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Hydrogen isotope in erbium oxide: Adsorption, penetration, diffusion, and vacancy trapping

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HIGHLIGHTS

- H adsorption on cubic Er_2O_3 surface results in electron transfer from H to the surface.
- The H penetration energy of at least 1.6 eV is required for cubic Er_2O_3 surface.
- The dominated mechanisms of H diffusion in bulk Er_2O_3 are elucidated.
- H diffusion near or at vacancies in Er_2O_3 is an exothermic reaction.

ARTICLE INFO

ABSTRACT

In this study, we report results using first-principles density functional theory calculations for four critical aspects of the interaction: H adsorption on Er_2O_3 surface, surface-to-subsurface penetration of H into Er_2O_3, bulk diffusion of H in Er_2O_3, and trapping of H at vacancies. We identify surface stable adsorption positions and find that H prefers to transfer electrons to the surfaces and form covalent bonds with the nearest neighboring four oxygen atoms. For low surface coverage of H as in our case (0.89×10^{14} H/cm^2), a penetration energy of at least 1.60 eV is required for cubic Er_2O_3 surfaces. Further, the H diffusion barrier between the planes defined by Er_2O_3 units along the favorable $\langle 1\,1\,1 \rangle$ direction is found to be very small – 0.16 eV – whereas higher barriers of 0.41 eV and 1.64 eV are required for diffusion across the planes, somewhat higher than the diffusion energy barrier of 0.20 eV observed experimentally at 873 K. In addition, we predict that interstitial H is exothermically trapped when it approaches a vacancy with the vacancy defect behaving as an electron trap since the H-vacancy defect is found to be more stable than the intrinsic defect.

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1. Introduction

One of the key components of the D–T fuelling cycle in fusion blanket systems is tritium recovery. Tritium permeation barrier (TPB) plays an important role in the recovery by containing and handling deuterium and tritium within the reactor building and by controlling hydrogen isotope release to the environment without incurring exorbitant costs [1,2]. Erbium oxide (Er_2O_3) has attracted much attention as TPB material owing to its high permeation reduction factor (PRF) as well as high stability under strong

reducing atmosphere [3,4]. The Er_2O_3 coating has been investigated as insulator for liquid lithium blanket system. In addition, Er_2O_3 has one of the lowest Gibbs free energy of formation among all binary oxide ceramics [5,6]. As a result, Er_2O_3 has been selected as one of the candidate materials for TPB coatings.

TPB coatings suppressing H isotope permeation explain the importance of interaction between atomic hydrogen and erbium oxide [7]. Hence, a thorough examination of the interaction requires to be performed both experimentally and theoretically. In the interaction, it is necessary to understand the thermodynamics and kinetics of hydrogen adsorption on Er_2O_3 surfaces and the subsequent behavior of hydrogen in bulk Er_2O_3, including its penetration, diffusion, and trapping. As reported in Refs. [8,9], density functional theory (DFT) calculations have become a valuable tool to elucidate the structures and determine the dynamics of interstitial H in metals, alloys, and ceramics. DFT

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has been used to successfully predict the microscopic behavior of H in oxides such as Cr_2O_3, TiO_2, SiO_2, and Al_2O_3 [10–13]. Therefore, it is essential to apply DFT calculations to investigate the interaction between atomic hydrogen and Er_2O_3.

Interest in the adsorption of hydrogen atoms on Er_2O_3 surfaces stems mainly from its relevance in TPB coatings. Cubic $Er_2O_3(0\,0\,1)$ surface was studied based on the experimental result that the $(0\,0\,1)$ surface is the most stable after long-time hydrogen isotope (deuterium) permeation [7,14], when compared to other surfaces such as $(1\,1\,1)$ and $(1\,1\,0)$. Because of this, we have placed emphasis on the cubic $Er_2O_3(0\,0\,1)$ surface itself and then discussed H adsorption and penetration on and through this surface, respectively, via DFT calculations. Subsequently, we analyze H diffusion in bulk Er_2O_3 and H trapping at vacancies. We provide computational details in Section 2 and then present and discuss our results in Section 3. Finally, we summarize our work in Section 4.

2. Computational details

The computational simulations in this study were performed using spin-polarized DFT calculations as implemented in the Vienna Ab Initio Simulation Package (VASP), and the Generalized Gradient Approximation (GGA) of Perdew and Wang 91 (PW91) [15] for electron exchange and correlation. PW91 contains much of the underlying physics of exchange and correction interactions of local density approximation (LDA). Although Perdew, Burke, and Ernzerhof (PBE) is based on PW91 and contains the correct features of LDA, some important features of PW91 are sacrificed. These include (1) correct second-order gradient coefficients for the exchange energy (E_x) and the correlation energy (E_C) in the slowly non-adiabatic limit, and (2) correct non-uniform scaling of E_x under the limiting condition where the reduced gradient (s) tends to infinity (∞) [16,17]. Hence, PW91 is used rather than PBE in the DFT calculations. The kinetic energy cutoff for the plane-wave basis set is set to 500.0 eV for all DFT calculations: increasing the cutoff resulted in variations in the total energy of <2 meV/atom (0.192 kJ/mol/atom). The surface and the adsorbate systems have been simulated using a slab model, which includes 12–16 relaxed and unrelaxed atomic layers and a vacuum region (>1.0 nm). Periodic boundary conditions have been used, with the one electron pseudo-orbitals expanded over a plane wave basis set. The expansion includes all plane waves whose kinetic energy is less than a predetermined cutoff energy E_{cut}, i.e., $h^{-2}k^2/2m < E_{cut}$, where h is Planck's constant, k is the wave vector and m is the electronic mass. The k points were obtained from the Monkhorst–Pack scheme [18].

