



# Zirconium-peroxo embedded in non-stoichiometric yttria stabilized zirconia (110) from first-principles

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## ABSTRACT

Metal-peroxo species on oxides are recognized as important intermediates for catalytic reactions on oxides. In this work, surface structures of stoichiometric and non-stoichiometric yttria stabilized zirconia (YSZ) were investigated for the low index surfaces (111), (110), and (100) by using first principles electronic structure calculations, and the energetic stabilities of non-stoichiometric surfaces with respect to the stoichiometric ones were calculated as a function of oxygen chemical potential. In the oxygen-rich condition, a unique form of zirconium-peroxo embedded in the lattice oxygen sites was found in YSZ(110); the embedded peroxo was recently confirmed in experimental observations for TiO<sub>2</sub> anatase (101) (M. Setvín *et al.*, *Science* **341** (2013) 988) and cubic In<sub>2</sub>O<sub>3</sub> (001) (D. R. Hagleitner *et al.*, *Phys. Rev. B* **85** (2012) 115441). The electronic structure of the embedded peroxo found in O-rich YSZ(110) was analyzed in details by means of orbital energy diagrams and density of states.

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## 1. Introduction

Yttria-stabilized zirconia (YSZ) has been widely used in many fields of technologies because of its high ionic conductivity, superior chemical and mechanical stability. For example, YSZ is used as catalyst supports [1], solid electrolytes in solid oxide fuel cells [2] and gas sensors [3]. High ionic conductivity at high temperature is achieved by oxygen vacancies V<sub>O</sub><sup>2+</sup> introduced by yttria dopants to keep charge neutrality. For the application to gas sensors, the activation of gases on the YSZ surface is also important. Shishkin and Ziegler have reported first-principles calculations for oxidation of H<sub>2</sub> and CH<sub>4</sub> at high temperature on an oxygen-rich cubic YSZ (111) surface (O-rich YSZ(111)), in which an oxygen vacancy is filled with an excess oxygen atom [4]. They also revealed that the oxidations of the molecules are not activated on a stoichiometric cubic YSZ (111) surface (sYSZ(111)) [4]. The computational results correspond well to the experimental observation that CH<sub>4</sub> can be oxidized on the oxygen enriched YSZ surface [5–7]. In the last few years, the oxidation of NO<sub>2</sub> [8] and the heterogeneous CO oxidation [9] on O-rich YSZ(111) have also been simulated with first-principles calculations. In fact, the stability of the non-stoichiometric cubic YSZ (111)

surface in terms of the defect formation energy of surface oxygen vacancy has been discussed, and the large defect formation energy, small relaxation and the presence of the highly localized gap state have been pointed out [10]. However, in spite of the many studies on the reactions, the understanding of the oxygen adsorbed state and the stability of non-stoichiometric surface, O-rich and O-poor surfaces especially in cubic YSZ is insufficient.

In this study we investigated the electronic structures of the low index surfaces of stoichiometric and non-stoichiometric cubic YSZ, and explain how different electronic and ionic states of adsorbed oxygen appear depending on the surface indices and environmental conditions. First, we determined sYSZ(111), sYSZ(110), and sYSZ(100) configurations with the most stable positions of the defects (i.e., the positions of dopant-Y and oxygen vacancies introduced by the dopant) by using first-principles calculations. By using the stable sYSZ slab models, we determined the configurations of non-stoichiometric YSZ slabs. The electric density of states (DOS) of the stoichiometric and the non-stoichiometric slabs are discussed. The analysis of DOS revealed that the adsorbed excess oxygen atoms are recognized as oxygen ions O<sup>2-</sup> in most cases, but especially in YSZ(110) at an oxygen rich condition, an excess oxygen atom adsorbed in an oxygen vacancy site creates the peroxo state O<sub>2</sub><sup>2-</sup> with a neighboring lattice oxygen on the surface. Since the peroxo species are important ingredients for catalytic applications [11,12], the concept on how the peroxo state can appear on YSZ(110) at an oxygen rich condition will be a good guideline for the construction of functional surfaces.

