

Ab initio atomistic thermodynamics study on the sulfur tolerance mechanism of the oxygen-enriched yttria-stabilized zirconia surface



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ABSTRACT

The first-principles method based on density functional theory (DFT) is used to investigate the reaction mechanism for the adsorption of H₂S on the oxygen-enriched yttria-stabilized zirconia (YSZ + O) (111) surface. It is found that the H₂S dissociation processes have low energy barriers (<0.5 eV) and high exothermicities (2.5 eV), and the dissociative S atoms may result in the poisoning of the YSZ + O surface by forming the SO and the hyposulfite (SO₂²⁻) species with very strong bonds to the surface. In addition, using the *ab initio* atomistic thermodynamics method, the surface regeneration or de-sulfurization process of a sulfur-poisoned (i.e. sulfur-covered) YSZ + O(111) surface is studied. According to the phase diagram, the adsorbed atomic sulfur can be oxidized to SO₂ and removed from the YSZ + O surface by introducing oxidizing reagents, e.g. O₂ and H₂O.

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1. Introduction

Due to its characteristics of withstanding the harsh thermal, mechanical, chemical environments found in automotive exhausts, and (at elevated temperatures) high oxygen ion conductivity, yttria-stabilized zirconia (YSZ) is widely used in thermal barrier coatings [1], robust oxide ion conducting electrolytes [2], high-temperature solid-state electrochemical gas sensors [3,4], and solid oxide fuel cells (SOFCs) [5,6]. For maintaining charge neutrality of the YSZ system, the oxygen vacancies are created during the substitution of Zr⁴⁺ by Y³⁺ in the YSZ lattice. Under practical operating conditions of SOFCs, these oxygen vacancies are mobile to give rise to oxygen ionic conductivity via vacancy diffusion mechanism, and can be filled by O²⁻ migrating through the crystal lattice of YSZ, to form an oxygen-enriched YSZ surface, YSZ + O(111). The O²⁻ ions supplied to the intrinsic vacancy of YSZ originate from the electrochemical reaction of O₂ at an electrode, which depends on the actual SOFC fuel gas operation and polarization conditions in the anode polarization measurement [2,7].

A considerable number of researches have been done on the molecule adsorption onto a YSZ(111) surface containing naturally occurring oxygen vacancies, and an oxygen-enriched YSZ + O(111) surface [7–13]. The surfaces are built based upon the previous *ab initio* studies of YSZ(111)/YSZ + O(111) surfaces by Shishkin and Ziegler who examined the adsorption of methane, oxygen, and hydrogen onto the YSZ(111) and oxygen-rich YSZ + O(111) surfaces [11,13], and found

that compared to the chemically inert YSZ surface, the YSZ + O is very active. For example, the combined theoretical and experimental studies of Alexandr Gorski et al. have shown that the adsorption of CO/H₂ on the YSZ + O surface will form CO₂/H₂O, while the YSZ surface resulting from surface oxygen depleting operating conditions is virtually inert toward CO and H₂ oxidation [7]. The DFT study of Michael Breedon et al. found that the binding of NO₂ with a surface oxygen atom of the YSZ + O(111) surface could yield an adsorbed NO₂, nitrate, or cis-peroxynitrite (OONO) molecule, while the adsorption of NO₂ on the YSZ surface only results in the weak molecular adsorption [4].

However, the YSZ-based (Ni/YSZ) anode for SOFCs is highly susceptible to deactivation (poisoning) by contaminants commonly encountered in readily available fuels, especially sulfur-containing compounds [5]. For example, at typical SOFC operating temperatures (>927 K), even trace amounts of H₂S (a few ppm) severely influence the performance of Ni/YSZ anodes [5,6,14–16]. Our recent DFT study on the adsorption of H₂S on the YSZ(111) surface has shown that the sulfur poisoning of the YSZ(111) surface with H₂S would be prevented by the co-adsorbed hydrogen [17]. Since the oxygen-enriched YSZ + O(111) surface exists in the practical operating conditions of SOFCs, its properties upon exposure to H₂S is quite relevant to the understanding of the sulfur tolerance mechanism of the Ni/YSZ anode. To the best of our knowledge, no direct experimental evidences and theoretical studies are available in this respect.

Here we use the first-principles method based on density functional theory (DFT) to study the mechanism and the minimum energy path (MEP) for the sulfurization process of the YSZ + O upon exposure to H₂S. Furthermore, since the removal of the adsorbed sulfur from surfaces is a critical step toward sulfur tolerance, using the *ab initio*

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atomistic thermodynamics method, we construct the phase diagram for the regeneration of the sulfur-poisoned YSZ + O(111) surface and further explore the sulfur tolerance properties of the YSZ + O surface under SOFC operating conditions. The structure of YSZ surfaces with extra supplied oxygen and its implications in catalysis are discussed in detail.

2. Model and computational details

2.1. Systems and optimization

In order to generate the YSZ + O(111) surface, as previously described by Shishkin and Ziegler [11], firstly, we model the $\text{ZrO}_2(111)$ surface as a slab with three O–Zr–O triple layers, and then Yttrium doping is introduced into the surface model by substituting two Zr atoms with two Y atoms in the topmost and subsurface layers, as shown in Fig. 1(a). In order to keep the charge balance, a single oxygen atom is removed from the subsurface to create an intrinsic oxygen vacancy, which results in a stoichiometric YSZ(111). The model has been used in our recent study to investigate the adsorption and dissociation of H_2S on the YSZ(111) surface [17]. As stated in the introduction, the intrinsic oxygen vacancy may be filled by an O^{2-} migrating through the lattice under practical operating conditions of SOFCs, which results in an YSZ + O(111) surface as shown in Fig. 1(a).