The sampling of the Brillouin zone was performed using k-points of $4 \times 4 \times 1$ for a (1×1) surface unit cell, which includes 24 Er and 36 O atoms. For the bulk Er_2O_3 consisting of 32 Er and 48 O atoms, we used a mesh size of $4 \times 4 \times 4$ for k-point sampling. The k-points above have been tested to converge to <1 meV/atom (0.096 kJ/mol/atom). Atomic relaxations were performed using a conjugate gradient alogirithm [19] with the force on each atom converged to less than 1 meV/nm (0.096 kJ/mol/nm). During the optimization, both the adsorbate (H) and the Er and O atoms in the top four atomic layers of the slab are allowed to relax while the remaining Er and O atoms of the slab are frozen at bulk optimized configurations, as indicated in Fig. 3(b). The relaxations in the inner atoms are rather small (<0.1%) even if all the atoms are fully relaxed. Further, the number of atomic layers in the slab as well as the vacuum depth needed were carefully tested, i.e., increasing the number of atomic layers from 12 to 16 while keeping the top four relaxed and the other inner layers frozen, alters the energy of H adsorption by <0.05 eV. In addition, dipole corrections originally introduced by Neugebauer and Scheffler [20] have been included in order to correct the errors introduced by the use of periodic

boundary conditions. Thus, the adsorption energy (E_{ads}) of the adsorbate H with the dipole correction can be calculated as

$$(E_{ads})_d = E(S)_{H\to d} - E(S) - 0.5E(H_2) \qquad (1)$$

where $E(S)_{H\to d}$ refers to the energy of the system when the H atom is distance d apart from the Er_2O_3 surface, $E(S)$ is the energy of the Er_2O_3 surface, and $0.5E(H_2)$ is the energy of atomic hydrogen as half of the molecular hydrogen energy. (1×1) and (1×2) surface cells were tested using the three-dimensional slab models for H adsorption. Enlarging the size doesn't result in the change of H adsorption energy. H diffusion on the surface and from the surface to the solute site in the bulk has been calculated using the nudged elastic band (NEB) method [21] as implemented in DFT calculations. Twelve images were used in the NEB calculation.

To gain a further understanding of the interaction between the H atom and the cubic $Er_2O_3(0\,0\,1)$ surface, we have presented the difference of charge density plot calculated using the following equation:

$$\Delta\rho = \rho_{(H/S)} - \left(\rho_{(S)}^{frozen} + \rho_{(H)}^{frozen}\right) \qquad (2)$$

where is the electron density for the adsorbate-Er_2O_3 system in its minimum-energy configuration, is the electron density of the cubic $Er_2O_3(0\,0\,1)$ surface that is kept frozen in the positions of the H adsorbate-surface system, and is the electron density of the isolated H atom/H_2 molecule at the same position as in the adsorbate-surface system. The calculations of charge density were then carried out including the dipole correction.

In addition, we have attempted to find the minimum energy pathways and calculate diffusion barriers for H hopping into and out of a vacancy trap from a nearby interstitial site (e.g., tetrahedral site) by the NEB method using three images. H-vacancy interaction has also been studied by means of the projected density of states (PDOS) of perfect and imperfect Er_2O_3. The imperfection comes from point defects such as vacancies. Consideration of quantum effects [20] is important at low temperatures for light species such as atomic H. Therefore, zero-point-energy (ZPE) corrections have been considered at the high-symmetry adsorption sites by summing up the zero-point vibrational energies of the H's normal mode, i.e., where v_i is the real normal mode frequency [22,23].

3. Results and discussions

3.1. Bulk properties

Cubic Er_2O_3 belongs to space group Ia3 and a unit cell has 32 Er atoms occupying the 8a and 24d equipoints and 48 O atoms occupying 48e equipoints. A lattice constant of 1.0545 nm derived by DFT calculations and fitted to Birch–Murnaghan 3rd-order equation of state (EOS) [24] corresponds well with the experimental data of 1.05431 nm [5]. The corresponding bulk modulus has also been calculated using the above equation as $B_o = 148.0$ GPa, in good agreement with the experimental result $B_o = 140.7$ GPa [6,24] within a deviation of 5%. The electronic density of states (DOS) of bulk Er_2O_3 has been calculated using GGA, as shown in Fig. 1. The valence band maximum (VBM) exhibits mainly O 2p features while the conduction band minimum (CBM) mainly consists of Er 5d electrons, in which all 4f electrons are localized and may fully be treated as valence states. This suggests that strong ionic characteristics with weak covalency exist in Er—O bonding in bulk Er_2O_3.

In addition, band structures of Er_2O_3 have been calculated at 45 regularly spaced k points in the irreducible portion of the Brillouin zone (BZ) by straightforward matrix diagonalization. Calculated band structures along the high-symmetry axes of the BZ for Er_2O_3 are shown in Fig. 2. The calculated direct GGA gap of 4.01 eV at Γ is an underestimation compared to the experimental data of 5.30 eV