus potentially self-compensate, i.e., in the absence of other defects or impurities, it would appear that N_O donors ($+3$, $+4$ or $+5$ charge states) could charge-compensate the N_O acceptors. This will be discussed in more detail when we compare the formation energies of N_O and oxygen vacancies in Sec. 3.4.

In the negative charge state, N_O^- retains the configuration of the O atom,

100 with N-Zr bond lengths approximately equal to the bulk Zr-O bonds. The positive charge states of N_O all exhibit configurations similar to what is shown in Fig. 2(a) for N_O^{+3} , where the N atom undergoes a large off-site displacement and forms two N-O bonds similar in bond length.

Figure 2: Atomic configuration of (a) N_O^{+3} and (b) N_{Zr}^- in tetragonal ZrO_2 .

3.2. Nitrogen in other configurations

105 Figure 3 shows the formation energies of nitrogen in various configurations, for different values of the oxygen chemical potential. Some of the information that was included in Fig. 1 for N_O is included in Fig. 3(a), but only the line segments corresponding to the lowest formation at each Fermi level are shown here. In addition to substituting on the oxygen site, nitrogen can substitute on
110 the Zr site, or form a nitrogen interstitial.

On the cation site in tetragonal ZrO_2 , N_{Zr} is characterized by an offsite displacement towards three of the O nearest neighbors. It can occur in three different charge states: +1, 0, and -1. Figure 3 shows that N_{Zr} would be stable only under very oxygen-rich conditions, which are unlikely to occur during
115 growth. If it would incorporate, it would be mainly in the negative charge state, in which the structure is characterized by bonding of N to three O atoms with N-O bond lengths of 1.39, 1.40, and 1.45 Å [see Fig. 2(b)].

The nitrogen interstitial prefers to incorporate on a site coordinated by two O atoms as nearest neighbors in tetragonal ZrO_2 . It can occur in a variety of
120 charge states. However, as is evident from Fig. 3, its formation energy is so high

Figure 3: Formation energy as a function of Fermi level for nitrogen in various configurations in tetragonal ZrO_2 for (a) $\mu_{\text{O}} = -2.63$ eV (skull melting growth conditions), (b) $\mu_{\text{O}} = -1.40$ eV (wet-chemical co-precipitation conditions), and (c) $\mu_{\text{O}} = 0$ eV (oxygen-rich conditions). The formation energy of oxygen vacancies is included as well.

that it is never a relevant configuration under any conditions.

3.3. Oxygen vacancies and charge equilibrium

We now address how nitrogen in its various configurations interacts with oxygen vacancies in ZrO_2 . V_{O} has a $(+2/+1)$ level 3.64 eV and a $(+1/0)$ level 4.49 eV above the VBM, implying that the defect will be in the +2 charge state for relevant Fermi levels. The position of the Fermi level is determined by overall charge neutrality. To a very good approximation, this can be obtained by inspection of the formation-energy plots, by finding the crossing point of the formation energies of the lowest-energy positively charged and negatively charged defects or impurities. This constitutes a good approximation because

Figure 4: Formation energy as a function of Fermi level for nitrogen in various configurations in monoclinic ZrO_2 for (a) $\mu_{\text{O}} = -2.63$ eV (skull melting growth conditions), (b) $\mu_{\text{O}} = -1.40$ eV (wet-chemical co-precipitation conditions), and (c) $\mu_{\text{O}} = 0$ eV (oxygen-rich conditions). The formation energy of oxygen vacancies is included as well.

defect concentrations decrease exponentially with increasing formation energy, and therefore the lowest-energy defect at each Fermi-level position will dominate. The formation energy of V_{O}^{+2} is low enough that for all possible oxygen chemical potentials it constitutes the lowest-energy positive charge state that will provide charge compensation for the negatively charged nitrogen impurities. The intersection of the formation energies of V_{O} and N_{O} pins the Fermi level such that it is the oxygen vacancy, rather than any donor states of any of the configurations of the nitrogen impurity, that provides the charge balance in ZrO_2 .

140 3.4. Monoclinic ZrO_2

The results presented above were for the tetragonal phase of ZrO_2 . Since the structure, bonding, and band gap of the monoclinic phase are similar to those of the tetragonal phase, we expect similar behavior of the point defects and impurities, and indeed this is revealed by our calculations.

145 As shown in Fig. 4, for both $\mu_{\text{O}} = -1.40$ eV and $\mu_{\text{O}} = -2.63$ eV, nitrogen on the fourfold coordinated oxygen site in monoclinic ZrO_2 is the most stable nitrogen configuration. It occurs in the $+3$ and -1 charge states, and exhibits a $(+3/-1)$ transition level at 1.73 eV above the VBM. $\text{N}_{\text{O}_4}^-$ is stable for Fermi levels above 1.73 eV. It behaves like the original fourfold coordinated O atom
150 and has N-Zr bond lengths similar to the bond lengths in bulk ZrO_2 .

On the cation site in monoclinic ZrO_2 , N_{Zr}^+ forms N-O bonds with the three threefold coordinated oxygen atoms. The four fourfold coordinated oxygen atoms exhibit dangling bonds. The N-O bond lengths are greater in length in the neutral and -1 charge state.

155 The oxygen vacancy exhibits a $(+2/+1)$ level at 3.66 eV and a $(+1/0)$ level at 4.15 eV above the VBM, in agreement with previous hybrid functional calculations[29]. As in tetragonal ZrO_2 , the Fermi level is pinned in the middle of the band gap by V_{O}^{+2} and N_{O}^- . The position of the Fermi level and the formation energy at the crossing point of V_{O}^{+2} and N_{O}^- is similar between tetragonal
160 and monoclinic ZrO_2 . Although nitrogen is also stable in positive charge states, these states are not lower in energy than V_{O}^{+2} and hence do not affect the charge neutrality between V_{O}^{+2} and N_{O}^- described in Eq. (1).