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## 2. Methodology

We performed first-principles calculations of the stoichiometric and non-stoichiometric YSZ surfaces by using the Vienna ab initio simulation package (VASP) [13,14] with Perdew–Burke–Ernzerhof type [15] generalized gradient approximation for the exchange–correlation functional in the density functional theory (DFT). The core electrons were replaced by projector-augmented wave (PAW) [16,17], and wave functions were expanded in a basis set of plane waves up to a cutoff energy of 400 eV. We chose a Monkhorst–Pack  $3 \times 3 \times 1$  k-point grid [18] for the first Brillouin zone sampling. Visualization of the YSZ slab models was performed with VESTA [19]. To discuss the surface stability as a function of the oxygen chemical potential  $\mu_O$  in the range of the oxidation to reduction limits, we defined the surface energy  $\gamma$  as follows [20]:

$$\gamma^{(hkl)} = \left( E_{tot}^{(hkl)} - n_{Zr}\mu_{Zr} - n_Y\mu_Y - n_O\mu_O \right) / A_V. \quad (1)$$

$E_{tot}^{(hkl)}$  is the total energy of a  $(hkl)$  slab at 0 K.  $n_i$  and  $\mu_i$  are the number and chemical potential of atom  $i$  in the slab, respectively. The surface area in a supercell is represented as  $A$ . The values of  $\mu_{Zr}$ ,  $\mu_Y$  and  $\mu_O$  are constrained with the equilibrium conditions as,

$$\mu_{ZrO_2} = \mu_{Zr} + 2\mu_O \quad \text{and} \quad \mu_{Y_2O_3} = 2\mu_Y + 3\mu_O.$$

The range of the oxygen chemical potential from the oxidation limit ( $\mu_O = \mu_{O_2}/2$ ) to the reduction limit ( $\mu_O = (\mu_{ZrO_2} - \mu_{Zr})/2$ ) is obtained from total energy calculations of the oxygen gas, cubic  $ZrO_2$  and hcp Zr metal [21]. Since the oxygen chemical potential is also related to the oxygen partial pressure and temperature as

$$\mu_O = \mu_O(T, p) = \mu_O(T, p^\circ) + 1/2kT \ln \left( \frac{p}{p^\circ} \right), \quad (2)$$

the calculated surface energy in Eq. (1) can be represented also as a function of oxygen partial pressure at temperature  $T$ . In Eq. (2),  $p^\circ$  of 1 atm is adopted [22,23]. The reference chemical potential  $\mu_O(0K, p^\circ)$  is defined as 0, and the following equation and Eq. (2) enable us to obtain the relationship between the oxygen chemical potential and oxygen partial pressure at any temperature,

$$\begin{aligned} \mu_O(T, p^\circ) &= \mu_O(0K, p^\circ) + 1/2\Delta G_{O_2}(T, p^\circ) \\ &= 1/2[H_{O_2}(T, p^\circ) - H_{O_2}(0K, p^\circ)] - 1/2T[S_{O_2}(T, p^\circ) - S_{O_2}(0K, p^\circ)], \end{aligned} \quad (3)$$

where  $G$  is the Gibbs free energy,  $H$  is the enthalpy, and  $S$  is the entropy.  $H$  and  $S$  of an oxygen gas at various temperatures were obtained in the JANAF Thermochemical Tables [24].

## 3. Result and discussion

### 3.1. The stable configurations of the defects

To find the stable defect configurations of the YSZ slabs, we performed first-principles calculations of the  $2 \times 2 \times 1$  sYSZ (111), (110) and (100) supercells. We used the 12, 5 and 9 atomic layer slabs for (111), (110) and (100), respectively. The sYSZ(111), (110) and (100) consist of 16, 20 and 16  $ZrO_2$  formula units, respectively. Fig. 1 shows the stoichiometric slabs, in which the defects are located at the most stable positions after structural optimization, and the non-stoichiometric slabs obtained from the stable stoichiometric slabs. Green, gray and red spheres express  $Zr^{4+}$ ,  $Y^{3+}$  and  $O^{2-}$  ions at the surfaces, respectively. The broken circles indicate the oxygen vacancies. The sYSZ slabs including two Y atoms and an oxygen vacancy at various positions were calculated to obtain the most stable configuration of the defects;  $Y_2O_3$  concentrations thus correspond to 6.3, 5.0 and 6.3 mol.% for (111), (110) and (100), respectively. The combinations of the defect positions

