First Principles Study of **Nanoscale Mechanism of** Oxygen Adsorption on Lanthanum Zirconate Surfaces

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ABSTRACT

Lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$) is a rare-earth pyrochlore material, which has been proposed as a promising thermal barrier coating (TBC) material due to its low thermal conductivity and high temperature phase stability. At elevated temperatures, degradation of $\text{La}_2\text{Zr}_2\text{O}_7$ may occur due to adsorption of oxygen (O_2) on $\text{La}_2\text{Zr}_2\text{O}_7$ surfaces. This paper investigates **nanoscale mechanism of** O_2 adsorption on $\text{La}_2\text{Zr}_2\text{O}_7$ coating surfaces using the density functional theory (DFT) calculations. $\text{La}_2\text{Zr}_2\text{O}_7$ surface energies on (001), (011) and (111) planes are calculated. The surface free energy of (011) plane is lower than **those of** (001) and (111) planes. On (001), (011) and (111) planes of $\text{La}_2\text{Zr}_2\text{O}_7$, the lowest adsorption energy occurs at 4-fold site, bridge site, and 3-fold-FCC site, respectively. Among all calculated cases, the lowest adsorption energy site is 3-fold-FCC on (111) plane, which is confirmed by the Bader charge transfer analyses. Charge density difference analyses show that the 3-fold-FCC site on (111) surface has the largest charge density, suggesting the strongest interaction between O_2 and $\text{La}_2\text{Zr}_2\text{O}_7$ surface.

Keywords: Lanthanum zirconate; density functional theory; O₂ adsorption

1. INTRODUCTION

Thermal barrier coatings (TBCs), which comprise multiple ceramic and metallic coating layers, insulate blades or combustion components of gas turbine engine and improve energy efficiency and lifetime of engines [1]. $\text{La}_2\text{Zr}_2\text{O}_7$, a rare-earth based TBCs material, has recently become popular because of its desirable high-temperature thermal and physical properties. Compared with the current state-of-the-art TBCs 8wt% Y_2O_3 -stabilized ZrO_2 (YSZ), $\text{La}_2\text{Zr}_2\text{O}_7$ has the following advantages: a relatively low thermal conductivity, no phase transition, low sintering activity, and high chemical stability [2-5]. Interfacial damage in TBCs due to the oxidation has been widely investigated by experiment. Zhu *et al.* found that the oxidation process of bond coat and substrate significantly reduced the coating adherence, resulting in delamination at both the top coat/bond coat and bond coat/substrate interfaces, due to the adsorption of oxidizing gas and oxidation process [6]. Evans studied the oxidation induced failure of YSZ/MCrAlY TBC system [7]. The final spallation often occurred by buckling or release of strain energy within the TBC top coat and the thermally grown oxide (TGO) layer due to oxidation induced phase or volume change. In addition, advanced application of TBC materials requires understanding of the ideal material properties and mechanism of interaction between TBC materials and its environment. Specifically, an atomic-level investigation of TBC materials becomes essential. However, the pursuit of the nano-properties requires high precision nano-devices, which makes it particularly challenging to characterize the properties in nanoscale [8]. As a result of that, theoretical method becomes a feasible approach to investigate the gas adsorption mechanism in nanoscale.

Density functional theory (DFT) calculations were used in this paper to investigate the O_2 adsorption mechanism on $\text{La}_2\text{Zr}_2\text{O}_7$ surface. DFT is an alternative approach to finding the solution to the Schrödinger equation, which is the fundamental equation to describe the quantum behavior of atoms and molecules [9-11]. In our previous work, several thermal and mechanical

properties of $\text{La}_2\text{Zr}_2\text{O}_7$ were calculated using DFT calculations, including specific heat, Young's modulus, thermal conductivity, coefficients of thermal expansion (CTE) [12, 13]. In terms of gas adsorption process, Wallin *et al.* studied O and O_2 adsorption process on $\alpha\text{-Al}_2\text{O}_3$ (0001) surface using the DFT method. Four atomic Al_2O_3 layers were built, and adsorption energies were calculated at various positions. Charge density was analyzed to interpret the adsorption mechanism. Atomic O was found to have strong interaction with the double layer Al-Al terminated surface, where O_2 molecules were found to easily dissociate on this surface [14]. Li *et al.* studied the oxygen adsorption process on Cr_2AlC (0001) surface. The surface energy, adsorption energy, bonding character, and electronic structure of Cr_2AlC (0001) surface with or without single O atom and molecular O_2 were investigated by the DFT calculations. The result showed that the O strongly bonded to the Al atom on the surface [15]. In addition, we have previously studied carbon dioxide adsorption process on $\text{La}_2\text{Zr}_2\text{O}_7$ surface using nano-scale slab models [16]. The results showed that (011) plane was the most thermodynamically stable plane due to its lowest surface energy.