3.5. Carbon impurities

We now examine the potential impact of incorporation of C impurities, first
165 in tetragonal ZrO_2 .

As shown in Fig. 5, for Fermi levels below midgap C on the oxygen site is stable in the $+4$ charge state. The atomic configuration involves C_{O} moving offsite and forming a C-O bond of 1.18 Å. In the negative charge state, C_{O} does not move offsite and forms C-Zr bonds similar in length to bulk Zr-O bonds.

Figure 5: Formation energy as a function of Fermi level for carbon in various configurations, V_O , and the lowest energy N defect in tetragonal ZrO_2 for (a) $\mu_O = -2.63$ eV (skull melting growth conditions), (b) $\mu_O = -1.40$ eV (wet-chemical co-precipitation conditions), and (c) $\mu_O = 0$ eV (oxygen-rich conditions).

Carbon is isoelectronic with Zr, and C_{Zr}^0 is thus expected to occur mainly in a neutral charge state. However, for Fermi levels high in the gap the -1 charge state can be stabilized, as shown in Fig. 5. Similar to N on the Zr site, C_{Zr}^0 enters a threefold bonding arrangement with the nearby O atoms, as shown in Fig. 7(a). The formation energy is low enough for C to be incorporated, possibly as an unintentional impurity, but because the dominant charge state is neutral it does not affect charge equilibration. The carbon interstitial, finally, has very low formation energies in the $+4$ charge state, C_i^{+4} , but only for Fermi levels in the lower part of the band gap. These Fermi levels will, in general, not be accessible for growth conditions near equilibrium since C and N defects have negative formation energy there, and therefore ZrO_2 will not be stable; even in

Figure 6: Formation energy as a function of Fermi level for carbon in various configurations, V_O, and the lowest energy N defect in monoclinic ZrO₂ for (a) $\mu_{\text{O}} = -2.63$ eV (skull melting growth conditions), (b) $\mu_{\text{O}} = -1.40$ eV (wet-chemical co-precipitation conditions), and (c) $\mu_{\text{O}} = 0$ eV (oxygen-rich conditions).

Figure 7: Atomic configurations for (a) C_{Zr} in the neutral charge state and (b) C_i in the +4 charge state in tetragonal ZrO₂.

the case of more C- and N-poor conditions, V_O has negative formation energy for Fermi levels near the VBM even under O-rich conditions. C_i⁺⁴ also enters a threefold bonding arrangement with three O atoms, as shown in Fig. 7(b).

In Fig. 5 we also plot the formation energy of the V_O and the lowest energy
185 N defect for each condition (reproduced from Fig. 3). We see that for the defects
and conditions considered, the Fermi level will be pinned near the mid gap by
 V_O^{+2} and either N_O^- or N_{Zr}^- . Therefore, we conclude that in tetragonal ZrO_2 , for
all conditions considered, the presence of C will not affect the compensation of
 V_O^{+2} by $N_{O/Zr}^-$ assumed in Eq. (1).

190 The behavior of C in monoclinic ZrO_2 , shown in Fig. 6, is more sensitive to
the growth conditions but similar conclusions can be reached. For $\mu_O = -2.63$
eV [Fig. 6(a)], C on the oxygen site is stable in the +4 charge state with both
 CO_3 and CO_4 having similar formation energies. Their atomic configuration is
very similar with both CO_3 and CO_4 moving offsite and forming two C-O bonds
195 of 1.29 and 1.30 Å. In the -1 and -2 charge state, CO_3 and CO_4 remain on site
and form C-Zr bonds similar in length to bulk Zr-O bonds.

C_{Zr} is again stable in the neutral charge state for most Fermi levels in the
band gap, with C entering a threefold bonding arrangement with the nearby
oxygen atoms. The $(0/-1)$ transition level of C_{Zr} occurs at 4.67 eV above the
200 VBM. Results for this charge-state transition level of C in monoclinic ZrO_2 were
previously published[30]. In Figs. 6(b) and (c), C_{Zr} has low formation energy
over the range where the Fermi level is pinned by V_O^{+2} and N_{Zr}^- , though it is in
the neutral charge state and will not compensate the V_O^{+2} .

Interstitial carbon C_i is again most stable for Fermi levels in the lower part
205 of the band gap, with C_i^{+4} in a threefold bonding arrangement similar to that
in tetragonal ZrO_2 .

Similar to the conclusion for the tetragonal phase, while carbon has low
formation energies and may be present in high concentrations, its presence does
not alter the charge neutrality between V_O^{+2} and $N_{O/Zr}^-$.

210 4. Conclusions

We report the electronic properties of carbon and nitrogen impurities in
 ZrO_2 through first principles calculations. We go beyond previous first princi-

ples studies on these defects by using a hybrid functional, which allows for more
 accurate predictions of formation energies and defect levels, and by comprehen-
 215 sively addressing all possible atomic configurations and charge states. We find
 that although nitrogen is present in positive charge states, the dominant defects
 are N_{O}^- and V_{O}^{+2} . This picture is consistent with the Kröger-Vink reaction in
 Eq. (1). Additionally, carbon impurities with their low formation energy may
 be present in high concentrations in ZrO_2 used for SOFCs. Carbon is stable in
 220 donor charge states in ZrO_2 but does not affect the charge neutrality between
 N_{O}^- and V_{O}^{+2} .

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