The DFT plane wave calculations are performed using the Vienna *ab initio* simulation package (VASP) [18–20] with the projector augmented wave method (PAW) [21,22] and the Perdew–Burke–Ernzerhof (PBE) [23] functional. The wave functions are expanded in plane waves with a cut off energy of 408 eV. The calculations of the YSZ + O(111) slab model are carried out using the Brillouin zone sampling with a $(2 \times 2 \times 1)$ Monkhorst-Pack k-points grid. A vacuum gap of 15 Å is introduced between the slabs and the structures are optimized until the forces on each atom are less than 0.02 eV/Å.

As done in ref. [17], the geometrical parameters of the free H_2S , SH and S are computed in a $10 \times 10 \times 10 \text{ \AA}^3$ cubic box with the Monkhorst-Pack mesh k-points grid of $8 \times 8 \times 8$ for the Brillouin zone integrations. For the adsorption, a molecule (H_2S , SH or S) is placed on one side of the relaxed slabs. One O–Zr–O triple layer at the bottom is fixed and the ions in the remaining layers, as well as the adsorbates, are allowed to fully relax.

2.2. Computational methods

The adsorption energy is defined by

$$E_{\text{ads}} = E_{\text{adsorbate}} + E_{\text{YSZ+O}} - E_{\text{adsorbate/YSZ+O}} \quad (1)$$

where $E_{\text{adsorbate}}$ is the energy of a free H_2S , SH or S, and $E_{\text{adsorbate/YSZ+O}}$ and $E_{\text{YSZ+O}}$ are the calculated energies of the support (YSZ + O) with and without adsorbate (H_2S , SH or S), respectively. Positive adsorption energy corresponds to a stable adsorption structure.

The desorption energy of a SO molecule product from the YSZ surface is defined as

$$E_{\text{de}} = E_{\text{SO/YSZ}} - E_{\text{YSZ}} - E_{\text{SO}} \quad (2)$$

where E_{SO} is the calculated total energy for the ground state of an optimized SO molecule in gas phase, and E_{YSZ} and $E_{\text{SO/YSZ}}$ are the total energies of the YSZ systems without and with the SO species. Positive energies correspond to exothermic processes.

The electronic structure and bonding features are analyzed by means of the density of states (DOS), the electron localization functions (ELF) [24,25] and the charge density difference ($\Delta\rho$) induced by the adsorption. The ELF can serve as a useful tool for characterizing the bonding between adsorbate and surfaces and provides a measure of bond order. Bader charge analysis [26] is applied to assign charges to atoms and fragments. The $\Delta\rho$ maps describe the electron density rearrangement resulting from the adsorption, and are calculated from

$$\Delta\rho(\mathbf{r}) = \rho_{\text{adsorbate/YSZ+O}} - \rho_{\text{YSZ+O}} - \rho_{\text{adsorbate}} \quad (3)$$

here it is necessary to use the same atomic positions for all the three terms, namely, those from the optimized adsorbate/YSZ + O systems. The climbing image nudged elastic band method (CI-NEB) is employed for the transition states (TS) search [27,28].

What's more, considering the effect of temperature and partial pressure of various gases, we calculated the Gibbs free energy $G(T, P)$ of the whole system by applying the thermodynamic corrections on the DFT computed energy, denoted by E^{DFT} , which represents the Gibbs free energy at 0 K in vacuum or the Helmholtz free energy at 0 K, as done elsewhere [29–33].

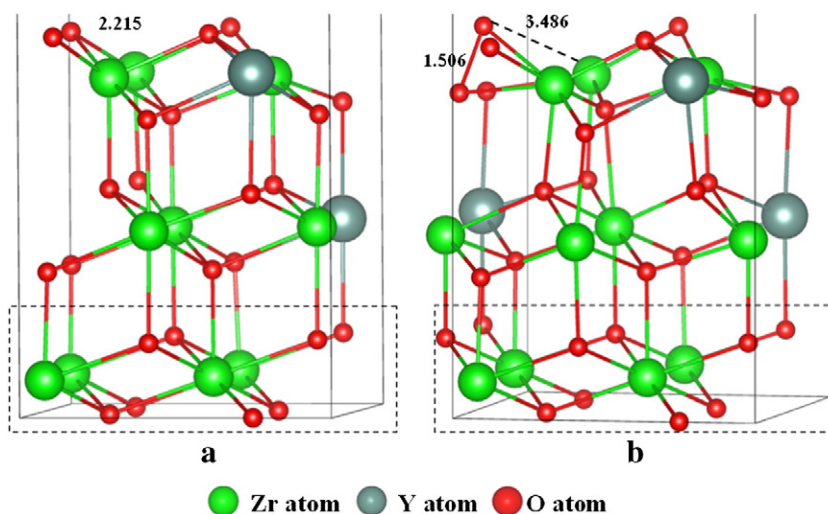


Fig. 1. (color on line) Slab models for the undistorted (YSZ + O) (111) surface (a) and the distorted (YSZ + O-distorted) (111) surface (b). The bottom three atomic layers (in the dashed rectangular box) are fixed at their bulk positions in the calculations. The slabs are repeated in the z-direction (vertical) and separated by vacuum gaps of 15 Å. The green, gray and red balls represent the Zr, Y, and O atoms, respectively.

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