Oxygen adsorption on TBC surface is the first step of the oxidation process. However, no previous study was found about the O_2 adsorption on $\text{La}_2\text{Zr}_2\text{O}_7$ surfaces. In this paper, the surface energies of $\text{La}_2\text{Zr}_2\text{O}_7$ (001), (011) and (111) planes are calculated. Then adsorption energies of O_2 on these planes are studied. The electronic density difference and charge transfer analyses are carried out to investigate the adsorption mechanisms of O_2 on $\text{La}_2\text{Zr}_2\text{O}_7$ surfaces.

2. COMPUTATIONAL DETAILS

All calculations are conducted using DFT based plane wave method with the Vienna *ab initio* simulation package (VASP) [9, 10, 17-19]. Generalized gradient approximation (GGA)

functional is used to simulate the adsorption process [20-22]. The standard potentials of the projector augmented wave (PAW) of GGA are used to describe the ion cores [23, 24].

In terms of the atomistic structure model **in nanoscale**, $\text{La}_2\text{Zr}_2\text{O}_7$ is a rare-earth pyrochlore crystal. Pyrochlore is a cubic crystal structure (space group $Fd-3m$). The lanthanum (La) atoms occupy at 16d positions (1/2, 1/2, 1/2), and zirconium (Zr) atoms take 16c positions (0, 0, 0). There are two different oxygen (O) positions. The **O** atoms locate at 48f positions (x, 1/8, 1/8), while **O'** atom occupy at 8b positions (3/8, 3/8, 3/8) [25]. The unit cell of $\text{La}_2\text{Zr}_2\text{O}_7$ **in nanoscale** has 16 La atoms, 16 Zr atoms and 56 O atoms, where each octahedron contains one **Zr** atom and six **O** atoms. **The relaxed lattice parameter of the $\text{La}_2\text{Zr}_2\text{O}_7$ conventional cell model is 1.0882 nm.**

To study the adsorption on different planes, three surfaces on (001), (011) and (111) planes are cut from a $\text{La}_2\text{Zr}_2\text{O}_7$ unit cell. More than five layers of atoms are included in the slab models, as shown in Fig. 1. All surfaces are fully relaxed with two layers of atoms on the bottom fixed at a cut-off energy of 500 eV. The positions of unconstrained atoms are optimized until the force change between two steps is smaller than 0.03 eV/Å. All atom electrons are also relaxed until the band structure energy change and total free energy change between two steps are less than 1×10^{-4} eV. Discretized k mesh ($3 \times 3 \times 1$), generated by the Monkhorst-Pack method [26], is used in Brillouin zone for energy integration. Oxygen molecules are initially placed at a height of 1.2 Å above each surface.

Fig. 1. Computational slab models of various $\text{La}_2\text{Zr}_2\text{O}_7$ planes: (a) (001) plane, (b) (011) plane, and (c) (111) plane. The blue, green, and red balls indicate La atoms, Zr atoms, and O atoms, respectively.

The proposed O_2 molecule adsorption sites on each surface plane are shown in Fig. 2. Position A is the bridge site located between one La atom and one Zr atom. Position B is the 4-fold site, which exists on (001) and (011) planes. Position C is the 3-fold-FCC site, and position D is the 3-fold-HCP site. Positions C and D only exist on (111) surface. In Fig. 2a and Fig. 2b, the dash lines highlight the second layer atoms, and remaining atoms are located on the top layer. In Fig. 2c, the dash lines highlight the top layer atoms. The dot lines highlight all the second layer atoms. The remaining atoms are located in the third layer.

Fig. 2. **O₂ molecule** adsorption sites on La₂Zr₂O₇ surface planes: (a) (001) plane, (b) (011) plane, and (c) (111) plane. **The blue and green balls indicate La and Zr atoms, respectively.**

The surface energy is calculated by using the following equation [27]:

$$\gamma = \frac{1}{2A} (E_{slab} - N_s E_{bulk/atom}) \quad (1)$$

where **A** is the surface area of each slab; **N_s** is the number of atoms; **E_{slab}** is the free energy; **E_{bulk/atom}** is the total free energy per atom for the La₂Zr₂O₇ unit cell. The calculated total free

energy of a $\text{La}_2\text{Zr}_2\text{O}_7$ unit cell is 803.74 eV. The factor 1/2 is used because each slab has two surfaces.

The gas adsorption energy (E_{ads}) can be calculated using the following relationship [28]:

$$E_{ads} = E_{tot} - E_{slab} - E_{adsorbate} \quad (2)$$

where E_{tot} represents the total free energy of the optimized $\text{O}_2 + \text{La}_2\text{Zr}_2\text{O}_7$ slab system; E_{slab} is the total energy of the $\text{La}_2\text{Zr}_2\text{O}_7$ slab; $E_{adsorbate}$ is the free energy of isolated gas phase O_2 molecule.

Finally, Bader charge calculations and charge density difference analyses are conducted to understand the electron transfer during the oxygen adsorption process [29-31].