investigated in this study were restricted as follows. Two Zr atoms in the top layers defined in Fig. 1 were substituted by two Y atoms, and an O atom in the top layer was removed from the slabs, which lead to 448 configurations for each surface, and we calculated all the configurations by taking symmetry relations into account. Bottom layers depicted in Fig. 1 were fixed to the bulk atomic positions during optimization procedure. In all cases in Fig. 1, the two Y atoms located at the topmost surface and sub-surface were consequently calculated to be the most stable. The oxygen vacancies are positioned at the third and first atomic layers for sYSZ(111) and sYSZ(110), respectively, as shown in Fig. 1. Note that in the  $ZrO_2$  (100), according to the (100) surface composition we have intrinsic oxygen vacancy sites which have to be introduced before the Y-doping. To determine the intrinsic vacancy sites firstly, we assumed following two conditions: (1) the number of dangling-bond of Zr is minimized, and (2) the most nearest-neighbor position between intrinsic vacancy sites is avoided for strong coulomb interaction. Consequently, we obtained the intrinsic oxygen vacancy sites on the topmost and lowermost layers, as shown in the sYSZ(100) initial structures in Fig. 1(c). The oxygen vacancy introduced by the Y-doping is positioned at the third layer, and the vacancy is still positioned at the third layer after the relaxation. On the other hand, an intrinsic oxygen vacancy at the topmost layer is moved to the third layer after the relaxation, as shown in the side view of the relaxed sYSZ(100) in Fig. 1(c). Note that other three intrinsic vacancies at the topmost layer are probably positioned at the topmost layer even after the relaxation, but the positions cannot be depicted because of the significant structural changes at the surface. Fig. 2 shows the total energies per formula unit and the surface energies of all calculated sYSZ slabs. The total energy differences between minimum and maximum values of each surface are 0.18, 0.20 and 0.25 eV for sYSZ(111), sYSZ(110) and sYSZ(100), respectively. The energy difference of sYSZ(100) is more strongly dependent on the defect positions than those in sYSZ(111) and sYSZ(110). Fig. 2 also shows that sYSZ(111) configurations are clearly more stable than sYSZ(110) and sYSZ(100) configurations.

### 3.2. Analysis of the YSZ surface stability

The surface energies of the most stable configurations calculated by using Eq. (1) are compared with those reported in Ref. [25] in Table 1. The energetic trend in sYSZ(111), (110) and (100) calculated in our slab models is consistent with that in the previous work by Ballabio and co-workers (i.e. (111) < (110) < (100)) [25]; positive small number corresponds to a stable surface. In Ref. [25], the Y atoms were fixed to the positions obtained in the bulk model [26]. Our slab models show the smaller surface energies than those in Ref. [25], which is partially related to the computational condition that the relative positions of dopant-Y and oxygen vacancies in our calculations were determined using the slab models.

Assuming that the three surface indices are the major surface orientations in YSZ, we can calculate the major surfaces in YSZ, we can calculate the relative surface area  $A^{(hkl)}$  of each surface at thermodynamic equilibrium expressed as,

$$A^{(hkl)}(T) = \sum_{i \in (hkl)} e^{-\frac{\gamma_i^{(hkl)}}{k_B T}} / \sum_{(h'k'l')} \sum_{j \in (h'k'l')} e^{-\frac{\gamma_j^{(h'k'l')}}{k_B T}}, \quad (4)$$

where  $k_B$  is Boltzmann's constant, and the surface index  $hkl$  ( $h'k'l'$ ) is restricted to 111, 110 and 100 in this study. The indices  $i$  and  $j$  indicate the calculated configurations included in Fig. 2(b). Fig. 3 shows the calculated relative surface area of these surfaces. Since the energy difference prominently affects  $A^{(hkl)}$  at low temperature,  $A^{(111)}$  is calculated to be about 1 at the low temperatures. Although the sYSZ(111) relative surface area is obviously larger than those of (110) and (100) in the temperature range shown in Fig. 3, the sYSZ(110) and (100) surface areas gradually increase with an increase in temperature. At 1000 K,  $A$ 's of sYSZ(111), (110)

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