3. RESULTS AND DISCUSSION

3.1 Surface energy

The calculated surface energies and related free energies of $\text{La}_2\text{Zr}_2\text{O}_7$ slabs (E_{slab}) on (001), (011), and (111) planes are summarized in Table 1. (011) plane has the lowest surface energy than those of (001) and (111) planes. Therefore, the (011) plane is the most thermodynamically stable plane in $\text{La}_2\text{Zr}_2\text{O}_7$, compared with (111) and (001) planes.

Table 1. Calculated energies on different planes

Adsorbent plane	Surface area ($\text{\AA}^2$)	Number of atoms (N_s)	E_{slab} (eV)	Surface energy γ (eV/ $\text{\AA}^2$)
(001)	58.3192	44	-369.9194	0.2814
(011)	83.6264	44	-371.1802	0.1835

(111)	51.2105	66	-569.5299	0.3249
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3.2 Adsorption energy

The calculated adsorption energies of each site are listed in Table 2. The energies are exothermic, which means O atoms are spontaneously adsorbed onto $\text{La}_2\text{Zr}_2\text{O}_7$ surface. For O_2 molecule adsorption on the (001) plane, the 4-fold site has the lowest adsorption energy, indicating it is the most favorable adsorption site on the (001) plane. On the (011) plane, the lowest adsorption energy occurs at the La-Zr bridge site. On the (111) plane, there are two 3-fold positions. The lowest adsorption energy occurs at the 3-fold-FCC position, suggesting it is the most thermodynamically favorable adsorption site on the (111) plane. Comparing adsorption energies at all sites on different planes, the most favorable adsorption position is at the 3-fold-FCC site on the (111) plane.

Table 2. Calculated oxygen adsorption energies on various $\text{La}_2\text{Zr}_2\text{O}_7$ surfaces

$\text{La}_2\text{Zr}_2\text{O}_7$ plane	A: bridge position (La-Zr) (eV)	B: 4-fold position (eV)	C: 3-fold-FCC position (eV)	D: 3-fold-HCP position (eV)
(001)	3.5127	5.1148	-	-
(011)	5.0240	1.3080	-	-
(111)	3.5795	-	5.5302	3.8070

3.3 Charge transfer and charge density difference

To better understand the adsorption mechanisms, Bader method [29] is used for charge transfer analyses to quantify the amount of charge transferred between O_2 and $La_2Zr_2O_7$ surfaces. Bader charges are calculated for each single atom in every adsorption model. Positive values of Bader charges indicate gaining electrons compared with the equilibrium structure. Negative values of Bader charges represent electron loss. In each adsorption case, the electron loss and electron gain should be balanced.

Table 3 lists the calculated electron charge transfer from $La_2Zr_2O_7$ surface to O_2 molecule. Higher charge transfer values imply a stronger interaction between O_2 molecule and $La_2Zr_2O_7$ surface. From Table 3, the largest electron charge transfer occurs at the 3-fold-FCC site of the (111) surface.

Table 3. Charge transferr between O_2 and $La_2Zr_2O_7$ surfaces

$La_2Zr_2O_7$ plane	A: bridge position (La-Zr) (e)	B: 4-fold position (e)	C: 3-fold-FCC position (e)	D: 3-fold-HCP position (e)
(001)	1.3368	1.5305	-	-
(011)	1.5024	0.7796	-	-
(111)	1.3479	-	1.8815	1.4692

To illustrate the electron charge distribution, charge density difference contours at all adsorption sites are plotted in Fig. 3. Red color represents electron gain, while dark blue color represents electrons loss. All the O atoms obtain electron, indicated by red color. The 3-fold-FCC site on the (111) plane has the highest electron charge density around the O_2 molecule, which is consistent with the charge transfer calculations listed in Table 3.

Fig. 3. Charge density differences of O₂ **molecule** adsorption on La₂Zr₂O₇ surfaces: (a) bridge site on (001) plane, (b) 4-fold site on (001) plane, (c) bridge site on (011) plane, (d) 4-fold site on (011) plane, (e) bridge site on (111) plane, (f) 3-fold-FCC site on (111) plane, and (g) 3-fold-HCP site on (111) plane.

4. CONCLUSIONS

This work investigates the O₂ molecule adsorption mechanisms on La₂Zr₂O₇ surface in nano-scale structure. The conclusions are summarized below.

1. On the (001), (011) and (111) planes of La₂Zr₂O₇, the lowest adsorption energy occurs at the 4-fold site, bridge site, and 3-fold-FCC site, respectively.
2. Among all calculated cases, the lowest adsorption energy site is the 3-fold-FCC on (111) plane, which is confirmed by Bader charge transfer analyses. The largest charge transfer is 1.8815 e at the 3-fold-FCC site on the (111) plane. Charge density difference analyses show that the 3-fold-FCC site on the (111) surface has the largest charge density, suggesting there is the strongest interaction between O₂ and La₂Zr₂O₇ surface.
3. The (011) plane is the most thermodynamically stable plane among the (001), (011), and (111) planes in La₂Zr₂O₇.

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